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Interactive comment on "Contrasting winter and summer VOC mixing ratios at a forest site in the Western Mediterranean Basin: the effect of local biogenic emissions" by R. Seco et al.

Anonymous Referee #1

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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

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many possibilities but no clear statement of their own viewpoint.

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?

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.

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.

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

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 μ g m⁻³).

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?

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.

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.

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 hight (slow) that play a role in that case.

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

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 C8925

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?

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

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.

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.

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.

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. 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.

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?

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?

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.

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

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 20389, 2011.

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