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Atmospheric Measurement Techniques
Discussions

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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We would like to thank Anonymous Referee 1 for his/her valuable comments. Please find below our response (2) and manuscript modification (3).

(1) 1) Figure 6: It does not seem that the linearity between the two parameters is statistically relevant. Notating R2 values would be helpful. The explanation about the observed inconsistency in the text (Page 5084 line 20 to Page 5085 Line 2) is not comprehensive enough for readers to understand the physical reasons for the experimental results. In the description, both techniques are using an exactly identical reactor

then between the analytical systems what could be possible causes for the observed different behavior if the inhomogeneity in the reactor could cause the observed inconsistency? In addition, the argument about different reaction rates between propaneand propene, explained for a main cause for the inconsistency needs further clarification.

(2) We have reformulated the explanation in the text in a more comprehensive way (see below). The R2 values are also added on figure 6 and help demonstrating that the choice of not considering a linear dependency for the correction factor on the pyrrole/OH of CRM-LSCE was correct. Indeed the values of reactivity obtained from CRM-LSCE were corrected for a mean value obtained from all the experiments conducted with propane and ethane on the field. For CRM-MD the experimental results showed a fair linear dependency between the correction factor and pyrrole/OH, and the reactivity values were corrected for the linear fit obtained from the experimental tests. Although the decrease of the correction factor towards the pyrrole/OH in fig. 6 looks barely linear for the pyrrole/OH values investigated on the field, the same trend was also noticed on a larger pyrrole/OH interval and by the modelling results reported by Michoud et al., 2015.

(3) replace lines 6-29 page 17 with: "However, for pyrrole-to-OH in the range 1.2-2.6 as the one of this study and showed in figure 6, such linear dependency seems to be fairly significant only for CRM-MD (R2=0.546) while it is not relevant for CRM-LSCE (R2=0.206). Therefore the data set from CRM-MD was corrected with the equation from the linear fit reported on fig. 6 while the data set from CRM-LSCE was corrected with a mean value of the correction factors obtained from the experiments conducted on the field. Since we obtained close corrections for our data sets (0.98 correction factor for CRM-LSCE, 0.97 for CRM-MD on average), this data processing did not substantially influence the correlation between the results from the two instruments. Table 2 reports a summary of the corrections resulting from our tests and their impact on the measures. The second important point to notice from fig. 6 is the larger variability in correction factors from the experiments observed for CRM-LSCE compared to CRM-

MD (1σ on the correction factor equals to 0.22 for CRM-LSCE and 0.07 for CRM-MD). We think that the main difference is attributable to a possible different mixing efficiency occurring inside the reactors where the two arms for air and nitrogen/OH are pointing. Although our reactors have the same shape, covering material and same flow rates injected, we suspect that even small differences in the length and pointing of the injection arms inside the reactor might provoke a different mixing and hence radical segregation inside the two systems. These differences in radical segregation could lead to differences in kinetics inside the two reactors. We need to further investigate different reactors to actually verify this hypothesis. To prevent that such small differences determine a wrong interpretation of the measured reactivity we consider therefore important that each CRM undergoes the experimental quantification of this correction factor; not only to assess the right correction for the kinetics regime but also to determine the specific reactor performance. Propane and ethane also showed slightly different behavior when used as test gases for the CRM calibration. Different rate coefficients with OH could explain this behavior, since for the same injected reactivity different concentration of the selected test gas are needed, hence the higher the concentration the closer the system is in the pseudo first order kinetics assumption. Additional experimental tests performed in the laboratory with a more reactive test gas as isoprene, and by modelled results of compounds with different reactivity conducted in the same pyrrole/OH range and discussed in the paper of Michoud et al., (2015), supported this hypothesis. However, the larger variability in the correction factors from all experimental field tests (propane and ethane) makes differences among test gases behavior not significant in the evaluated range of pyrrole/OH, hence a mean value or a linear fit including all experimental results is suitable to correct the reactivity." Replace fig. 6. and caption with Fig.1 enclosed and the following caption:

Figure 6. Correction factor of reactivity for the kinetics regime reported versus pyrrole-to-OH ratio in the reactors. Correction for CRM-LSCE is represented in red while correction for CRM-MD is represented in blue. Full circles refer to the experiments conducted with propane while hollow circles refer to the experiments with ethane as gas

standard. Linear fits include coefficient values ± 1σ.

(1) 2) Figure 7 and 8: It is appeared that the statistics are driven by the high reactivity points, higher than 50 s-1. As most of ambient OH reactivity probably below 50 s-1, it will be more informative to show plots for lower reactivity data points only between 0 to 50 s-1.

(2) Indeed, for a comparison of ambient air OH reactivity at the site is more meaningful exploring a narrower region as 0-50 s-1. Therefore we included two more panels in Fig. 7 (panel E and F) where the raw data of reactivity and the final corrected results in the range 0-50 s-1 are showed. All linear least squares fits include only the data points above the LoD of the two systems (3 s-1, 3σ). All data points obtained from the measurements are kept in the panels for information. We also modified the y axes in fig. 8 which is now in the logarithmic scale, following the minor comment of Anonymous Referee 2.

(3) replace lines 1-2 page 20 with: With: "A linear least squares fit is also applied to the same data sets in a narrower range of reactivity values between 0 and 50 s-1 which is more relevant for the ambient OH reactivity values at the field site. For this range of values the variability among data is higher compared to the data points in the range 0-300 s-1 (R2 from 0.667 to 0.543 vs R2 from 0.706 to 0.717). However, the agreement among CRM-LSCE and CRM-MD reactivity data sets also increases with the corrections applied when the 0-50 s-1 range is considered. From the raw data to the final reactivity in the interval 0-50 s-1 the slope of the fits varies from 0.74 (raw data), 0.93 (humidity corrected data), 0.92 (kinetics corrected data) to 0.96 (dilution corrected, final result). Therefore the two data sets show a good agreement, within the instrumental uncertainties, also for reactivity values below 50 s-1." Replace fig. 7 and fig. 7 caption with Fig.2 enclosed and the following caption:

Figure 7. Linear least squares fits of Total OH reactivity measured by CRM-LSCE versus Total OH reactivity measured by CRM-MD. Panels from top left to bottom right

show: correlation among raw results (A); correlation among data corrected for humidity (B); correlation among data corrected for humidity and deviation from pseudo first order kinetics (C); correlation among data corrected for humidity; kinetics regime and dilution inside the reactor (D); correlation among raw values in the range 0-50 s-1 (E); correlation among final values in the range 0-50 s-1. (F). Coefficient values are extracted from the equation: OH reactivity CRM-LSCE=b(OH reactivity CRM-MD)+a and report 1σ standard deviation. The regressions are applied to the values above the instrumental LOD only.

(1) Minor comment: There are a couple of acronyms without clarifications in the abstract.

(2) The acronyms are now clarified in the abstract (see below).

(3) replace 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.“ And replace lines 16-18 page 2 with: “ This study highlights that ambient measurements of OH reactivity with differently configured CRM instruments yield consistent results in a low NOx (NO+NO2), terpene rich environment, despite differential corrections relevant to each instrument.“

References: Michoud, V., Hansen, R. F., Locoge, N., Stevens, P. S., and Dusanter, S.: Detailed characterizations of a Comparative Reactivity Method (CRM) instrument: experiments vs. modelling, Atmos. Meas. Tech. Discuss., 8, 3803-3850, doi:10.5194/amtd-8-3803-2015, 2015

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

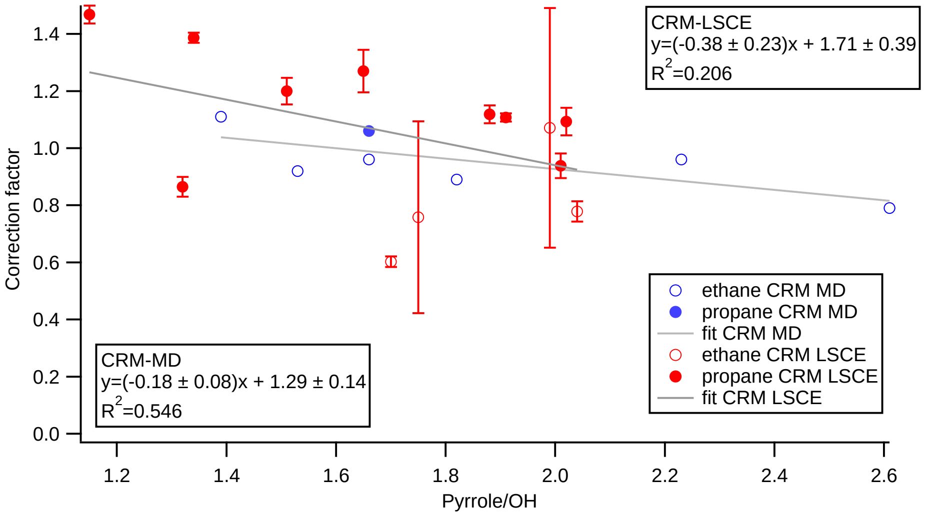

Fig. 1.

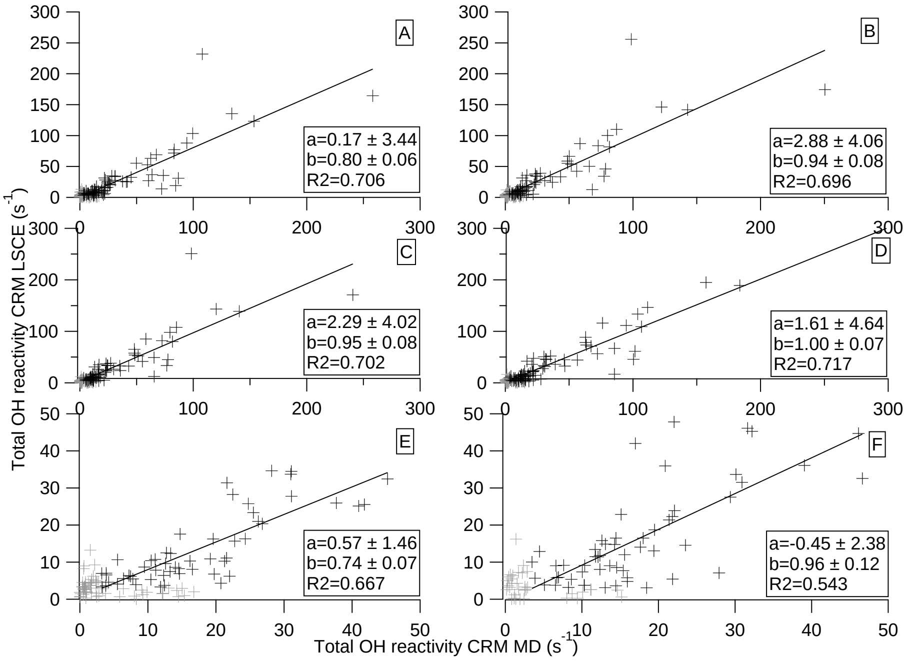
Total OH reactivity CRM LSCE (s^{-1})
Total OH reactivity CRM MD (s^{-1})
A
a=0.17 ± 3.44
b=0.80 ± 0.06
R2=0.706
B
a=2.88 ± 4.06
b=0.94 ± 0.08
R2=0.696
C
a=2.29 ± 4.02
b=0.95 ± 0.08
R2=0.702
D
a=1.61 ± 4.64
b=1.00 ± 0.07
R2=0.717
E
a=0.57 ± 1.46
b=0.74 ± 0.07
R2=0.667
F
a=-0.45 ± 2.38
b=0.96 ± 0.12
R2=0.543
0
50
100
150
200
250
300
0
10
20
30
40
50

Fig. 2.