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Interactive Comment

Interactive comment on "OH reactivity and concentrations of Biogenic Volatile Organic Compounds in a Mediterranean forest of downy oak trees" *by* N. Zannoni et al.

Anonymous Referee #1

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The total OH reactivity, the overall loss rate of hydroxyl (OH) radicals, is a fundamental property of air and has recently been of special interest in forested ecosystems. In contrast to urban environments it was found repeatedly that the summed individual measurements of OH reactive compounds could not account for the directly observed total OH reactivity. Here, Zannoni et al. (2015) present the first measurements of total OH reactivity in air within and above a Mediterranean forest. In parallel to the OH reactivity, a multitude of individual OH sink compounds were measured which allowed a solid comparison. The OH reactivity budget was dominated by isoprene, the forest's primarily emitted volatile organic compound (VOC), and overall little missing reactivity was observed. The presented manuscript falls within the scope of ACP and is certainly of interest for the atmospheric science community.

The method used for observations of the total OH reactivity was the Comparative Reactivity Method (CRM), which is one of three measurement principles currently used for monitoring the total OH reactivity. It was thoroughly discussed and within the text it was referred to recent, more technical, publications (e.g. Zannoni et al. 2015, AMTD). The set-up within the Mediterranean oak forest aimed for sampling air from within the forest canopy and from above the canopy. It is unfortunate, that the two heights within and above the canopy were sampled on different periods (i.e. 2 days within, 2 days above) during the measurement campaign. A frequently switching (e.g. 2-10 min) inlet system would have allowed to directly compare the total OH reactivity within and above the forest canopy, and hence provided information about forest emissions and dynamic exchange processes. Nevertheless, the discussion of the total OH reactivity within and above the forest canopy as well as the nocturnal missing reactivity observed during two nights with increased ambient temperature is interesting, and overall add to our understanding of atmospheric oxidation processes. I recommend the submitted manuscript for publication in ACP after addressing the following minor comments:

1) The abstract is relatively long and especially the first paragraph (until l.14) reads more like an introduction. It would be nice to shorten it a little, highlight more the importance and novelty of this study, and emphasize the key-findings.

2) Even though overall the text is easy to read, there are several flaws in formulations and sentence-structures. For example, in p.22050, l.11 the sentence probably ends after “troposphere” and similarly in l. 14 the sentence probably ends after the reference. Since I am not a native English speaker, I do not want to try and correct the English formulations. But I recommend to ask a native speaker to pre-review the text prior to the final publication.

3) p.22050, l.10: Biogenic volatile organic compounds are globally the most abundant

class of reactive organic compounds in the troposphere. Regionally, such as in urban environments, anthropogenically emitted compounds may dominate the atmospheric OH reactivity.

4) p. 22051, l. 16-17: The definition “low NOx” or “high NOx” can be misleading (see Wennberg 2013, “Let’s abandon the “High NOx” and “low NOx” terminology”).

5) p.22053, l. 15: Please, replace “close” with “examine”.

6) p.22053, l.19: I think it should be “determined” instead of “sampled”.

7) p.22054, l. 3-4: The closest city and town to the measurement site are Marseille and Manosque. Could you please include, how many inhabitants do live there? Also, I cannot see the cities in Figure 1. It would be nice to have their location pictured in Fig.1, especially since you refer to it in the text.

8) p.22054, l.16: You determined the leaf area index (LAI) during August 2010 as 2.4. Was it measured again afterwards in another year or another season? Is it not likely to change with time? 9) Section 2.1 Description of the field site: What was the dominant wind direction? Is the footprint of sampled air predominantly influenced by the oak forest?

10) p.22055, l.7: I find the description of the set-up confusing. You have two PFA sampling lines on a mast. Are these two lines for the two instruments or for the two heights? Or do you have two lines at each height? How long were the lines? Did you have filters? Also, you write later (p.22055, l. 13) that you kept the lines heated, about 1°C above ambient temperature. So, did the line temperature vary according to the diel variation of ambient temperature? p.22055, l.21: The residence time in the lines for the CRM and PTR-MS instruments differed by about 10 seconds. Why did you not adjust these two flows to have the same residence time? Also, if you have individual lines for each instrument, did you test the two lines against each other? Can you rule out any line effect that would bias the CRM and PTR-MS observations for the comparison?

11) p.22055, l.18: C2 and C3 describe concentration levels detected during the CRM measurements and were not explained before. The CRM technique is later explained in section 2.3. Please, remove the CRM specific terminology from this paragraph, or reorder the paragraphs, or explain it carefully e.g. as zero air and ambient measurements.

12) p.22055, l.25: At what height exactly did you install the extra line for sampling tubes for offline GC-MS analysis?

13) p.22055, l.29: Why was the monoterpene concentration measured by the PTR-MS only every 5 minutes? Similar to comment 11), the PTR-MS technique and details about the instrumental field campaign set-up are presented later in Section 2.4.1. Hence, at this point it needs more explanation or it should be removed from the paragraph.

14) p.22056, l.1-4: What height did the NOx and ozone (O3) instruments sample from?

15) p.22056, l.13: Please, exchange “to take up” with “to react with”.

16) p.22056, l. 22: How did you produce the zero air? Did you adjust the humidity during zero air (C2) measurements to the ambient humidity? Since the OH is generated inside the glass reactor of the CRM, its levels depend on the humidity of the sample. If during the comparison C2 (zero air+OH+pyrrole) and C3 (ambient air+OH+pyrrole) do not have the same humidity, the OH levels inside the reactor will be different. Hence, the total OH reactivity is under- or overestimated.

17) p.22057, l.5: Was the total OH reactivity obtained as average every 10 minutes? What was the time resolution of the raw values?

18) p.22057, l.9: Generally it would be more accurate to write “OH reactivity”. There are other oxidants such as O3 or nitrate radicals (NO3) that react with most of the atmospheric constituents as well.

19) p.22057, l.12: You write that propane represents a proxy of an unknown air mass.

Why is that? I would think that the average reaction rate with OH of an air mass depends on its origin. A biogenic air mass might contain more reactive compounds (such as isoprene, monoterpenes) than an anthropogenic air mass (for which carbon monoxide (CO) or nitrogen dioxide (NO2) dominate).

20) p.22057, l.15-21: The correction described in this paragraph differs from previously published CRM studies (e.g. Sinha et al. 2008). Therefore, it would be good to include the graph that is described here either in the manuscript directly, or as supplementary information.

21) p. 22057, l. 20-21: How large were these two corrections relative to the measured total OH reactivity? It would be interesting to learn about the relative impact of these corrections.

22) p.22057, l. 23-26: Here you talk about the calibration of the PTR-MS instrument that was used for pyrrole detection. The instrument was calibrated in dry and wet conditions. You should briefly explain why this is necessary, and refer to Sinha et al. (2010) who pointed out that the PTR-MS sensitivity to pyrrole depends strongly on humidity.

23) p. 22058, l. 11: This is not a sentence.

24) p.22058, l.23 and p.22059, l.18-24: The PTR-MS was calibrated with a standard gas mixture containing several volatile organic compounds. Particularly, m/z 71 was calibrated with crotonaldehyde. The atmospheric signal, however, was identified as isoprene products including methacrolein (MACR), methyl vinyl ketone (MVK) and isoprene hydroperoxides (ISOPOOH). First, I wonder if the PTR-MS sensitivity would be different for these compounds. Then, I think this section could be improved by explaining at first that m/z 71 typically was assigned to the sum of MVK and MACR, and only recently the mentioned interference of ISOPOOH was discovered. Could you please modify this part in the text?

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25) p.22059, l.2: The PTR-MS sensitivity depends on humidity for most of the compounds in the standard gas mixture used for calibration. Were the calibrations performed in dry or in wet conditions? Did you try to match typical ambient humidity levels?

26) Could you please check the acronyms used in the entire manuscript? Generally, I found that sometimes they were not introduced properly or differ from how they are used later. For example: p.22058, l.13 “PTR-QMS” is later “PTR-MS” (p.22059, l.14). Or: “MEK” (p.22059, l.25) is not defined when first mentioned as methyl ethyl ketone. Similar later for formaldehyde: “HCHO” (p.22060, l.19).

27) p.22060, l.6: Losses are typically enhanced by stainless steel tubing and Nafion dryers. Did you test your set-up for losses?

28) p.22062, l.3: The samples for GC-MS offline analysis were stored at 4°C and analyzed within a month in the laboratory. Did you test if there are any losses of your compounds of interest during this procedure? How large do you estimate such losses?

29) p.22062, l.12: It is really unfortunate that CO was not measured during the field campaign. I would think that usually atmospheric CO levels are quite variable and dependent on transport processes and regional pollution. Since you had to use the average of springtime measurements, could you as well report how variable the atmospheric CO levels were in spring 2012? Did you include this variability in the uncertainty of the total OH reactivity calculation?

30) Section 3.1 Trace gases profiles and atmospheric regime: I do not understand the meaning of this title. Do you mean diel profiles? Vertical profiles? And what do you mean with atmospheric regime?

31) p. 22063, l.11: “. . .isoprene covariates perfectly with PAR” Could you please provide the correlation coefficient?

32) p.22063, l. 13-15: To be precise, you could add the exact hour of the day when the

peaks occur. If you do so, I think that isoprene above the canopy would peak at about 20 CEST (Fig. 2). This is after sunset. Can you explain why isoprene has its maximum that late in the day above the canopy?

33) p.22064, l.8 and 10: You present the daily maximum inside the canopy for methanol and isoprene as 14 ppbv and 23 ppbv. Are these values averages?

34) p.22064, l.12: What are 24h statistics? I am not familiar with this terminology.

35) p.22064, l.21: Please, add "...with ethane being the most abundant..."

36) p.22065, l.19-28: Could you make clear which height was sampled from at which day? So, during 11 June 2014 the instrument measured from 2m. You describe the temporal variation of total OH reactivity with two maxima during daytime. If you look at it differently, it could be a slight drop around noon. Could it be that at noon, when light intensity and temperature levels are at their maximum, the oaks favor photorespiration and tend to close their stomata? This would reduce the direct emission of reactive species at midday. Interestingly, the shape of total OH reactivity during daytime above the canopy differs slightly from within the canopy. It follows less the diurnal cycle of light and temperature, but gradually increases during the daytime to reach peak levels at about 21 CEST. Could you comment on that?

37) p.22066, l.22: How did you estimate 25% uncertainty for the calculated total OH reactivity? This value seems very small with respect to the high uncertainty every single reaction rate constant has. Additionally, the CO level was assumed to be constant which probably further increases the uncertainty of this value. It would be interesting to add a small paragraph about the uncertainty of the calculated OH reactivity to the experimental section.

38) p.22067, l.3-p.22068, l.6: This is a very interesting paragraph. But it is written in a way that is difficult to understand. Could you please simplify and be more specific with the presentation. For example l.13-14: Why do you assume equal OH reactivity

above and within the canopy? And l.16: I am not familiar with the expression “9 point percentage”. p.22067, l. 15: Please, write correctly 30°C and 32°C. p.22068, l.3: Erase “definitely”.

39) p.22068, l.25: You write that isoprene concentrations flattered much faster than its oxidation products. As reason you refer to its higher reaction rate. Most probably, it is as well the close proximity to the source, that causes the high variability. As a measure for short term you could provide the relative standard deviation (see e.g. Noelscher et al. 2012, ACP).

40) p.22069, l.2: You state that ISOP.OXs/isoprene anticovariate with ozone as can be seen in Figures 9 and 10. I can see in Figure 9 that the increase of ISOP.OXs/isoprene falls together with the decrease in ozone. However, I cannot see such a behaviour in Figure 10. Therefore, I think it is too strong to talk about an anticorrelation. Can you provide a correlation coefficient of ISOP.OXs/isoprene with ozone to prove an anticorrelation?

41) p.22069, l.2 and Figures 9 and 10: Ozone levels are relatively high (about 50 ppb) for a forested environment. Do you have any explanation for such high ambient ozone mixing ratios?

42) p.22069, l.9 and following paragraphs: In order to explain the missing reactivity that was observed during two nights, you point to nighttime chemistry or lateron to surface oxidation reactions. Could you please also discuss the effect of boundary layer dynamics such as dilution or enhanced deposition during nighttime? What about humidity dependent emissions from the soil or microbial communities on leaves?

43) p.22071, l.1: I do not think that forest environments may be called “perfect laboratories”. The experiment examining the total OH reactivity in air within or above a forest is not a controlled study. Often even laboratory work is by far not perfect as the technical set-up, instrumental limitations, or other unknowns bias the scientific results.

44) Table 3 presents mean mixing ratios of the PTR-MS detected compounds. If you additionally include the standard deviation or standard error, you could emphasize the variability of the total OH reactivity.

45) Figure 1 shows the measurement site. Could you please point to the cities mentioned in the text? And could you also show where the instruments and the inlet set-up are located in the oak forest?

46) Figure 2: The diel mean (?) profiles of isoprene, isoprene oxidation products, formaldehyde, PAR and temperature are presented for inside and above the canopy. At which height was the temperature measured?

47) For several figures, please make sure that the labels or description text is not moved into axes or figure elements (such as in Figure 3, 7 and 8).

48) It would be nice to point out at which height the presented data was measured. Similarly as in Figure 2, could you please add a box with “inside/above canopy” to the Figures 5, 6, 7, 8, 9, and 10?

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