

Interactive comment on “Summertime OH reactivity from a receptor coastal site in the Mediterranean basin” by Nora Zannoni et al.

Anonymous Referee #1

Received and published: 30 December 2016

The manuscript presents OH reactivity measurements from a receptor site in the Western Mediterranean. OH reactivity represents an important top-down constraint on the amount of (OH) reactive species, which is directly relevant to radical cycling. At this site, which has low anthropogenic influence the OH reactivity furthermore mainly reflects the reactivity of biogenic volatile organic compounds (BVOCs) and their oxidation products. Important is also that the site has high terpene/isoprene ratios with a large contribution of alpha-terpinene, likely distinct from other sites for which OH reactivity has been reported. The manuscript thus presents a valuable data set providing insight into our understanding of contribution of BVOCs and their oxidation products to radical cycling. Two periods are identified that show larger discrepancies between the measured reactivity and that calculated from observed BVOCs and their reaction products. The work is an important addition to understanding the emission and fate reactive car-

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bon in the atmosphere and should be published after the following comments have been addressed.

1. It would be very helpful to learn a little more about the OH reactivity measurement.

(i) How does the instrument sample the air and does this allow for observations of sesquiterpenes in the OH reactivity instrument or will they likely be lost. This is important for the comparison with calculated reactivity as sesquiterpenes were not observed.

(ii) Definition of OH reactivity. There are a number of compounds in the atmosphere that after attack of OH can recycle OH rapidly. Probably the best known examples would be MACR, which recycles OH with a rate constant of 0.5 s⁻¹ (Crounse et al. JPCA 116, 5756-5762, 2012, probably too slow to have an effect), isoprene hydroxy hydroperoxides forming isoprene epoxydiols, which likely recycle OH extremely fast, and RO₂ that can recycle OH via reaction with HO₂, (Praske et al. JPCA 119, 4562-4572, 2015, for example). Depending on the HO₂ concentration in the instrument and the residence time, this could result in an underestimate of the actual OH reaction rate. It should be simple to model this, for the example of MVK+OH with the instrumental HO₂ and residence time between OH addition and detection of pyrrole in the PTR.

2. P. 3 line 13: I did not see how this work “better elucidates the chemical processes, including ozone and secondary organic aerosol formation . . . over the Mediterranean basin”. This requires more than comparing observed with calculated concentrations, i.e., a more quantitative framework addressing these chemical processes, ozone, SOA. I suggest removing this statement and simply stating, what the very nice observational data at one specific location in the Mediterranean set actually shows, which is what the two bullet points do.

3. There are too many references to work in preparation.

(i) P. 12 line 27-30. The comparison GC and PTR has to be shown. It is mentioned that isoprene correlated well for the GC and PTR but they could be off by a large factor.

This has to be shown in the manuscript. In extension of this, how were the GC and PTR measurements calibrated? Uncertainty in these directly relates to uncertainty in calculated reactivity. Extending the section on the (O)VOC measurements would be very helpful to this end. How was the terpene reactivity calculated, was the speciated one from the GC scaled up to give the same total as the PTR measurement? I also recommend extending table 1, to include the rate constants used.

(ii) More importantly, I recommend removing the PMF factorization aspect from the manuscript. As the actual PMF factorization is not presented it is impossible to evaluate this. For example, how high is the covariance between these factors, or in other words, in how far are these factors significant. I also think that this section is speculative and does not add much value to the manuscript. For example, it is stated that the first period (23/7-27/7) is “dominated” by OVOCs, referring to figure 2. Inspection of figure 2, to me, does not show any such dominance. In fact, to me it looks like the primary BVOCs dominate during the day, but I could be wrong. I also don’t see how such a clear distinction as is made in the manuscript that the first period discrepancy is caused by “higher oxygenated chemicals” and for the second period by “oxidation products of BVOCs” is possible. This again requires a much more quantitative framework than presented here. The conclusion section thus is not very conclusive but rather has a lot of speculation. This does not detract from the importance of the observational data set and comparison with calculated reactivity.

4. p. 10 line 1 and line 17-19: The measured reactivity peaks around 16:00. However, no calculated contribution peaks at that time but rather around 14:00, hence the statement that the OH reactivity diurnal profiles resembles the one of the BVOC OH reactivity, which is significantly lower at 16:00 is not correct. This lag in the shape of the OH reactivity with respect to BVOCs, could lend support to oxidation products being important, which typically build up during the day, unless they are very short lived.

Additional/technical comments:

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P. 1 line 27 “inferred” I would say that “calculated” from measured reactive gases. Inferred to me sounds like a vague, estimated process, but it is actually calculated here.

P. 2 line 3 “the biogenic volatile compounds” I assume this means with the reactivity calculated from the concentrations of biogenic VOCs. As written it is vague and could mean concentration of BVOCs, which probably is not ideal, as different BVOCs have different diurnal profiles, as pointed out in the manuscript.

p. 2 line 5 associated respectively “with” instead of “to”

p. 2 line 7. biogenic “gas” not “gases”

p.2 line 7 delete “the” before “missing”

p.2 line 14: typically I see volatile organic compounds written in lower case, even if explaining the acronym.

p. 2 line 17 “all reactive compounds”, strictly “compounds reactive with OH”

p. 2 line 18 product “of” not “between”

p. 2 line 25 associated “with”

p.2 line 26 delete “either” before “secondary generated”

p. 2 line 28. I don’t think Portugal has a shore line on the Mediterranean, rather the strait of Gibraltar defines the western end of it, but I could be wrong.

p. 3 line 1-2. Is it relevant afterward in the manuscript that these species have not been identified anywhere else? It seems out of context.

p. 3 line 6, delete “a”

p.3 line 10-12: I am not sure that one paper proves this. Other regions of the world are even less sampled. I would suggest rephrasing as that additional observations are useful, but a minor point.

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P. 3 line 18 “site” not “side”

P. 3 line 27 “local anthropogenic pollutants” is a little vague. Does it mean the same compounds could be coming from somewhere else?

P. 4 line 19: “measurements of gases and aerosol properties over a total surface area of ~ 100 square meters”. Please clarify, you measured the species across the whole area and nowhere else or the instruments were distributed over this area?

p. 8 line 17: “Here, . . . here”

p. 9 line 16 either “maximum” or “peak”

p. 9 line 31: To me the reactivity in figure 3 looks as it goes to about $4s^{-1}$ but not below $3s^{-1}$ at night.

P. 10 line 22: delete “to” in front of “the largest fraction”

P. 10 line 26 “larger” than what or simply state “large”

P. 11 line 18: Is it true that monoterpenes in all plant species have only-temperature dependent emission?

P. 11 line 14-30. It would be very helpful to have references to all reaction rate constants used for the calculated reactivities (I may have missed this, and apologize if I did).

P. 11 line 26: I do not understand the “hence” used here

P. 12 line 7. Perhaps clarify how the discrepancy is calculated, i.e., calculated was 56% lower than measured, was 56% of measured, or measured was 56% higher than calculated etc.

P. 12 line 15: On the other “hand”

P. 12 line 16 “of “ the wind sector

P. 12 line 22-23. Again, at least during the day BVOCs dominate OVOCs, so the

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statement as made, does not seem accurate.

p. 13 line 9: “or” monoterpenes.

p. 13 line 17-18: “Figure 6 shows the variability of the volume mixing ratios of BVOCs and oxidation products with local drivers such as temperature. . .”

P. 14 line 2 “effective” What does it mean for wind speed to be effective for monoterpenes?

P. 14 line 5 “small” instead of “little”

P. 17 line 11: Perhaps the term “secondary biogenic VOCs” could be redefined as it is a little unusual.

Figure 2: Does others not include methane, which probably contributes around 0.3 s⁻¹.

Figure 3: Please add a total calculated reactivity trace, which would be very helpful.

Figure 7: Please show the same for the second period.

Lastly, the manuscript may benefit from language editing by a native speaker, if this is possible.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-684, 2016.

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