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Atmospheric Measurement Techniques
Discussions
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Interactive comment on "Intercomparison of two Comparative Reactivity Method instruments in the Mediterranean basin during summer 2013" *by* N. Zannoni et al.

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First we would like to thank the Anonymous referee #2 for his/her helpful comments. Please find below our answers.

(1) 1) It is not clear from the title and the abstract that it is mainly a plant emissions observation and that the OH reactivity measurements were carried out in an enclosure. In fact, only after 15 pages (at pg. 5080) it is explained that the ambient reactivity was close to the LOD of the systems, so they decided to measure the reactivity of plants, placing the inlets in a small enclosure with plants to exclude ambient air. Therefore

from lines 1-5 of pg. 5080, seems that, due to low ambient reactivity this study regards only plant emissions. Finally, on pg. 5086, lines 16-18 it is clear that the campaign was divided in three parts: 2 days of plant emissions (8-9 July), 2 days of ambient measurements (10-11 July) and 2 days (12-13 July) of plant emissions. In my opinion this mix of measurement (ambient and enclosure) must be cleared starting from the abstract. From fig. 8 seems that during the ambient observations the CRM-LSCE systematically overestimate the OH reactivity compared to the CRM-MD, whereas in the enclosure measurements for the same low level of OH reactivity the agreement between the two systems is much better. Is this discrepancy explainable? Is this due to a possible interference in the CRM-LSCE in ambient atmosphere?

(2) We agree with Anonymous Referee #2, hence we clarified the campaign timing in the abstract, in the introduction, and in the figure 8 caption. It has to be noticed that measurements in the enclosure were not performed in a real plant enclosure (see fig. 4 for some details). Due to the low ambient reactivity during the days of the intercomparison we decided to move our sampling lines to the closest source of VOCs, i.e. the plant, and due to strong wind at the site we covered the sampling lines with a flask. The discrepancy between enclosure measurements and ambient measurements is possibly due to a slight different sampling. For ambient measurements our sampling lines where above our two trailers, which were roughly 30 m distant from each other. In this case, for CRM-MD a shorter line was used and the residence time achieved in the two instruments was about the same (∼3s). Data sets from the instruments were also processed the same way: correction for humidity differences, for the kinetics regime, and dilution inside the reactor. We did not apply any correction for OH recycling due to NO in ambient air, since the levels of NO were low during the whole time of the campaign (NO was on average 0.08 ±0.07 ppbv, while NO2 was on average 0.5±0.14 ppbv which would have given a negligible correction between 0.1 and 0.2 s-1). Therefore we think that main differences for this data set could be given by the different sampling point (30 m far) and strong wind at the field site during those days. Moreover, samplings were performed at different altitudes (different of few meters) which could also

cause the slight differences observed in OH reactivity measurements, due to probable vertical gradients of biogenic VOCs in the emission area such as our measurement site. More clear details about the sampling are added in Table 1 and in the text; the mix of enclosure and ambient measurements is clarified from the abstract.

(3) please substitute lines 8-10 page 2 with:" Herein we present an intercomparison exercise of two CRM instruments, CRM-LSCE (Laboratoire des Sciences du Climat et de l'Environnement) and CRM-MD (Mines Douai), conducted during July 2013 at the Mediterranean site of Ersa, Cape Corsica, France. The intercomparison exercise included tests to assess the corrections needed by the two instruments to process the raw data sets as well as OH reactivity observations. The observation was divided in three parts: 2 days of plant emissions (8-9 July), 2 days of ambient measurements (10-11 July) and 2 days (12-13 July) of plant emissions." And replace lines 22-24 page 5 with: "OH reactivity conducted in ambient air (10-11 July) and from a plant enclosure (8-9 July and 12-13 July) to cover a broad range of OH reactivity (from the limit of detection, LOD, of the instruments up to 300 s-1)." Replace fig. 8 caption with: "Figure 8. Time series of enclosure kOH (8-9/07), ambient kOH (10-11/07), enclosure kOH (12-13/07) measured by CRM-LSCE (red) and CRM-MD (blue). Total monoterpenes signal measured by CRM-LSCE as protonated unfragmented m/z 137 is reported with the green line. " Please modify the text in lines 12-16 page 12 with: (ii) The sampling point during the ambient kOH experiment: the sampling lines of the two instruments were placed on top of each trailer, about 30 m far from each other, and 2 m different in height. The length of the sampling lines was the same, while the outer diameter size and sampling flow rates differ to have a similar residence time of the sample in the lines of about 3 s. (iii) The length of the sampling line during the enclosure kOH experiment: approximately 30 m for CRM-MD and 5.5 m for CRM-LSCE. A longer sampling line was used for CRM-MD to perform collocated measurements with CRM-LSCE. However, the sampling flow rate was adjusted to 2 L min-1 to get similar residence times in the sampling lines of the two instruments (approximately 14 s and 16 s for CRM-LSCE and CRM-MD, respectively).

Please substitute Table 1 with Table 1 (here as Fig.2)

(1) 2) I'm not sure that mixing the data (enclosure and ambient) to carry the intercomparison is fine: how about the observational environment? Since the enclosure is completely different from the open atmosphere: Are you confident that you were in the same situation in terms of possible interference and/or instruments performance that you allow to consider and analyse all the data together?

(2) We think that the way we designed the experiment, qualified the instruments and processed the data sets allows us to treat the data sets from the different experiments in the same way. We performed calibrations of the instruments, and tests to assess the corrections at both scales: in ambient air and in the enclosure and used mean values from the results of all these tests conducted on the field. This gives us enough confidence to treat the data sets from the different experiments in the same way.

Minor comments: (1) a) Pg. 5078, lines 15-14: The length of the sampling lines of the two system is very different: 30 m. vs 5.5 m. You acknowledge a similar residence time and a Teflon pump for the system with the longer line. I suppose that the pump is placed between the line and the reactor to have a similar residence time. If this is the case, please specify this and all other evidences that show that the intercomparison is fine even if the experimental setup is different for the two systems.

(2) yes, a pump was placed between the sampling line and the reactor of CRM-MD. The sampling flow was kept to 2 sL/min, the length of the sampling line was 30 m and the residence time achieved was ∼16 s (details available in Table 1, above). These details are integrated in the text.

(3) please, modify the text in lines 17-20 page 12 with: (iv) The sampling strategy: CRM-MD is equipped with a Teflon pump between the sampling line and the reactor while CRM-LSCE has the sampling line directly connected to the reactor, without any pump. The extra flow from the pump is vented through an open T-connector and similar sampling flow rates are achieved for both instruments. In addition, the sampling line

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of CRM-LSCE has a PTFE filter at the inlet to exclude particles with a diameter larger than 0.25 μm entering the reactor, while CRM-MD has no filters at the inlet.

(1) b) Pg. 5084, lines 3-4: The humidity correction results in an increase of the CRM-LSCE reactivity and in the decrease of that of the CRM-MD: how do you explain this opposite behavior?

(2) We think that such behavior can be explained by the use of a particles filter at the inlet of the sampling line of CRM-LSCE (PTFE filter, excluding particles with diameter above 0.25 micron), while no filters were used for CRM-MD. We noticed that a filter, to exclude small particles entering the reactor, can retain water contained in air when humid air is sampled and release water when dry air is sampled. We think this is the main reason why the difference in humidity we are observing in CRM-LSCE between C2 and C3 is not always in the same sense (C2 always drier than C3 or viceversa), while for CRM-MD C2 is always more humid than C3. We included this information in the text.

(3) The information is included in: lines 12-20 page 12: (iii) The sampling strategy: CRM-MD is equipped with a Teflon pump between the sampling line and the reactor while CRM-LSCE has the sampling line directly connected to the reactor, without any pump. The extra flow from the pump is vented through an open T-connector and similar sampling flow rates are achieved for both instruments. In addition, the sampling line of CRM-LSCE has a PTFE filter at the inlet to exclude particles with a diameter larger than 0.25 μm entering the reactor, while CRM-MD has no filters at the inlet. The explanation of the opposite behavior is added in line 9 page 16: “We believe that this opposite behavior was due to a difference we had in the sampling set-up. CRM-LSCE usually operates with a PTFE filter at the inlet of the sampling line to prevent atmospheric particles entering the reactor; while CRM-MD did not use any filter for the intercomparison exercise. The PTFE filter might have act as water reservoir; retaining water vapors when the air was very humid and releasing water vapors when the air was dry. Therefore, using a filter at the inlet leads to both C2 drier or more humid than C3,

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depending on atmospheric conditions; while C2 of CRM-MD was always more humid than ambient air. "

(1) c) Fig. 7: For all the panels there is a group of data where there is a big difference between the two systems: the CRM-MD measures between 50 and 100 s-1 of OH reactivity, whereas the CRM-LSCE between 0 and 50 s-1. Do you have an explanation for this?

(2) Most points were taken between 7:30 and 11:00 on 12/07/2013 and were associated to a quick release of VOCs by the plant induced by us. It is possible that during this action we did not catch the plant reactivity at the same time. It has to be noticed that even if we synchronized our sampling at its best, and tried to achieve similar residence times in the sampling lines, a data point of reactivity for each instrument is a mean value of about 10 points, among which usually five need to be neglected due to valve switching. When the plant was induced to emit VOCs its emission was quick and not stable: between 7:30 and 11:00 the m/z 137 measured by CRM-LSCE was on average 14±20 cps, and over 5 minutes data peak it was 50±56 cps. Such high variability in monoterpenes concentration might have been catchable only by a couple of points of reactivity, hence even small differences in synchronization and time needed to condition the sampling lines (1/8" OD for CRM-LSCE while $\frac{1}{4}$" OD for CRM-MD) as well as dwell time of the PTR-MS can lead to few discrepancies.

(1) d) Fig. 8: A log-scale in the y axis would be better to help to see details of the low OH reactivity measurements. (2) We modified fig. 8 with the log scale on the y axes. (3) Please replace fig. 8 and caption with Fig.1 and the caption below:

Figure 8. Time series of enclosure kOH (8-9/07), ambient kOH (10-11/07), enclosure kOH (12-13/07) measured by CRM-LSCE (red) and CRM-MD (blue). Total monoterpenes signal measured by CRM-LSCE as protonated unfragmented m/z 137 is reported with the green line.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 5065, 2015.

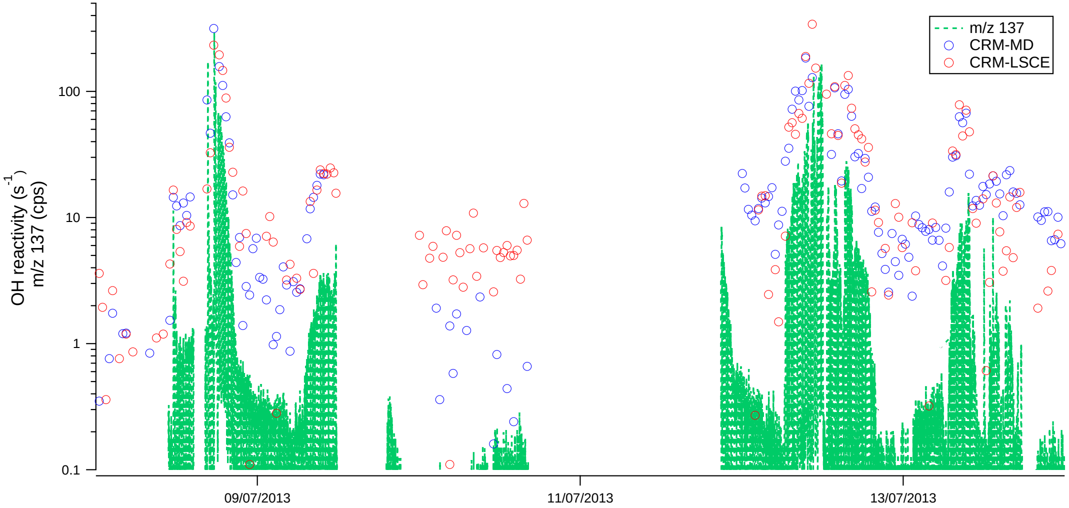
m/z 137
CRM-MD
CRM-LSCE
OH reactivity (s^{-1})
m/z 137 (cps)
100
10
1
0.1
09/07/2013
11/07/2013
13/07/2013

Fig. 1.

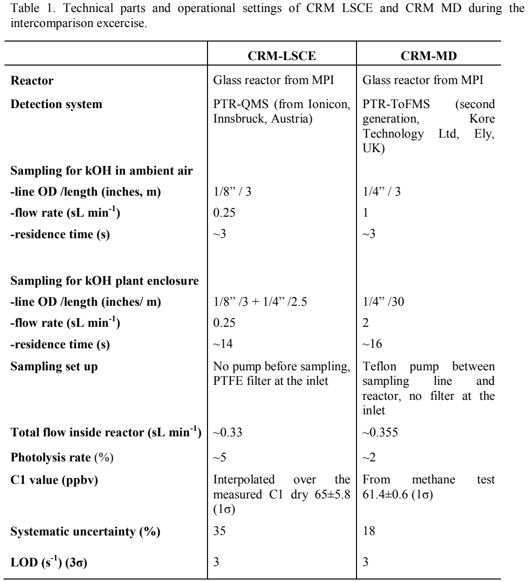

Table 1. Technical parts and operational settings of CRM LSCE and CRM MD during the intercomparison excercise.

	CRM-LSCE	CRM-MD
Reactor	Glass reactor from MPI	Glass reactor from MPI
Detection system	PTR-QMS (from Ionicon, Innsbruck, Austria)	PTR-ToFMS (second generation, Kore Technology Ltd, Ely, UK)
Sampling for kOH in ambient air		
-line OD /length (inches, m)	1/8” / 3	1/4” / 3
-flow rate (sL min^{-1})	0.25	1
-residence time (s)	~3	~3
Sampling for kOH plant enclosure		
-line OD /length (inches/ m)	1/8” /3 + 1/4” /2.5	1/4” /30
-flow rate (sL min^{-1})	0.25	2
-residence time (s)	~14	~16
Sampling set up	No pump before sampling, PTFE filter at the inlet	Teflon pump between sampling line and reactor, no filter at the inlet
Total flow inside reactor (sL min^{-1})	~0.33	~0.355
Photolysis rate (%)	~5	~2
C1 value (ppbv)	Interpolated over the measured C1 dry 65±5.8 (1σ)	From methane test 61.4±0.6 (1σ)
Systematic uncertainty (%)	35	18
LOD (s^{-1}) (3σ)	3	3

Fig. 2.