SUPPLEMENTARY MATERIAL OF THE ARTICLE:

Contrasting winter and summer VOC mixing ratios at a forest site in the Western Mediterranean Basin: the effect of local biogenic emissions

Roger Seco[1], Josep Peñuelas[1], Iolanda Filella[1], Joan Llusià[1], Roberto Molowny-Horas[2], Simon Schallhart[3], Axel Metzger[4], Markus Müller[3], Armin Hansel[3]

1. Relationships between variables

The correlation coefficients between all the available data variables (VOC mixing ratios, wind, temperature, solar radiation, and NO_2 and O_3) were calculated to conduct a preliminary screening of possible relationships (see table S1). For this purpose the Statistica (StatSoft Inc., Tulsa, USA) package was used.

In addition, wavelet analysis was applied to analyze the relationship between VOC mixing ratios and ozone concentrations in summer. Wavelet analysis is best suited for studying transient signals (oscillatory or non-oscillatory), or signals whose amplitude varies in time. This method is widely used in the field of general signal processing, in cases where the signal is localized both in time and frequency (Torrence and Compo 1998). Since we are interested in the relationship between transient signals that may be present in two different time series, we have calculated the crosswavelet transform and wavelet coherence pairwise to the dataset (for an introduction to this topic, see Grinsted et al. 2004). The wavelet coherence can be thought of as a "localized correlation coefficient in time frequency space" (Grinsted et al. 2004). The calculations have been performed in MATLAB R2009b (MathWorks, Natick, MA, USA).

The wavelet analysis with ozone and VOC mixing ratios in summer showed that the maximum coherence between the two signals occurred with a period of one day (i.e. ozone correlated with VOC data as regards having a similar daily cycle). The phase between each VOC and ozone was different however. OxVOCs and aromatics were in general in phase (i.e. their mixing ratios and ozone concentrations varied simultaneously), whereas monoterpene levels peaked before those of ozone. Fig. S1 shows the cross wavelet analysis output graphs corresponding to acetic acid (representing oxVOCs), benzene (representing aromatics) and monoterpenes. Acetic acid showed an additional correlation with ozone, with a period of around half a day, in some days of the first half (up to the 2nd of August) of the measures (Fig. S1). This could be attributed to a small rise in both compounds taking place at night.

Table S1. Correlation coefficients between 60-minute averages of VOCs, ozone, nitrogen dioxide and meteorological variables for both periods of the campaign: winter (lower-left side of the table) and summer (upper-right part). All numbers shown are significant ($p < 0.01$) Pearson's correlation coefficients ($353 \leq n \leq 608$ for winter; $343 \leq n \leq 348$ for summer). Wind data has been divided into its wind direction vectorial components (x and y) weighted by the wind speed. ns = not significant.

Sum Win	Acetaldehyde	Acetic acid	Acetone	Formic acid/ ethanol	Methanol	Isoprene	MVK/ MACR	Monoterpenes	Benzene	Toluene	C8-aromatics	Acetonitrile	O_3	NO_2	Solar rad.	Temp.	Wind (x, y)
Acetaldehyde	-	0.86	0.88	0.77	0.65	0.72	0.86	0.51	0.86	0.83	0.80	0.41	0.55	0.76	0.47	0.58	0.46, -0.49
Acetic acid	0.91	-	0.93	0.92	0.72	0.72	0.80	0.58	0.80	0.77	0.67	0.50	0.80	0.66	0.56	0.78	0.48, -0.54
Acetone	0.89	0.91	-	0.88	0.73	0.75	0.83	0.60	0.83	0.77	0.67	0.52	0.72	0.63	0.55	0.73	0.51, -0.56
Formic acid/ ethanol	0.94	0.91	0.85	-	0.65	0.80	0.79	0.72	0.76	0.74	0.59	0.44	0.81	0.58	0.71	0.89	0.58, -0.65
Methanol	0.80	0.88	0.87	0.77	-	0.54	0.58	0.51	0.54	0.54	0.47	0.34	0.42	0.44	0.37	0.50	0.35, -0.38
Isoprene	0.81	0.76	0.72	0.81	0.62	-	0.83	0.88	0.76	0.77	0.63	0.37	0.61	0.56	0.75	0.80	0.73, -0.76
MVK/MACR	0.94	0.89	0.86	0.90	0.79	0.88	-	0.61	0.81	0.80	0.75	0.31	0.58	0.68	0.51	0.68	0.54, -0.57
Monoterpenes	0.72	0.70	0.63	0.73	0.56	0.66	0.66	-	0.57	0.61	0.40	0.32	0.53	0.31	0.84	0.79	0.72, -0.78
Benzene	0.68	0.58	0.58	0.70	0.34	0.75	0.69	0.54	-	0.89	0.83	0.51	0.60	0.80	0.53	0.63	0.52, -0.55
Toluene	0.76	0.74	0.67	0.85	0.52	0.81	0.75	0.68	0.83	-	0.93	0.46	0.49	0.86	0.54	0.63	0.49, -0.53
C8-aromatics	0.69	0.69	0.60	0.79	0.46	0.78	0.70	0.63	0.81	0.98	-	0.41	0.33	0.89	0.32	0.44	0.34, -0.36
Acetonitrile	0.72	0.76	0.82	0.68	0.80	0.65	0.71	0.55	0.43	0.57	0.52	-	0.51	0.37	0.35	0.42	0.29, -0.30
O_3	0.25	0.35	0.48	0.20	0.42	ns	0.14	0.16	ns	-0.16	-0.22	0.35	-	0.38	0.59	0.82	0.50, -0.57
NO_2	0.70	0.60	0.56	0.74	0.40	0.71	0.68	0.55	0.78	0.91	0.93	0.43	-0.16	-	0.28	0.42	0.32, -0.32
Solar radiation	0.14	0.13	0.12	0.11	0.14	0.13	0.15	0.22	ns	ns	ns	ns	0.19	ns	-	0.82	0.64, -0.76
Temperature	0.57	0.59	0.60	0.49	0.70	0.38	0.51	0.55	ns	0.23	0.17	0.60	0.47	0.21	0.28	-	0.57, -0.69
Wind (x, y)	0.28, -0.38	0.29, -0.40	0.32, -0.40	0.26, -0.36	0.28, -0.37	0.21, -0.24	0.22, -0.30	0.45, -0.52	0.16, -0.16	0.22, -0.23	0.17, -0.18	0.23, -0.28	0.17, -0.32	0.24, -0.22	ns, -0.22	0.35, -0.49	-

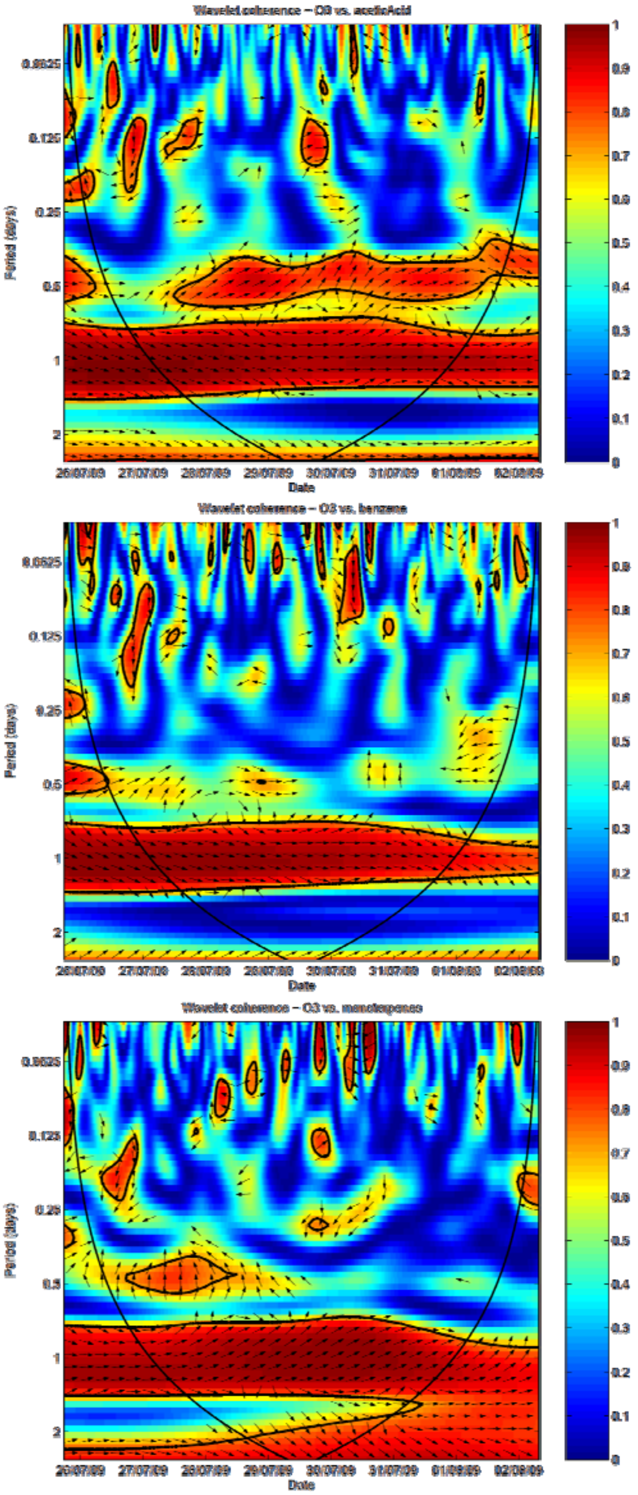

Fig. S1. Cross wavelet analysis output using ozone concentration data versus VOC mixing ratios: acetic acid (top panel), benzene (middle panel) and monoterpenes (bottom panel) mixing ratios. It shows the coherence in a scale from 0 to 1, the latter representing complete coherence between the two signals. In those areas enclosed by a thick line the coherence is significantly ($p<0.05$) different from zero, as calculated via 1000 Monte carlo simulations (Grinsted et al., 2004). Superimposed to the coloured diagrams there are arrows whose direction is related to the phase between the signals. An arrow pointing to the right corresponds to two signals which are in-phase. If the arrow points downward, ozone leads the VOC by 90º, whereas if it points upward it is the VOC that leads ozone concentration by 90º.

2. VOC to NO_x ratios and ozone formation

The relationship between O_3, NO_x and VOCs is driven by complex nonlinear photochemistry (Atkinson 2000). The ozone concentration measured at MSY is the result of photochemical production that has occurred over several hours (Sillman 1999) in the air masses advected to MSY. These air masses, loaded with pollutants from the metropolitan area of Barcelona, mix with the new biogenic VOCs locally emitted at MSY, and this mixing process may enhance the production of ozone. Ozone production depends on the VOC/NO_x ratio of the air (Finlayson-Pitts and Pitts 1993). It has been reported that a ratio below 4 is characteristic of VOC-sensitive conditions, when an increase in the concentration of VOCs leads to higher production of ozone. The contrary situation, a ratio above 15 defines NO_x-sensitive situations, those where an increase in NO_x levels promotes ozone formation. Ratios between 4 and 15 are those that are better suited for ozone production, with an optimum at ratios around 8.

Fig. S2 shows the average time course of VOC to NO_x ratios at MSY. In winter, almost all day the ratios are in the optimum range for ozone production. In summer, the MSY valley atmosphere in the early morning has NO_x-sensitive conditions (VOC/NO_x > 15) due to the high local biogenic emissions and the low concentrations of NO_x, that may change to more favorable conditions for ozone production when the breeze advects NO_x from the metropolitan area (NO_x start arriving at around 10:00 h).

It should be noted that these calculations have been performed taking into account

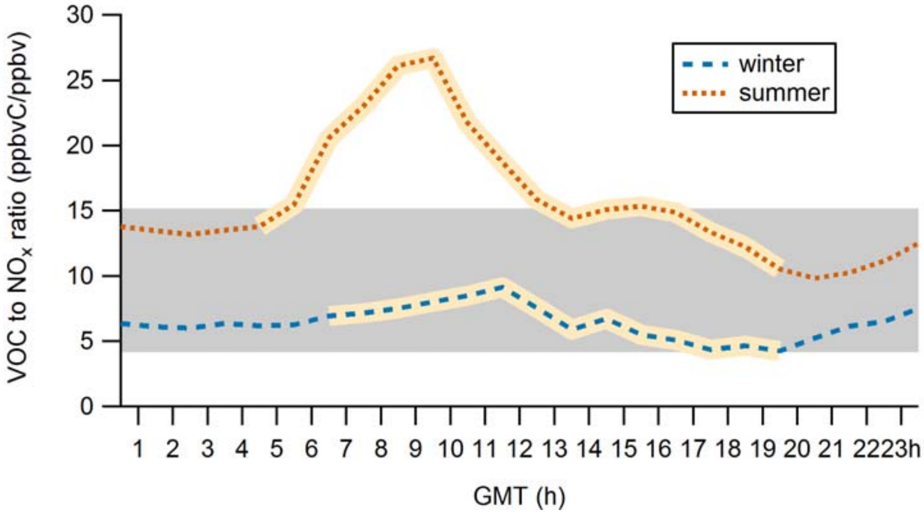

Fig. S2. Mean daily cycle of VOC to NO_x ratios at MSY in winter and summer. The shaded area corresponds to the ratios between 4 and 15, which better promote the formation of ozone. Ratios below 4 define a VOC-sensitive situation, and ratios above 15 correspond to NO_x-sensitive conditions. The highlighted part of the traces indicates when solar radiation is present and thus ozone production can occur. The calculations used here only take into account the VOCs discussed in the paper.

only the VOCs discussed in this paper, and so these VOC to NO_x ratios should be considered minimum estimates.

3. Comparison of VOC mixing ratios with values reported in the literature

Table 3 of the main paper displays published mixing ratios of different VOCs measured at natural environments such as Nordic forests, other mixed forests, and a Mediterranean location.

In Nordic environments, like the boreal forest of Hyytiälä (Finland) or a sub-artic wetland in Sweden, oxVOCs (methanol, acetone and acetaldehyde) were in the same order of magnitude but somewhat lower than at MSY, both in winter and summer, and isoprenoids were similar in winter and clearly lower in summer. Only some occasional peaks of these VOCs were similar or higher than at MSY (Holst et al. 2010, Lappalainen et al. 2009, Rinne et al. 2005, Ruuskanen et al. 2009). These results are in accordance with the lower temperatures found in Scandinavia (which prompt lower physiological activity of the vegetation, resulting in minor VOC emissions) compared to MSY. One of these studies found very similar benzene mixing ratios to MSY, both in winter and in summer in Hyytiälä, Finland, while reported values for acetonitrile were very low in summer, even less than those at MSY in winter (Ruuskanen et al. 2009).

Jordan et al. (2009) have recently published a long-term study of VOCs at a rural area near the coast in New Hampshire (East USA). The oxVOC mixing ratios reported were generally lower than at MSY in both seasons, with the exception of acetaldehyde in winter that was within the lower range of the MSY values. Monoterpene average mixing ratios were higher in winter and also in spring than those at MSY in winter, while in summer they were in the same range of values as at MSY. Isoprene and MVK/MACR, in turn, were in the same range of values as at MSY for both seasons but with slightly higher mixing ratios. In addition, isoprene and MVK/MACR daily cycles peaked during the daytime, as opposed to monoterpenes which had a nighttime maximum. Benzene measurements were in the range of MSY but with higher medians for both seasons, together with toluene and C8-aromatics in the same range, but generally lower medians. Finally, winter and spring mixing ratios of acetonitrile were similar to the MSY winter ratios, while summer acetonitrile mixing ratios were lower than at MSY.

Mielke et al. (2010) have also reported that monoterpene mixing ratios were at a maximum during the night in a mixed forest in Michigan (USA) in summer, with values that were lower in average but higher at night than those at MSY. A different mixed forest in Jülich (NW Germany) presented similar minimum methanol averages but higher maximum methanol mixing ratios in summer compared to MSY, and lower values of monoterpenes, with the maximum at midday (Spirig et al. 2005). Both mixed forests at Michigan and Germany had higher midday isoprene mixing ratios than MSY in summer, with spikes up to 9 ppbv in the case of Jülich. For another German mixed forest near the city of Frankfurt reported isoprene summer mixing ratios were in the range of those at MSY, while the levels of aromatics were higher in summer than at MSY, with the exception of toluene that was within the same range (Steinbrecher et al. 2000).

For comments on the Mediterranean location, please refer to the main paper.

References

Atkinson, R.: Atmospheric chemistry of VOCs and NOx, Atmos. Environ., 34, 2063-2101, 2000.

Finlayson-Pitts, B. J. and Pitts, J. N.: Atmospheric Chemistry of Tropospheric Ozone Formation - Scientific and Regulatory Implications, J. Air Waste Manage. Assoc., 43, 1091-1100, 1993.

Grinsted, A., Moore, J. C. and Jevrejeva, S.: Application of the cross wavelet transform and wavelet coherence to geophysical time series, Nonlinear Processes in Geophysics, 11, 561-566, 2004.

Holst, T., Arneth, A., Hayward, S., Ekberg, A., Mastepanov, M., Jackowicz-Korczynski, M., Friborg, T., Crill, P. M. and Backstrand, K.: BVOC ecosystem flux measurements at a high latitude wetland site, Atmos. Chem. Phys., 10, 1617-1634, 2010.

Jordan, C., Fitz, E., Hagan, T., Sive, B., Frinak, E., Haase, K., Cottrell, L., Buckley, S. and Talbot, R.: Long-term study of VOCs measured with PTR-MS at a rural site in New Hampshire with urban influences, Atmos. Chem. Phys., 9, 4677-4697, 2009.

Lappalainen, H. K., Sevanto, S., Bäck, J., Ruuskanen, T. M., Kolari, P., Taipale, R., Rinne, J., Kulmala, M. and Hari, P.: Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors, Atmos. Chem. Phys., 9, 5447-5459, 2009.

Mielke, L. H., Pratt, K. A., Shepson, P. B., McLuckey, S. A., Wisthaler, A. and Hansel, A.: Quantitative Determination of Biogenic Volatile Organic Compounds in the Atmosphere Using Proton-Transfer Reaction Linear Ion Trap Mass Spectrometry, Anal. Chem., 82, 7952-7957, 2010.

Rinne, J., Ruuskanen, T. M., Reissell, A., Taipale, R., Hakola, H. and Kulmala, M.: On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem, Boreal Environ. Res., 10, 425-436, 2005.

Ruuskanen, T. M., Taipale, R., Rinne, J., Kajos, M. K., Hakola, H. and Kulmala, M.: Quantitative long-term measurements of VOC concentrations by PTR-MS: annual cycle at a boreal forest site, Atmos. Chem. Phys. Discuss., 9, 81-134, 2009.

Sillman, S.: The relation between ozone, NOx and hydrocarbons in urban and polluted rural environments, Atmos. Environ., 33, 1821-1845, 1999.

Spirig, C., Neftel, A., Ammann, C., Dommen, J., Grabmer, W., Thielmann, A., Schaub, A., Beauchamp, J., Wisthaler, A. and Hansel, A.: Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry, Atmos. Chem. Phys., 5, 465-481, 2005.

Steinbrecher, R., Klauer, M., Hauff, K., Stockwell, W. R., Jaeschke, W., Dietrich, T. and Herbert, F.: Biogenic and anthropogenic fluxes of non-methane hydrocarbons over an urban-impacted forest, Frankfurter Stadtwald, Germany, Atmos. Environ., 34, 3779-3788, 2000.

Torrence, C. and Compo, G. P.: A practical guide to wavelet analysis, Bull. Am. Meteorol. Soc., 79, 61-78, 1998.