

## ***Interactive comment on “Seasonal variation and origins of volatile organic compounds observed during two years at a western Mediterranean remote background site (Ersa, Cape Corsica)” by Cécile Debevec et al.***

**Anonymous Referee #1**

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This manuscript presents an analysis of the VOC concentrations and temporal trends over a 2 years long observation campaign at a remote site located in Corsica and representative of the northwest part of the Mediterranean background atmosphere. The monthly, seasonal and interannual variabilities of 21 NMHCs and 4 OVOCs are reported. Source apportionment using positive matrix factorization in combination with back trajectories analysis was carried out on a selection of 14 NMHC species. Not surprisingly, the five factors solution chosen fails to apportion the selected VOCs into their specific emission sources, as the air masses that reach the remote site are already

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mixed and processed. Finally, the NMHC temporal concentration trends are compared to those observed in the 17 other European background stations at the same period. Overall, while a significant spatial variability in concentration levels is found, especially in winter, similar seasonal trends are observed.

The work provides valuable scientific information as long term VOCs datasets in background sites are still rather scarce in the Mediterranean region. To my point of view this topic together with the comparison with the 17 other background sites located in Europe is the most interesting feature of the manuscript. On the other hand, I have some concerns regarding the added value brought by the PMF analysis on a limited set of VOCs and the relevance of the solution as meteorology (boundary layer, air mass circulation, temperature) seems to be the main factor driving the temporal trends in a remote background site. The authors should more clearly elaborate on the limits of the PMF with respect to the limited set of VOCs and samples in such a remote site. As a general comment on language and structure, I find the manuscript in its current state unnecessarily long. Topics are repeated saying pretty much the same thing in different sections. For example, many points raised in section 4.1 (Determination of controlling factors) have already been discussed in the section 3.5 (VOC factor analysis) and points raised in section 4.2 (The particular case of winter) have partly been discussed in section 4.1 when fall-winter interannual trends are discussed. Same remark for sections 3.3 and 3.5. Some sections lack clarity (see specific comments). Overall, I find it very difficult to extract the main messages of the sections/paragraphs.

A major revision according to these mentioned general comments is consequently required before publication to ACP.

Specific comments – The introduction could be shortened and focused on the scientific context and goals of the study. For example, information given on the various national and international programs is not essential here (Page 3, line 8-13 ; Page 3, line 32 to Page 4, line 4) – It appears that the biweekly samples were collected between 09h00-13h00 UTC for 7 months and between 12h00-16h00 UTC for 15 months.

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The authors should comment the sampling strategy and tell whether this sampling time shift could impact the PMF analysis and the interannual variations, especially for species with strong diurnal variations such as biogenic VOCs. – Page 6, o It is not clear when these additional 150 off-line air samples were taken; over the 2-year period? at which frequency? Also some of the VOCs listed (6 C6 - C11 n-aldehydes) are not discussed at all afterwards, why ? o line 8 “44 C5-C16” Check consistency with table 1 where 50 VOC are listed to be sampled with the solid adsorbent. – Page 7, section 2.2.3 (“Additional high frequency VOC measurements performed at Ersa”) and 3.4.4 : the information provided in this section is already given in Section S3 (“comparison of VOC measurements with other ones performed at Ersa”). I suggest removing this section from the main text and to merge it with S3 – Page 7, section 2.2.4 (“Concurrent VOC measurements performed at other..”) I would suggest shortening this section merge it with section 5. Both sections start with the same 4 lines. – Page 8, line 6 : could the authors elaborate on the choice of the VOCs included in the PMF ? This is a rather limited range of VOCs, compared to other studies (see for example Abeleira et al., 2017, 46 VOCs; Yuan et al., 2012, 73 VOCs). Can the authors provide a rough estimate of their contribution to the total VOCs mass concentration? – Page 8, lines 4-11 are duplicates of lines 22-29- from the Section S1 – Page 8 line 16-20 It is said that the PMF model results reconstructs on average 99% of the total concentration of the 14 selected species, but in the meantime 5 out of the 14 selected are not properly captured by the PMF solution. Also, ethane and propane account for 50% of the VOC mass. In these given circumstances, is the percentage of total reconstructed mass relevant to assess the quality of the PMF solution? It would be helpful to include more information on the PMF preprocessing, and on the diagnostic plots (Q/Q(exp) values vs number of factors, scatter plots of the measured vs reconstructed concentrations, scaled residuals, if and why outliers were removed from the time series, etc..) – I understand that species not properly reconstructed by the PMF model should be categorized as “weak” in the model. This is not the case here, as seen in Table 2, where none of the 14 species are indicated as “weak”. Could the

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author justify this choice? – Page 8, line 19 The authors specify that “PMF model limitations to explain these species should be kept in mind when examining PMF results”. A more detailed discussion would be helpful for the reader to appreciate the limits of the proposed PMF solution. A rough estimate based on figure 8 indicates that these species make up approximately 80% of the concentration of Factor 2 (short lived species). – Page 9, starting to line 32 to page 10, line 3 : It is unclear what you mean here : “tests that revealed that results only highlighted local contributions . . .” is it related to exploratory tests with empirical weighting function ? Was it finally decided to apply such a weighting function? – Page 9, line 28 Can the author explain the meaning of shortening the back-trajectories? – Page 9, line 24-25 Please rephrase this sentence as we understand that longer 3-day back trajectories were considered in order to be in the same conditions as Michoud et al. – Page 11, section 3.2 Air mass origins and table 3: it is not clear why trajectories categorized as long have median transit time always shorter than the trajectories categorized as short. – Page 14 section 3.4.3 Oxygenated VOCs: this section is hard to follow, line 14-26 are only general considerations with no direct link to the observations. Why not starting with the trends observed (end of line 26, “Formaldehyde and acetaldehyde concentrations. . .” and use some of the general information to support the discussion. Same comment for acetone and MEK – Page 17, 3.5.1 Biogenic source: “Local biogenic source” instead ? – Page 17, line 6 “troposphere is” instead of “troposphere was”? – Page 17, line 1: “to the sum of measured VOC concentrations” : do you include OVOC in this calculation ? Anyway, because the list of the VOCs included in the PMF is not exhaustive, the average individual contribution of each factors to the sum of the measured VOCs should be considered with care. – Line 20, The term “regional” is rather vague, can you indicate which geographical areas are included? – Page 20 “Towards the best experimental strategy to characterize variation in VOC concentrations” Large parts of this section are copy/paste of the section S4 of the SI (page 20, line 28 to page 21, line 2 ; similar to page 10 of the supporting information, lines 1-6 ; page 21, lines 8-19 similar to page 12 of the SI, lines 22-34) – Page 21, line 25 “are” instead

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of “were” – Page 21 line 25 starting at “Note that..” to line 28 : I suggest to remove this information, it is not essential and distracts the reader from the topic of the section – Page 22, line 6-8 The authors attribute the high contribution of factor 2 (related to short lived species) in spring and summer to relatively nearby sources. Have the authors checked if the correlation with CO was improved in these specific conditions? – Page 24, line 24 I don’t understand the meaning of the last sentence. Please rephrase “As a consequence, this finding . . . may be reflected. . .” – Page 25 line 18 Please rephrase “were also be taken..”

Literature cited Abeleira, A., Pollack, I. B., Sive, B., Zhou, Y., Fischer, E. V., and Farmer, D. K.: Source characterization of volatile organic compounds in the Colorado Northern Front Range Metropolitan Area during spring and summer 2015, *J. Geophys. Res.-Atmos.*, 122, 3595–3613, <https://doi.org/10.1002/2016jd026227>, 2017. Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, *J. Geophys. Res.-Atmos.*, 117, 117, D24302, <https://doi.org/10.1029/2012jd018236>, 2012

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