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

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## 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 | Acetal-dehyde | Acetic acid | Acetone | Formic acid/ethanol | Metha-nol | Isoprene | MVK/MACR | Mono-terpenes | Benzene | Toluene | C8-aromatics | Aceto-nitrile | $O_3$ | $NO_2$ | 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 | - |

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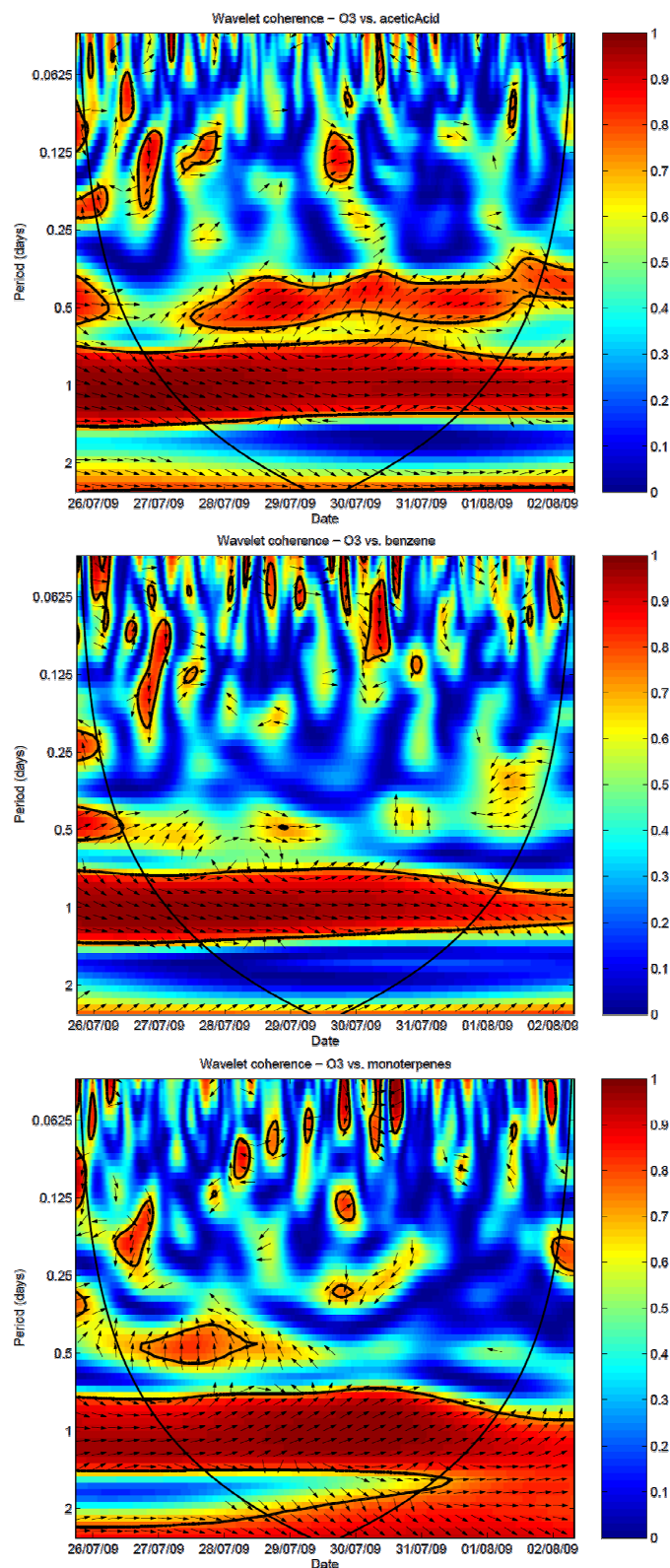
**Fig. S1**. Cross wavelet analysis output using ozone concentration data versus VOC mixing ratios: acetic acid (top panel), benzene (middle panel) and monoterpenes (bottom panel) mixing ratios. It shows the coherence in a scale from 0 to 1, the latter representing complete coherence between the two 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.

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

Table S2 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 photochemical activity and also 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.

**Table S2.** VOC mixing ratios (ppbv) reported in the literature for several natural environments (either Scandinavian ecosystems, other mixed forests and rural sites, or Mediterranean ecosystems). Numbers represent means or medians, while numbers in brackets represent maximum values reported by the authors. The numbers are followed by a letter to indicate the time of year when they were recorded (w for winter, s for summer). The Castelporziano Mediterranean values were obtained in May-June.

| Location | methanol | acetone | acetaldehyde | isoprene | monoterpenes | MVK/MACR | benzene | toluene | C8-aromatics | References |
|---|---|---|---|---|---|---|---|---|---|---|
| Hyytiälä forest (S Finland) | <0.7w 2s | <0.5w (4.5s) 1.5-1.7s | 0.16-0.33w 0.3s | 0.06w (0.5s) 0.14-0.2s | <0.1w 0.25-0.3s | | | | | [1]Lappalainen et al. (2009) |
| | 0.22w 1.9-3s | 0.33w 1.35-2.05s | 0.16w 0.25-0.39s | 0.05w 0.14-0.17s | 0.05-0.09w 0.29-0.37s | 0.07w 0.12-0.16s | 0.14w 0.04-0.07s | | | Ruuskanen et al. (2009) |
| | 3.5s (8.5s) | 1.5s (3.5s) | 1s (1.9s) | 0.1s (0.3s) | <1s (2.5s) | 0.1s (0.2s) | <0.05s (0.09s) | | | [2]Rinne et al. (2005) |
| sub-arctic wetland (N Sweden) | 2.8s (6s) | 1s (2.1s) | 0.2s (0.5s) | 0.38s (1.2s) | | | | | | Holst et al. (2010) |
| rural site with urban influences (New Hampshire, USA) | 0.97w 2.69s | 0.57w 2.11s | 0.33w 0.54s | 0.05w 0.42s | 0.10w 0.50s | 0.04w 0.33s | 0.20w 0.08s | 0.11w 0.14s | 0.10w 0.12s | Jordan et al. (2009) |
| mixed forest (Michigan, USA) | | | | 2s | 0.25s (0.97s) | | | | | [1]Mielke et al. (2010) |
| mixed deciduous forest (Jülich, NW Germany) | 13s (22s) | | | 2s (9s) | 0.5s (1s) | (0.4s (1.2s) | | | | [1,2]Spirig et al. (2005) |
| urban-impacted forest (Germany) | | | | (0.2-1.5s) | | | (0.5-2s) | (0.2-1.5s) | (0.5-1.5s) | [2]Steinbrecher et al. (2000) |
| Castelporziano Mediterranean ecosystem (Italy) | | 1.74 | 1.80 | 0.17-0.376 | | | 0.64 | 0.89 | | [1]Kalabokas et al. (1997) |
| | 1.6-3.5 | 0.96-2.1 | 0.44-1.3 | 0.1-0.14 | 0.13-0.30 | | | | | Davison et al. (2009) |
| Montseny (NE Spain) | 1.84w (9.76w) 4.92s (13.4s) | 1.1w (3.9w) 2.76s (5.95s) | 0.4w (1.88w) 0.78s (3.37s) | 0.04w (0.18w) 0.43s (1.25s) | 0.03w (0.23w) 0.64s (2.56s) | 0.02w (0.15w) 0.32s (1.04s) | 0.13w (0.47w) 0.05s (0.19s) | 0.18w (1.9w) 0.23s (1.34s) | 0.1w (1.33w) 0.17s (0.82s) | This study |

[1] These values correspond only to day-time or midday hours.
[2] Approximate values taken from graphs.

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