SUPPLEMENTARY MATERIAL OF THE ARTICLE:

Volatile Organic Compounds in the Western Mediterranean Basin: urban and rural winter measurements during the DAURE campaign

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1. Relationships between variables

The Pearson's correlation coefficients (*r*) 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.

Linear correlations between all of the VOC species showed variable correlation coefficients, but they were always significant ($p < 0.01$) above 0.52 at BCN and 0.34 at MSY, and with averages of 0.80 and 0.73 at BCN and MSY, respectively (Table S1). This demonstrates that all VOCs measured at each site showed similar diurnal trends.

Correlations between VOCs and other parameters were different at each site (Table S1). All the VOCs measured at BCN showed high correlations with NO_x ($0.60 < r < 0.85$) and quite high negative correlations with ozone ($-0.53 < r < -0.7$). This confirms that the main source of VOCs at the urban site can be linked to rush-hour traffic. Ozone, on the other hand, shows negative correlations because the emission of fresh NO promotes ozone scavenging through NO titration. In relation to meteorological parameters, VOCs at BCN showed some degree of correlation to wind, which may be linked to the sea breeze transporting air masses away from the city at the center of the day. VOCs at BCN had low or non significant correlations with solar radiation and temperature. The three oxVOCs reported plus isoprene and MVK/MACR showed low correlations with temperature and no correlation with solar radiation. On the contrary, monoterpenes and aromatics had no correlation with temperature and low negative correlations with solar radiation. Acetonitrile showed no correlation to neither of these two environmental parameters.

At MSY, VOCs generally showed good correlation to NO_2, as at BCN, but with lower values. Correlations with ozone were lower or inexistent. Wind and temperature correlations with VOCs were higher than at BCN, especially for oxVOCs, isoprenoids and acetonitrile. Correlation with solar radiation existed only for oxVOCs and isoprenoids.

Table S1. Correlation coefficients between 60-minute averages of VOCs, ozone, nitrogen oxides and meteorological variables for both locations of the campaign: MSY (lower-left side of the table) and BCN (upper-right part). All numbers shown are significant ($p < 0.01$) Pearson's correlation coefficients ($353 \leq n \leq 608$ for MSY; $321 \leq n \leq 400$ for BCN). Wind data has been divided into its wind direction vectorial components (x and y) weighted by the wind speed. ns = not significant. The data for MSY were previously reported in Seco et al. (2011).

MSY \ BCN	Acetal-dehyde	Acetic acid	Acetone	Ethanol	Metha-nol	Isoprene	MVK/ MACR	Mono-terpenes	Benzene	Toluene	C8-aromatics	Aceto-nitrile	O_3	NO	NO_2	Solar rad.	Temp.	Wind (x, y)
Acetaldehyde	-	0.78	0.87	-	-	0.82	0.86	0.71	0.81	0.84	0.76	0.81	-0.56	0.74	0.73	ns	0.18	0.25, -0.14
Acetic acid	0.91	-	0.88	-	-	0.72	0.77	0.52	0.70	0.71	0.67	0.67	-0.53	0.60	0.76	ns	0.44	0.42, -0.39
Acetone	0.89	0.91	-	-	-	0.85	0.87	0.73	0.83	0.86	0.80	0.85	-0.60	0.74	0.77	ns	0.30	0.32, -0.33
Ethanol	0.94	0.91	0.85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Methanol	0.80	0.88	0.87	0.77	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Isoprene	0.81	0.76	0.72	0.81	0.62	-	0.89	0.80	0.88	0.88	0.85	0.79	-0.62	0.80	0.77	ns	0.16	0.27, -0.19
MVK/MACR	0.94	0.89	0.86	0.90	0.79	0.88	-	0.75	0.87	0.87	0.83	0.78	-0.58	0.76	0.77	ns	0.24	0.31, -0.24
Monoterpenes	0.72	0.70	0.63	0.73	0.56	0.66	0.66	-	0.76	0.81	0.74	0.78	-0.69	0.70	0.71	-0.20	ns	0.18, ns
Benzene	0.68	0.58	0.58	0.70	0.34	0.75	0.69	0.54	-	0.92	0.95	0.79	-0.67	0.83	0.85	-0.17	ns	0.24, -0.14
Toluene	0.76	0.74	0.67	0.85	0.52	0.81	0.75	0.68	0.83	-	0.90	0.80	-0.70	0.84	0.84	-0.18	ns	0.25, -0.14
C8-aromatics	0.69	0.69	0.60	0.79	0.46	0.78	0.70	0.63	0.81	0.98	-	0.75	-0.65	0.78	0.83	-0.19	ns	0.19, -0.14
Acetonitrile	0.72	0.76	0.82	0.68	0.80	0.65	0.71	0.55	0.43	0.57	0.52	-	-0.61	0.68	0.71	ns	ns	0.18, -0.20
O_3	0.25	0.35	0.48	0.20	0.42	ns	0.14	0.16	ns	-0.16	-0.22	0.35	-	-0.58	-0.84	0.35	0.16	-0.17, ns
NO	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.69	ns	ns	ns, ns
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	-	-	-0.19	0.17	0.30, -0.28
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	-	0.73	ns, -0.41
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	-	0.41, -0.68
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	-

2. VOC and ozone relationships

2.1. 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. S1 shows the average time course of VOC to NO_x ratios at MSY and BCN during winter. At BCN, the higher local emissions of NO_x promoted the presence of VOC-sensitive conditions. At MSY, located farther away from the sources of NOx, almost all day the ratios were in the optimum range for ozone production.

It should be noted that these calculations have been performed taking into account only the VOCs discussed in this paper (moreover, BCN does not include methanol or ethanol), and so these VOC to NO_x ratios should be considered minimum estimates.

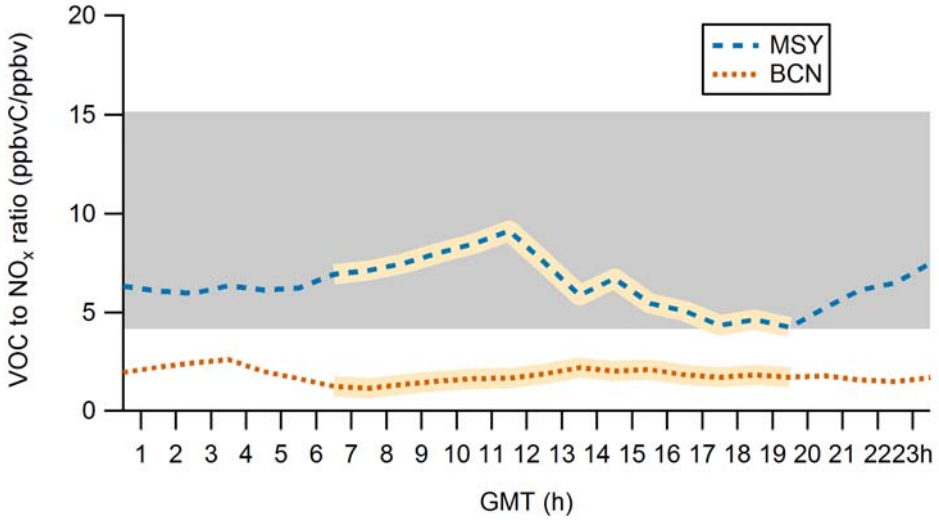

Fig. S1. Mean daily cycle of VOC to NO_x ratios at MSY and BCN in winter. The shaded area corresponds to the ratios between 4 and 15, which better promote the formation of ozone. Ratios below 4 define a VOC-sensitive situation, and ratios above 15 correspond to NO_x-sensitive conditions. The highlighted 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.

2.2. VOC species relative abundance and their ozone formation potential

According to their reactivity characteristics, each VOC has a different potential to produce ozone in the photochemical reactions in the atmosphere. To estimate and compare the relative contribution of the different VOCs to the formation of ozone at BCN, the ozone formation potentials of the different VOCs were calculated as the product of the individual VOC amount and its corresponding MIR (maximum incremental reactivity) factor (Carter, 1994). In this case, reactivities could be defined as the sensitivity of ozone concentration to the mass of individual organic compounds added to the air. The MIR values are useful in regions of high NO_x values, like BCN, because in the VOC-limited urban air mass the mixture is most sensitive to organic compounds due to low VOC to NO_x ratios. The MIR calculation does not take into account meteorological conditions or the importance of traffic and thus does not necessarily explain current ozone concentrations. However, it can still be used to identify species with high reactivities under certain conditions (Carter, 1994).

For MSY data, another reactivity scale was used: the Maximum Ozone Incremental Reactivity (MOIR, see Carter, 2010a). MOIR conditions are likely to happen at higher VOC to NO_x ratios than MIR, that are more favorable for ozone formation and more typical of aged urban air masses like the ones we detected at MSY. The MIR and MOIR factors used in our calculations were obtained from the documentation of the SAPRC-07 chemical mechanism developed by Carter (2010a, 2010b).

Fig. S2 displays the relative abundance of each VOC in relation to the other VOCs measured, both in terms of ppbv and of ppbv of carbon atoms. At BCN, as shown in the main text of this article (Fig. 3 and Table 2), several VOCs show similar average ppbv. With about 25-20% of the total measured ppbv, the dominant compounds are acetaldehyde, acetone, toluene and C8 aromatics. When the metric used is the relative amount of carbon atoms, aromatic VOCs stand out among the rest, and also monoterpenes contribute around 10-15% with their 10 atoms per molecule. It must be noted that BCN data do not include ethanol and methanol, and this absence is important since these are two of the most abundant VOCs at MSY. These two VOCs together with acetone account for about 70% of measured VOC ppbv at MSY (Fig. S2), with very small contributions from aromatics or isoprenoids. Carbon-wise, acetone is the major species at the rural site with around 20-30%, followed by other oxVOCs and with aromatics together summing up to 20-25%. With the low emissions of biogenic VOCs at MSY during winter, the main VOC species that are found in the atmosphere are long-

lived species like methanol, ethanol and acetone that can be easily transported over long distances.

The picture is quite different when looking at the reactivity with which each VOC species contributes to ozone formation (Fig. S3). At the BCN urban site, acetaldehyde alone contributes around 30-40% of the potential for ozone formation. The aromatics group contribute another 40-50%, followed by isoprene with around 10%. Of course that the share of methanol and ethanol, not measured at BCN, was not taken into account when calculating these percentages. At MSY, acetaldehyde shows the highest incremental reactivity of all VOCs measured, with around 30% of it. The short chain alcohols methanol and ethanol have around 20% each, highlighting their importance in new ozone production at the rural site. The remaining 20-30% of reactivity is due to acetone, acetic acid, and minor contributions of aromatics and isoprene.

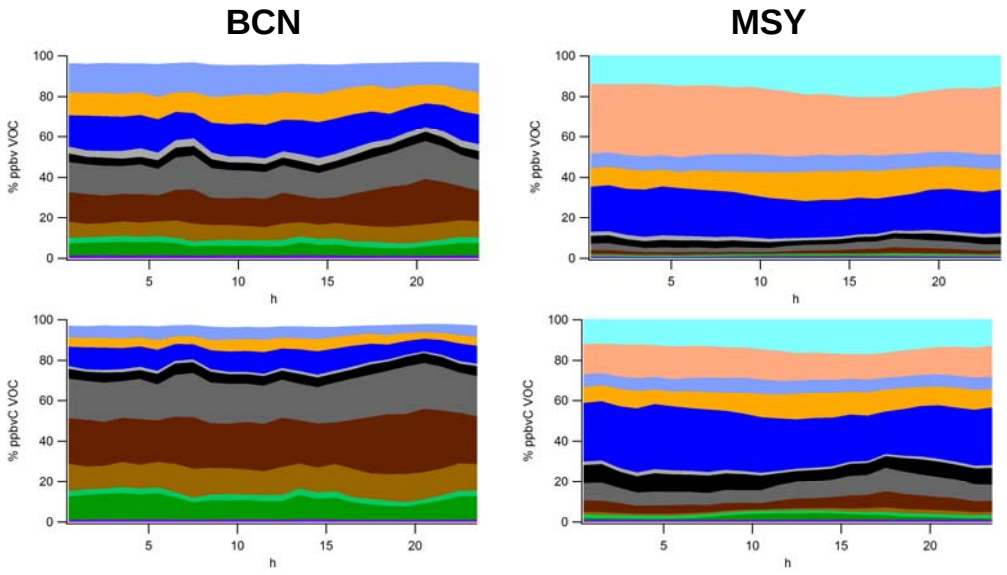

Fig. S2. Hourly mean abundance of each VOC species relative to the total VOC amount measured during the DAURE winter campaign at BCN (left panels) and MSY (right panels). The relative abundaces are shown in percent of VOC molecules (top panels) and percent of carbon atoms (bottom panels). The calculations used here only take into account the VOCs measured, and furthermore it has to be noticed that methanol and ethanol could not be correctly measured at BCN. See Fig. S3 for color legend.

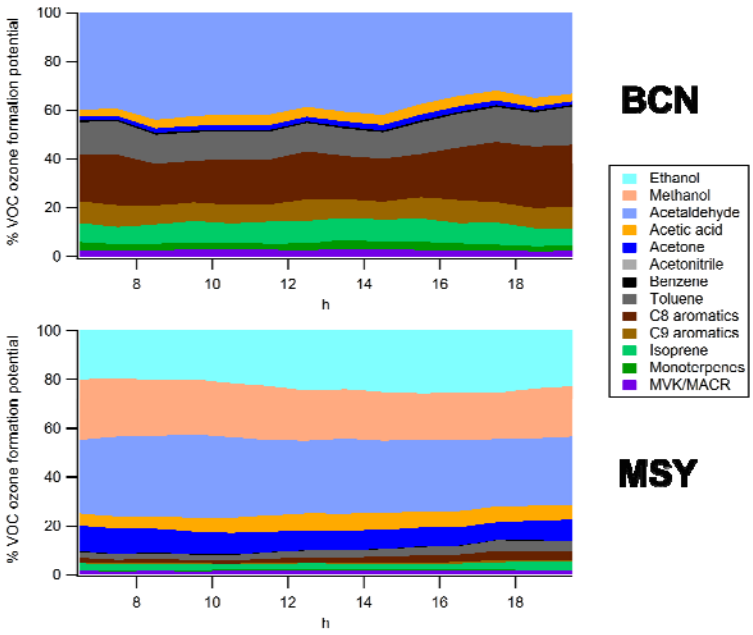

Fig. S3. Hourly mean ozone production incremental reactivity of each VOC species relative to the total VOC incremental reactivity calculated for the DAURE winter campaign at BCN (MIR scale, top panel) and MSY (MOIR scale, bottom panel). The calculations used here only take into account the VOCs measured, and furthermore it has to be noticed that methanol and ethanol could not be correctly measured at BCN.

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