Supplementary material

Concentrations and fluxes of isoprene and oxygenated VOCs at a French Mediterranean oak forest

C. Kalogridis[1], V. Gros[1], R.Sarda-Esteve[1], B. Langford[2], B. Loubet[3], B. Bonsang[1], N. Bonnaire[1], E. Nemitz[2], A-C.Genard[4], C. Boissard[1], C. Fernandez[4], E. Ormeño[4], D. Baisnée[1] ,I.Reiter[5] and J. Lathière[1]

[1]{Laboratoire des Sciences du Climat et de l'Environnement (LSCE-IPSL), Unité Mixte CEA-CNRS-UVSQ (Commissariat à l'Energie Atomique, Centre National de la Recherche Scientifique, Université de Versailles Saint-Quentin-en-Yvelines), F-91198 Gif-sur-Yvette, France.}

[2]{Centre for Ecology & Hydrology (CEH), Bush Estate, Penicuik, EH26 0QB, UK}

[3]{Environnement et Grandes Cultures, INRA, UMR EGC, Thiverval-Grignon, France}

[4]{Institut Méditerranéen d'Ecologie et Paléoécologie IMEP, 13397 Marseille, France}

[5]{Observatoire de Haute-Provence, CNRS 2207, 04870 Saint-Michel-l'Observatoire, France}

Correspondence to: C. Kalogridis (cerise.kalogridis@lsce.ipsl.fr)

1. Calibration and volume mixing ratios (VMR) calculations

1.1 VOC present in the calibration gas standard

Calibration coefficients, also called normalized sensitivities (S_{norm}) were calculated for each atomic mass unit (amu, *m/z*) using the approach of Taipale et al., (2008). Normalized sensitivities S_{norm} were expressed in units of normalized counts/sec/ppbv (ncps/ppbv) as follows:

$$S_{norm} = \frac{I(RH_i^+)_{norm}}{VMR_{standar}}\ , \quad \text{(S1)}$$

$$I(RH_i^+)_{norm} = 10^6 \times \left(\frac{I(RH_i^+)}{m/z21*500+m/z37} - \frac{I(RH_i^+)_{zero}}{m/z21_{zero}*500+m/z37_{zero}}\right), \quad \text{(S2)}$$

where, $I(RH^{+}{}_{i})$ is the ion count signal at mass *m/z*$_{i}$ (units:cps), $I(RH^{+}{}_{i})_{zero}$ is the ion count signal at mass *m/z*$_{i}$ from the zero air (cps), *m/z* 21 and *m/z* 37 the counts of the primary ($H_3{}^{18}O^+$) and reagent clusters ($H_3{}^{16}O^+$ $H_2{}^{16}O^+$) (cps), *m/z* 21$_{zero}$ and *m/z* 37$_{zero}$ the counts of the primary and reagent clusters when measuring from the zero air (cps), $I(RH^{+}{}_{i})_{norm}$ the normalized ion count rate of $I(RH^+)$ (ncps) and VMR the volume mixing ratios (ppbv).

1.2 VOC not present in the calibration gas standard

We calculated the normalized sensitive $S_{norm\text{-}calculated}$ for VOC not present in our calibration gas standard (acetic acid and hydroxyacetone) using the procedure described by De Gouw and Warneke (2006). Transmission coefficients for RH^+ and H_3O^+ ions were determined from the PTR-MS transmission curve established by Ionicon engineers in the same configuration we operated the PTR-MS (U_{drift}=600V, P_{drift}=2.2V) during the campaign. $S_{norm\text{-}calculated}$ was expressed as follows:

$$S_{norm\_calculated} = \frac{T(RH^{+}{}_{i})}{T(H_3O^+)} \times k_i \times \frac{L^2 \times P_{drift}{}^2 \times Na \times T_{std}{}^2}{10^3 \times U_{drift} \times \mu_0 \times V_m \times P_{std}{}^2 \times T_{drift}{}^2} \qquad \text{(S3)}$$

where $T(RH^{+}{}_{i})$ and $T(H_3O^+)$ are the transmission efficiencies for RH^+ and H_3O^+ ions, respectively, k_i (cm^3 s^{-1}) are the proton transfer reaction rate coefficients taken from Zhao and Zhang (2004), L (9.2 cm) is the drift length, U_{drift} (600V) is the drift voltage, P_{drift} and T_{drift} are the pressure and temperature in the drift tube (2.2 mbar and 333.15 K respectively), P_{std} and T_{std} are the standar pression and temperature (1013 mbar and 273.15 K respectively], μ_o (2.8 cm^2 Vs^{-1}) is the reduced mobility of the primary ion and V_m (22400 cm^3) is the molar volume.

In both cases, VMR were calculated as the ratio of the normalized count rate of ions detected to the normalized sensitivity.

$$VMR = \frac{I(RH_i^+)_{norm}}{S_{norm}} \quad \text{or} \quad VMR = \frac{I(RH_i^+)_{norm}}{S_{norm\_calculated}} \qquad \text{(S4)}$$

However, due to the uncertainties associated to the proton transfer reaction rate coefficients k_i and the relative transmission curve, the accuracy of the calculated data using the calculated sensitivity $S_{norm\text{-}calculated}$ is significantly lower than the accuracy of the data based on the measured normalized sensitivities after gas calibration.

2. PTR-MS based water vapour flux measurements and comparison with a reference system.

Water vapour concentrations and fluxes were measured using a standard reference system based on the combination of a closed path infrared gas analyzer (IRGA, Model 7000, Li-COR) and the sonic anemometer. Both instruments were set to a sampling frequency of 20 Hz. Ambient air close to the sonic sensor head was continuously sampled through the main line (inlet at 10 m) leading to the IRGA instrument. Fluxes were calculated by the eddy covariance (EC) method, as implemented before by Loubet et al., (2011). Additionally a high frequency losses corrections was implemented based on the co-ogive method as in (Ammann et al., 2006)

EC water vapour fluxes from the standard reference system were also compared to DEC water vapour fluxes derived from the signal at *m/z* 37 of the PTR-MS (Ammann et al., 2006). The same anemometer was used for the DEC flux measurements with the PTR-MS as for the IRGA system.

In the PTR-MS, water vapour was detected at *m/z* 37, a mass corresponding to the cluster ion H_3O^+ H_2O^+ present in the drift tube. Water clusters in the drift tube originate from the ion source but also from the water vapour in the sample air. It is expected that the contribution of the ion source to the *m/z* 37 is relatively constant and thus, there is a quantitative relationship between the signal at *m/z* 37 and the concentration of the water vapour (Ammann et al., 2006). Ion counts at *m/z* 37 were calibrated against the reference IRGA concentration, in order to investigate the relationship between the *m/z* 37 signal and the water vapour concentration in the sampled air (Fig. S1).

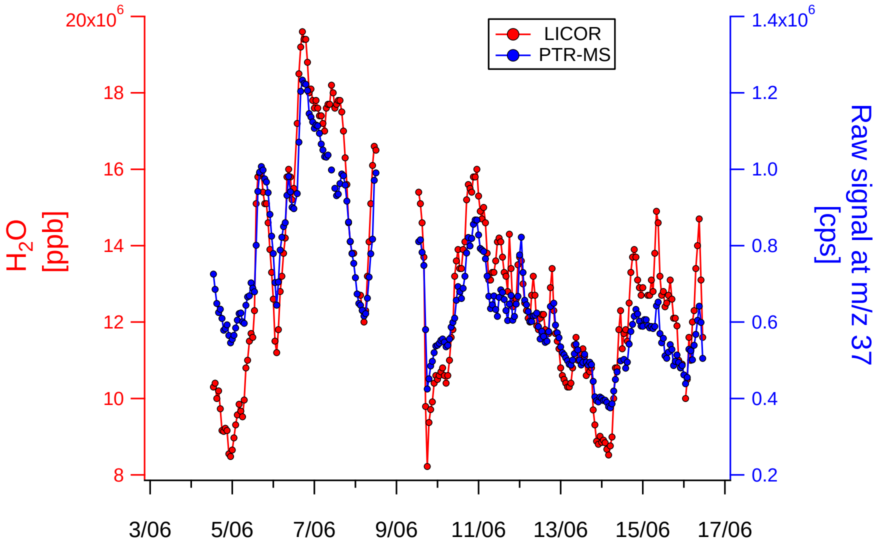

Figure S1. Time series of the PTR-MS *m/z* 37 signal (units: cps) and of water vapour as measured by the closed path infrared gas analyser IRGA.

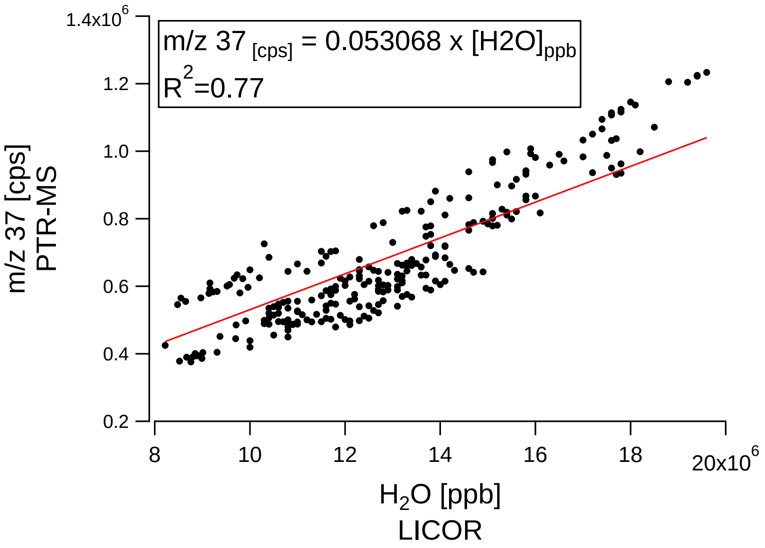

Figure S2. Relationship between the PTR-MS *m/z* 37 signal (units: cps) and the water vapour concentration (units: ppb) as measured by the closed path infrared gas analyser IRGA.

The raw signal at *m/z* 37 showed a linear relationship to the IRGA water vapour concentration with a coefficient of determination, R^2, of 0.77. The following equation was used for the calibration of water vapour concentration against the *m/z* 37 signal:

$$[H_2O]_{ppb} = m/z\,37_{cps} \times \frac{1}{0.053} \qquad \text{(S5)}$$

After calibration, *m/z* 37 fluxes were calculated in g.m^{-2}.s^{-1} with the same LabVIEW algorithm used for the other VOC fluxes and then converted in latent heat fluxes LE (units: W.m^{-2}) using the latent heat of evaporation constant (Lv =2400 J g^{-1} at 25°C) :

$$LE_{W.m^{-2}} = LE_{J\,s^{-1}\,m^{-2}} = F(water)_{g\,m^{-2}\,s^{-1}} \times Lv_{J\,g^{-1}} \quad \text{(S6)}$$

The resulting calibrated PTR-MS based latent heat fluxes are plotted along the IRGA fluxes in Fig S3.

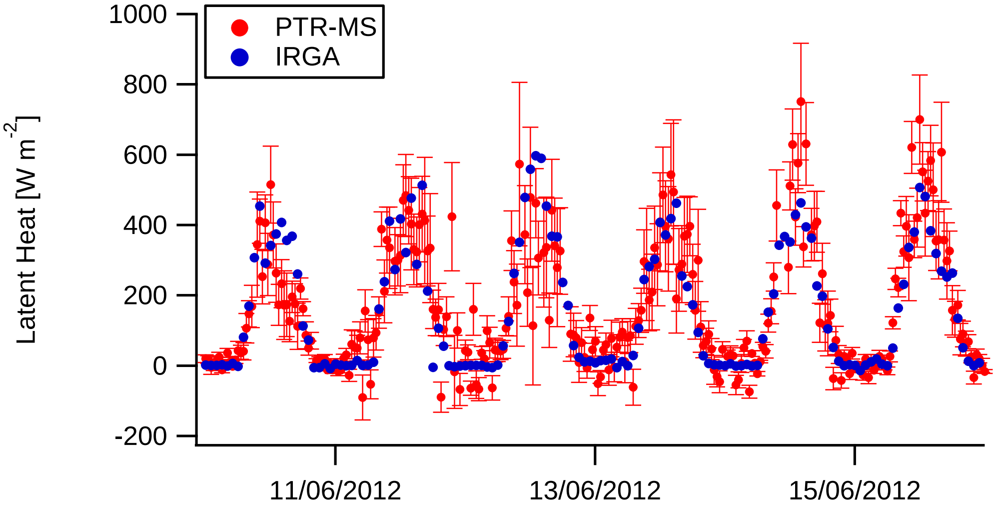

Figure S3. Time series of the PTR-MS based and IRGA latent heat fluxes

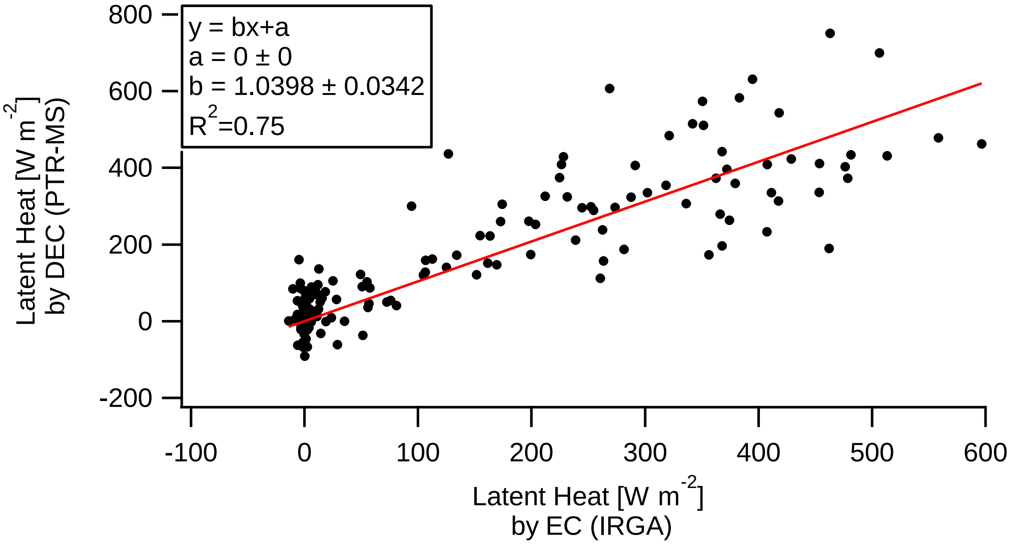

Figure S4. Relationship between the latent heat as measured by the PTR-MS and the closed path infrared gas analyser IRGA.

Water vapour fluxes obtained with the PTR-MS were highly comparable to the results of the IRGA reference system. A linear relation was found between the latent heat measured by DEC (PTR-MS) and conventional EC (IRGA), with a coefficient of correlation, R^2, of 0.75. This good agreement supports our PTR-MS eddy flux measurements of VOCs.

3 Comparison between DEC fluxes and vertical concentration gradients

Isoprene fluxes derived by DEC were also compared to the vertical gradient of isoprene concentration inside the canopy multiplied by the friction velocity:

$$u^* \times \frac{\partial C}{\partial z} = u^* \times \frac{c_{iso(2m)} - c_{iso(10m)}}{|z_{2m} - z_{10m}|} \qquad \text{(S7)}$$

Although one cannot quantitatively derive a flux from the gradient method, because the lower measurement height was not only within the roughness sublayer, but also located below some of the sources inside the canopy, the correlation found was fairly strong (R^2 = 0.6), lending further confidence to the DEC flux measurements (Figure S5). Here, the measured gradient stands for a proxy of the above-canopy gradient and u_* as a proxy for the eddy-diffusivity, which in reality depends further on atmospheric stability.

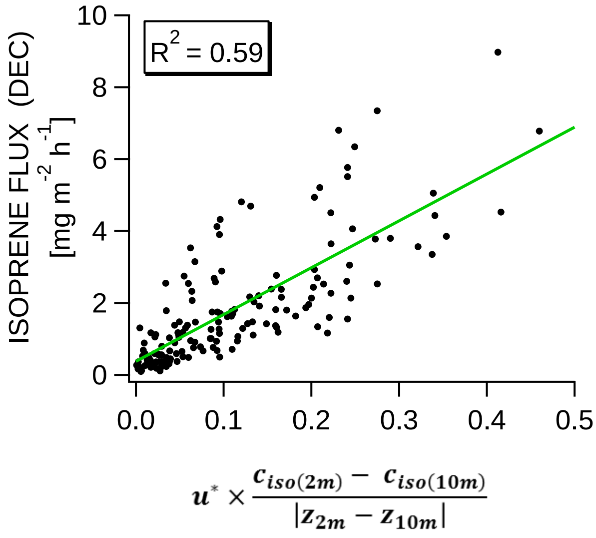

Figure S5. Correlation between isoprene fluxes measured above the canopy by DEC and the gradient of isoprene concentration (between 2 m and 10 m) multiplied by the friction velocity.

4 Time τ for diffusion transport of a trace gas

The turbulent transport time τ between the measurement height (z_{ref}) and the ground surface can be expressed as the transfer resistance through each layer multiplied by the layer height (Garland, 1977).

$$\tau = \tau_{in\_canopy} + \tau_{above\_canopy} \qquad \text{(S8.1)}$$

$$= Ra_{canopy} \, . \left(d + z_{0(M)}\right) + Ra_{zref} \, (z_{ref} - d - z_{0(M)}) \; \text{(S8.2)}$$

where d is the canopy displacement height and z_0 is the canopy roughness length. Estimates from the literature gives d =0.7*h_c where h_c is the canopy height, and $z_{0(M)}$ = 0.13*h_c . Turbulent resistances within and above the canopy, Ra_{canopy} and Ra_{zref} respectively, are expressed as:

$$Ra_{canopy} = \frac{h_c . \exp^{\propto_u}}{\propto_u . K_m(h_c)} \, . \left(\exp \frac{-\propto_u . z_{0(s)}}{h_c} - \exp \frac{-\propto_u . (d + z_0)}{h_c} \right) \qquad \text{(S9.1)}$$

$$Ra_{zref} = \frac{1}{k^2 \, . u(z_{ref})} \, . \left(\ln \frac{z_{ref} - d}{z_{0(T)}} - \Psi_H \left(\frac{z_{ref} - d}{L} \right) \right) . \left(\ln \frac{z_{ref} - d}{z_{0(M)}} - \Psi_M \left(\frac{z_{ref} - d}{L} \right) \right) \; \text{(S9.2)}$$

where k(=0.4) is the von Kármán constant, $z_{0(M)}$ and $z_{0(T)}$ are the canopy roughness lengh for temperature and momentum, $z_{0(s)}$ (=0.02 m; (Personne et al., 2009)) is the ground surface roughness length below the canopy; $\propto_u$ is the attenuation coefficient for the decrease of the wind speed inside the canopy, defined as LAI/2 (Yi, 2008), $K_m(h_c)$ is the eddy diffusivity at the canopy height; and Ψ_M and Ψ_M are dimensionless stability correction functions for heat and momentum (Dyer, 1974).

In the current study the transport time was estimated to be in the range of 30-60 s in daytime.

References

Ammann, C., Brunner, A., Spirig, C., Neftel, A., 2006. Technical note: Water vapour concentration and flux measurements with PTR-MS. Atmospheric Chemistry and Physics 6, 4643–4651.

De Gouw, J., Warneke, C., 2006. Measurements of volatile organic compounds in the earth’s atmosphere using proton-transfer-reaction mass spectrometry. Mass Spectrometry Reviews 26, 223–257.

Dyer, A.J., 1974. A review of flux-profile relationships. Boundary-Layer Meteorol 7, 363–372.

Garland, J.A., 1977. The Dry Deposition of Sulphur Dioxide to Land and Water Surfaces. Proc. R. Soc. Lond. A 354, 245–268.

Loubet, B., Laville, P., Lehuger, S., Larmanou, E., Fléchard, C., Mascher, N., Genermont, S., Roche, R., Ferrara, R.M., Stella, P., Personne, E., Durand, B., Decuq, C., Flura, D., Masson, S., Fanucci, O., Rampon, J.-N., Siemens, J., Kindler, R., Gabrielle, B., Schrumpf, M., Cellier, P., 2011. Carbon, nitrogen and Greenhouse gases budgets over a four years crop rotation in northern France. Plant Soil 343, 109–137.

Personne, E., Loubet, B., Herrmann, B., Mattsson, M., Schjoerring, J.K., Nemitz, E., Sutton, M.A., Cellier, P., 2009. SURFATM-NH3: a model combining the surface energy balance and bi-directional exchanges of ammonia applied at the field scale. Biogeosciences 6, 1371–1388.

Taipale, R., Ruuskanen, T.M., Rinne, J., Kajos, M.K., Hakola, H., Pohja, T., Kulmala, M., 2008. Technical Note: Quantitative long-term measurements of VOC concentrations by PTR-MS – measurement, calibration, and volume mixing ratio calculation methods. Atmos. Chem. Phys. 8, 6681–6698.

Yi, C., 2008. Momentum Transfer within Canopies. Journal of Applied Meteorology and Climatology 47, 262–275.

Zhao, J., Zhang, R., 2004. Proton transfer reaction rate constants between hydronium ion (H< sub> 3</sub> O< sup>+</sup>) and volatile organic compounds. Atmospheric Environment 38, 2177–2185.