

RESPONSE TO THE REVIEWERS FOR MANUSCRIPT ACP-2011-400

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

We are very grateful to the reviewers for their comments and for their careful reading of the paper. We have addressed each one of the points raised, and have altered text, figures and tables wherever appropriate to address the concerns raised. We believe that this has improved the paper, and thank the reviewers for their time and effort in pointing out where improvements could be made.

We look forward to having the editor's approval to submit a revised manuscript to be considered for final publication in ACP.

The *referees' comments* followed by our responses (R) are below.

Anonymous Referee #1

1- Seco et al. report ambient VOC mixing ratios over a Mediterranean forest site. The site is strongly influenced by the local landscape and wind regimes which is interesting. Especially the switch between air masses affected by the Barcelona urban area during the day and the change during the night where air masses flow mostly in the opposite direction.

The weakest points of the manuscript are the problem of the measure in windspeed as that renders without any justification all argumentations on travel-times of air masses passing over the urban area to pure speculations and the lack of finalising argumentations conclusively. In many parts, the authors get stuck with referring to many possibilities but no clear statement of their own viewpoint.

R: We have now solved this question of windspeed measurement by using a new calibration of the sensor in which we took into account the nearby meteorological stations. This has allowed us to avoid speculations.

2- Page 20396, 23ff: Please describe the sampling procedure to the cartridges in more detail. Flow of the pump, time and amount sampled. Did you use an ozone scrubber or not?

R: The sampling procedure was performed once per hour from 6am to 9pm on selected days, in order to obtain a daytime hourly profile of monoterpene speciation. The flow of the pump was 500 mL/min for 20 minutes, without ozone scrubber. This information has been added to this section in the manuscript.

3- Page 20399, 1ff: You speak about the "Atlantic advection scenario"? What do you mean with that? Just winds from the western directions or was that a special period during the campaign? There is no discussion or further remarks on that later in the manuscript.

R: This was a special period during the campaign when high speed winds from the western direction cleaned the atmosphere in all the region. It is a typical atmospheric phenomenon that is frequently observed in this Mediterranean region. The DAURE campaign overview paper in preparation by Pandolfi et al. will further explain the characteristics of the atmospheric scenarios observed during the campaign. In addition, the meteorological overview paper for the DAURE campaign (Jorba et al. 2011), which provides more information about the synoptic conditions of the campaign, is already available in discussion stage in ACPD. This information has been added to the text to make clear to the readers what is the Atlantic advection scenario and where they can find more information about it.

4- Page 20399, 3ff: You refer to problems recording the wind speeds in summer, well, can you give any grading about the bias of that measurements then? If it's by the software and the recording took place as seen by your graphs, that might have been just a problem of a calibration factor? This is important as you refer to air mass travel times later in your argumentations.

R: The wind speed recordings took place, but there was a calibration factor problem that we have now tackled by calibrating with an interpolation of the three nearby meteorological stations. Moreover, previous research conducted at the same site showed that average summer wind speeds are at least in the same range of winter wind speeds. All this information has now been added to the revised version of the manuscript in the methods section (2.3).

5- Page 20399, 7ff: You use for most of the reported substances mixing ratios, would it make sense to also use them for ozone and NO_x instead of the concentrations? What is the reason to use concentrations here?

R: The reason for this is that the original data from the NO_x and O₃ measuring equipments was given in concentrations. We agree with the reviewer that it would make sense to use mixing ratios with O₃ and NO₂ data, so we have now converted these datasets into mixing ratios (ppbv) in all the graphs and text, in order to have all the gaseous data in the same units throughout the manuscript. Additionally, in the text we have also kept the information in $\mu\text{g m}^{-3}$ to allow comparison with other papers cited in the text.

6- Page 20399, 15ff: You state the measurements of NO was most time below detection limit, any comment why? The device you listed should be able to measure around 100 ppt which is two times the detection limit given by specs of the manufacturer and that is about a factor ten smaller than the detection limit you have offered here ($1 \mu\text{g m}^{-3}$).

R: The reason for this is that these data were gathered by the government air monitoring agency. Up to the moment that our measurement campaign was held, this agency had only used these type of analyzers in urban areas to check for pollutants being higher than the legal limits, so the software that recorded the half hour averages of the data was only prepared to store "high concentration" numbers, the kind of "high concentration" numbers usually measured in a polluted city like Barcelona. The measuring campaign reported in this paper served to the monitoring agency managers to realize that, for more remote areas as MSY, they should change the software in the near future. But unfortunately more accurate data was not available for us in this campaign.

7- Page 20400, 20ff: The part about the "linear correlations" is not very well understandable. What was correlated to what? Why it is needed? Are you sure that a linear correlation can be done? Correlation between light or temperature and BVOCs is obviously not linear. Why did you use Pearson's correlation coefficient and not another one which is more robust in case of non-linear relations?

R: As stated in the 2.4 section, linear correlations were used to conduct a preliminary screening, to detect variables that show high or low values at the same time. As a preliminary screening, the table with the correlation coefficients was included only in the supplementary material. Please notice that it is well known that BVOC emission rates are not linearly related to PFD or temperature but here we are dealing with BVOC air concentrations, not directly with emissions.

8- Page 20401, 22ff: As you refer to the global range of methanol mixing ratios it might be good to also tell your mixing ratios here, additional to the reference to the graph.

R: Following this suggestion we have added to the text the values of maximum methanol mixing ratios recorded during winter and summer at MSY. The new sentence now reads: "At MSY methanol reached the highest mixing ratios among the VOCs measured in both seasons (Fig. 8; Table 2), with peaks up to 9.7 ppbv in winter and 13.4 ppbv in summer".

9- Page 20402, 1ff: Do you have any number or percentage about the share between the biogenic and anthropogenic fractions of OxVOCs. Especially as your site is influenced by air masses that are originated or have passed the Barcelona urban area.

R: Indeed it would be really interesting to be able to distinguish between the biogenic and anthropogenic fractions of oxVOCs. Unfortunately, we do not have such a number or percentage.

10- Page 20402, 21ff: Here, you state that leaf level emission have been increased by one order of magnitude between winter and summer and that your ambient mixing ratios did a similar increase. The next sentences state that in that case this increase would have been inhibited and the final sentence on that page tells that the vegetation source must have been stronger than the photochemical sink. Are you sure that you can argue like that? Is it possible to translate an increase in emission one to one into an

increase in the mixing ratio? To my opinion, there are as well more processes such as dilution by mixing and transport (fast), changes in boundary layer height (slow) that play a role in that case.

R: Given the concerns raised by both reviewers about this part of the text, we have removed the sentence about the photochemical inhibition of the increment in isoprenoid VOC mixing ratios. However, the enhanced emission by the holm oak forests of MSY, specially in the case of monoterpenes must have influenced the 10x increase in isoprenoid mixing ratios as explained in the text. This species is known for its capacity to emit monoterpenes, and the leaf-level measurements performed during the campaign showed a 10x increase in the emissions. These leaf cuvette results are now being compiled in a paper (Llusà et al., 2011, in preparation) that will soon be submitted for publication. We agree with the referee that other factors such as dilution by mixing and transport (fast) and changes in boundary layer (slow) play a role too, and have included a comment on that in the revised manuscript.

11- Page 20403, 9ff: I suggest "... with lowest daily..." instead of "... with less daily..." here.

R: We have changed this word in the revised version of the text.

12- Page 20403, 13ff: The section on acetonitrile is somehow lacking a clear discussion point. What do you want to point out here? If there is just the 6% of fuel combustion originated, what consequence that may have? The double mixing ratio in summer, is that a hint to more extensive burning events in the area? What conclusions do you get here?

R: In this section we provided basic information regarding the known sources of acetonitrile for those readers unfamiliar with that subject. We have included the acetonitrile data in the paper for those readers that may be interested in knowing its mixing ratios during this study and commented that it is a hint to more extensive burning events in summer. Although it was not a main focus of study, we have now included some additional information in the revised text (see answer 6 to referee #2).

13- Page 20404, 11ff: I would say "... described by Perez et al. (2008)..." instead of "...described elsewhere..."

R: We have corrected this expression in the revised version of the text.

14- Page 20405, 1ff: Maybe give the VOC/NOx ratios, that would be some information to help assessing the discussions on the origin of ozone at the site.

R: We have now included in the Supplementary material a graph showing the VOC to NOx ratios for both seasons at MSY, together with a discussion about them. We have shortly commented it in the main text.

15- Page 20405, 5ff: In the discussion on the ozone concentrations, I can not see the focus. In the following paragraph are loosely many possible reasons given why the ozone might be as such as measured at the site. However, that all can not be proven with the data presented here and so the part remains speculative. This paragraph need to be somehow made more clear and stringent in terms of the special situation of the strong influence by local landscape and wind regimes.

R: We have deleted part of this paragraph to avoid, as much as possible, speculation. We have, instead, highlighted the influence of local landscape and wind regimes, as suggested by the referee.

16- Page 20406, 15ff: Well, here and in some other places in the manuscript the comparison between the compounds lifetime vs potential travel-time might help to assess the situation better. In that sense the lack of a clear wind speed during summer is a clear drawback.

R We have solved this problem with the calibration now conducted using the data from the three nearby stations as explained in responses 1 and 4. We have moreover included some new fragments of text in discussion part of the revised manuscript explaining that given the average daytime wind speed of 2 m/s for both seasons, the air masses being advected to MSY can

travel around 7 km per hour. This locates the source of the detected monoterpenes (with atmospheric lifetimes around 1 hour) 7 km of distance from the MSY station, which agrees with the local origin by the valley vegetation. In the case of isoprene (with a lifetime of around 1.5 hours), its source can be located up to 11 km from MSY.

17- Page 20407, 1ff: The discussion on the methanol burst is rather strange to me as the typical morning burst is a very short term pulse and then mostly followed by longer a decay. The average day-courses here show quite another pattern, where the emission id highest around midday.

R: : Our reference to the methanol burst is a possible explanation to the first, small rise in mixing ratios occurring in the morning in the summertime. As the referee points out, it is normally a short term pulse of emission followed by a longer decay. It is likely that in the mixing ratios showed in Fig. 8 we only see the rise resulting from the short term emission pulse, and that the longer decay gets masked by the arrival of a much higher methanol amount advected by the wind from the plains below the MSY station. We have added this consideration to the revised version of the text.

18- In the further discussion on the possible conflict of m/z 93, well, what the authors believe is the right answer? Overlaid monoterpene fragment or toluene? The discussion stops here without some kind of conclusion on that problem.

R: We present these options as possibilities, although, as we said in this paragraph, the monoterpene fragment option has been determined to be practically insignificant by Ambrose et al (2010). Now we have added the following statement at the end of the sentence: "so the early morning toluene increase must be product of either toluene emissions from plants or from a local anthropic source".

19- Page 20408, 1ff: Are you sure that the VOC load is another because the air traveled via another valley or is that just a guess? Can you rule out other factors?

R: This statement is based on the wind speeds and directions, and the fact that the wind is then coming from another valley with different vegetation, much less dense and with isoprenoid emission factors reported to be lower (Hewitt and Street 1992).

20- Page 20408, 10ff: If the results given in the cited literature are "in accordance with lower photochemical activity and..." from where you know that it is as such? The sun angle is clearly lower in Finland as in Spain, but during summer the length of the day is substantially longer and 800 W m⁻² maximum global radiation are as well possible. I think you should have at least a citation if you state that. Maybe the main reason for the difference is the temperature?

R: We thank the reviewer for pointing this out. We have changed the phase and it now reads: "These results are in accordance with the lower physiological activity of the vegetation in Nordic regions linked to lower temperatures, thus resulting in lower emissions compared to the Mediterranean MSY".

21- Figure 8: The OxVOCs are lacking units on the right panel, even if they are the same, please put them. It is hard to see what range the graph covers.

R: Now the units for oxVOCs on the right panel of Fig. 8 are shown.

22- Appendix: Move the table with the comparison between the sites to the main text, that is a valuable information.

R: Following reviewer's advice we have moved the comparison table from the Supplementary Material to the main manuscript.

Anonymous Referee #2

1- This paper gives very interesting information on temporal variation of VOC in a typical Mediterranean forest influenced by urban emissions. Despite the potential for biogenic VOC emissions and photochemical reactions in the Mediterranean area is high, these types of studies are scarce. In consequence, this manuscript can contribute to obtain valuable data on VOC emissions in the south of Europe.

Although the scientific quality of the manuscript is high, I include below some questions/suggestions to be taken into account before final publication of the paper.

R: We thank the positive and encouraging evaluation of the referee and have incorporated his/her suggested improvements. See next responses to his/her queries.

2- Page 20396, line 25: Describe the characteristics of VOC sampling: type of pump, sampling flux (mL/min), duration of sampling, number of cartridges used, etc.

R: As already answered to reviewer #1 (response 2), we have included this information in the revised text.

3- Page 20399, line 2: Is there any other meteorological station in the vicinity of MSY confirming that during summer time wind speed was above the recorded values?

R: . Previous research conducted at the area and information from nearby meteorological stations (Santa Maria de Palautordera, Viladrau and Tagamanent) showed that average summer wind speeds are at least in the same range of winter wind speeds. This information has been added to the revised version of the manuscript. See responses 1 and 4 to referee #1.

4- Page 20399, line 14: Explain in more detail why NO concentrations were so low at MSY, specially in summer season (for instance, conversion to NO₂ by higher O₃ concentrations). Are there other remote stations in Catalunya where the same phenomenon has been observed?

R: In this section of the manuscript only the results are introduced. The reason why NO concentrations are so low is the lack of sources in the vicinity of the MSY station, as the majority of NO_x come from the nearby semi-urban and metropolitan areas, and NO is consumed by chemical reactions with O₃ and other compounds during its transport to MSY. We have now added a comment about this in the discussion part about ozone mixing ratios.

We have looked at the Catalan Government's publicly available 2011 summer data from the Montsec station, which is remote in a mountain area in the north-west of Catalonia (but likely influenced also by the semi-urban region of Lleida air masses), and the NO levels were also near zero most of the time (with some peaks up to 2 $\mu\text{g m}^{-3}$) and the NO₂ levels averaged 2 $\mu\text{g m}^{-3}$ (with occasional peaks up to 14 $\mu\text{g m}^{-3}$). In an other station, Bellver de Cerdanya, situated in a northern mountain environment (but near some towns) NO levels were more similar to NO₂ levels, but still lower (1-2 $\mu\text{g m}^{-3}$ averages for NO vs 4-6 $\mu\text{g m}^{-3}$ averages for NO₂). Again, all these measurements may have been conducted with the detection limits limitations explained to referee #1 (answer 6).

5- Page 20402, line23: In my opinion, the justification of the increase of isoprene mixing ratio in summer due to the increase of biogenic emissions is enough. However, it is not so obvious that under summer conditions increased photochemistry would inhibit the mixing ratios of VOC. Although this may be true, there are also several factors that can contribute to the same fact. For that reason, if no data are presented to support this argument, I wouldn't include the sentence.

R: Following the reviewer's suggestion, we have removed this sentence from the text.

6- Page 20403, line 19: *As mentioned in the text, acetonitrile is considered a biomass marker. The fact that the mixing ratio of this compound is much higher in summer (the double) suggests the influence of local or distance fires around the area of study. Do the authors have any information about the existence of fire episodes during the sampling period? If so, did these activities affect the concentrations of other organic compounds? Are there any small villages around the forest site where biomass is used for heating in winter? If so, have you detected any influence of such type of activities?*

R: Unfortunately we do not have information regarding fire episodes during the sample periods. The villages around the forest site use biomass for heating, specially in winter. And also during summer the controlled burning of agricultural waste is limited by law. These facts might promote higher winter mixing ratio, which did not happen. On the other hand, in summer forest fires are common in the Mediterranean area and the long atmospheric lifetime of acetonitrile could help it to reach the MSY area. We have now commented this in the revised manuscript. However, we have not observed an effect of burning in other VOCs, and also do not have data on forest fires in other Mediterranean areas that could impact MSY mixing ratios.

7- Page 20404, line 16: *Both biogenic and anthropogenic VOC mixing ratios are said to be linked to the mountain wind breezes. However, with the available information, authors cannot differentiate the percentage of contribution from each of these sources. Even in the case of typical biogenic compounds, like monoterpenes, data do not allow to extract certain conclusions about the source of these compounds, because the highest mixing ratios are detected when air masses are advected by the sea breeze (thus heavily affected from Barcelona city emissions). In order to confirm that biogenic VOC detected at MSY are locally emitted in the holm oak forest, it would be interesting to include some results from other type of studies (enclosed branches) supporting this hypothesis.*

R: Monoterpenes are the clearest case of local emission in the valley of MSY, because their mixing ratios start to increase when the solar radiation starts to rise too, when plants are becoming active. This happens before the breezes from the industrialized plains have started. Also the maximum mixing ratios of monoterpenes occur before the maximum of other VOCs that are clearly transported by the wind from distant places, like aromatic compounds. In addition, as answered to referee #1 (question 16), monoterpene atmospheric lifetime is around 1 hour, that with average wind speed of 2 m/s locates the source of the detected monoterpenes 7 km of distance from the MSY station, which agrees with the local origin by the valley vegetation.

We have plenty of experience regarding monoterpene emissions by holm oaks, and also the scientific literature is full of papers reporting that holm oaks are great monoterpene emitters. What's more, during this campaign we performed cuvette measurements of monoterpene emissions, covering whole diurnal cycles (from sunrise to sunset) for several days. The results of these measurements, as reported in the manuscript, showed that holm oak leaf-level monoterpene emissions increased around one order of magnitude in summer compared to winter emissions. These results are now being compiled in a paper (Llusià et al., 2011, in preparation) that will soon be submitted for publication.

8- Page 20407, line 14: *The relation between the wind regime and VOC mixing ratios doesn't seem to be very consistent. Have you found any significant correlation between both variables? It would be very interesting to see if this variation pattern is also present in other periods (not only during the 6th august).*

R: We prepared Fig. 9, with the data corresponding to the 6th of August, to illustrate a situation that was observed on several other days: VOC mixing ratios changed depending on the direction of the wind. Normally the change in wind direction was associated to day/night changes, and this is what can be seen in Fig 8 (mean daily cycles for each season), that all VOCs except monoterpenes increase at MSY a couple of hours after the wind has changed direction in the morning (bringing all the air masses from the nearby semi-urban and metropolitan areas to MSY), and all the VOCs decrease when the wind changes again in the evening. But there were other days with situations like that of August 6th, with wind changes in the middle of the day that were associated with changes in VOC mixing ratios.

In Table S1 of the Supplementary material, the linear correlations between the VOC mixing ratios and the wind (decomposed into its vectorial x and y components) can be found. Specially in summer (when there were more VOCs in the air), the correlation coefficients were significant and quite high ($0.30 \leq r \leq 0.78$ for $343 \leq n \leq 348$).

9- Page 20408, line 3: This affirmation is based in hypothesis. Do you have any information proving that heath communities are lower VOC emitters than oak trees? Include some references.

R: The heath community has much lower biomass than the holm oak forest and its emission factor of isoprenoids is also reported to be lower (Hewitt and Street 1992). We have now included this reference in the revised text.

10- Page 20408, line 20: This comparison is very interesting, as both types of areas are very similar. The different behaviour between Castelporziano and the MSY site in relation with monoterpene mixing ratios is well explained in the text.

R: We thank the reviewer for his/her positive evaluation of this part of the text.

11- Page 20410, line 17: According to the authors, the most important factor governing VOC mixing ratios is the wind regime of the mountain. In my opinion, more meteorological information is needed to support, as some of the results seem to be based on conjectures. In a future work, it would be very interesting to achieve a similar study in a holm oak forest located far away from the influence of a big city like Barcelona. This could help to elucidate if the observed VOC mixing ratios are mainly influenced by mountain winds and it would also give more real information about the sources of such emissions.

R: The data presented in this paper shows that vegetation can have a great influence on the VOC mixing ratios of the MSY zone. Specially comparing the winter and summer seasons, vegetation impact on VOC mixing ratios can be notorious. Besides this natural emissions' influence, the main factor governing VOC mixing ratios at MSY is the wind regime, as most part of the VOCs detected there are advected by the wind. Several previous papers dealing with particulate matter measurements concluded that this "metropolitan area-to-MSY" transport was effectively occurring (Pérez et al. 2008). Soon the DAURE campaign overview paper by Pandolfi et al will be submitted for publication, and together with the meteorological overview by Jorba et al (available in ACPD now) will provide more in-depth information about atmospheric circulation in MSY.

We agree with the referee that such a study in a forest far away from the influence of big cities would be really helpful to see what is the relationship between the mountain winds and the natural VOC emissions of the forest.

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