

Interactive comment on “Molecular characterization of gaseous and particulate oxygenated compounds at a remote site in Cape Corsica in the western Mediterranean basin” by Vincent Michoud et al.

Anonymous Referee #2

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The manuscript by Michoud et al. presents a method of analysis with TD-GC-MS of gas and particulate samples for the determination of oxygenated compounds. It compares the new method with alternative measurements in Cape Corsica and then uses data on the concentration of oxygenated compounds in the two phases to calculate partitioning coefficients. It finally compares the experimental values of partitioning coefficients with theoretical ones. I think that the manuscript could be published but after major revisions. I was also wondering whether an analytical chemistry journal might be more appropriate given that the methodological part is extensive. However, the study on

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partitioning coefficients makes it absolutely interesting and suitable for an atmospheric chemistry journal.

Major comments:

Full validation of the new method is not reported. Please add LOD, LOQ, precision and recovery for each compound in both matrices. Please add all data pertaining to line 1-6 on page 10 to the supplementary materials. Please add an example chromatogram showing the separation of the different compounds and please report all retention times.

Concerning the method used for the calculation of VOC concentrations, not all VOCs react with water cluster ion and those who react may react through a ligand-switching mechanism rather than proton transfer. The formula used for the calculations is not generally applicable to all VOCs and each VOC should be treated correctly (reaction with H_3O^+ only, reaction with both H_3O^+ and H_5O_2^+ , proton transfer with H_3O^+ and ligand-switching with H_5O_2^+). At line 30 page 10, the authors refer to the signal of the H_3O^+ ion. Is this measured on the isotope ^{18}O and then corrected for the isotopic abundance? Was the ^{18}O used also for measuring the signal of H_5O_2^+ ?

What was the extraction protocol for DNPH cartridges?

Please add LOD, LOQ, precisions and recovery for the GC-MS method described at page 12-13.

IC and HPLC-PAD analysis are mentioned but methods are not reported.

Line 13 page 17 and elsewhere: may you be quantitative in discussing the agreement between methods rather than reporting qualitative adjectives such as “fair agreement”?

Line 31 page 17, was the thermodegradation observed with the standards?

Line 9-16 page 18, did you check recovery and matrix effects to investigate the causes of this large disagreement between the results from the different methods?

Concerning the section 3.2.5 on the partitioning of oxygenated compounds between the two phases, I have a general concern about the input data from the TD-GC-MS measurements. For some compounds, there was a clear disagreement between TD-GC-MS results and alternative methods (e.g. glyoxal), so I am not confident that the data quality was always good enough to obtain reliable results on partitioning constants. Concerning more specifically the calculations, it is mentioned that TSP concentrations are used but there was no mention on the paper about TSP measurements and all TD-GC-MS analysis were done on PM_{2.5}. In equation 3, activity coefficients are used but there is no reference or table reporting which ones were used.

Minor comments and typos: The introduction is very long and could be more focused. For example, I would remove the paragraph from line 26 at page 3 to line 8 at page 4. It does not add much to the discussion. Line 6 page 7: did you check that the filter does not cause absorption of SVOCs? Line 21 page 10: how humid was the humid zero air? Line 18-20 page 12: why the calibration was performed only 2 months before and not on-site? Did you do any quality check? Why a collection efficiency of 0.5 was used rather than a composition-dependent one? Line 18-20 page 13, the elution gradient is missing. Line 23-25 page 15, how high the ratios? Was there any long-range transport of dusts that could have influenced these ratios? Line 14 page 21, are you referring to compounds that were in-between the LOD and LOQ? Line 29-30 page 21, I am not sure if the discussion around Henry's law constants is relevant here. The absolute solubility of a compound in water may be more relevant in this case if we are discussing a transfer from particulate into water rather than a gas-water equilibrium. Line 4 page 25, oligomer production can happen also at high relative humidity and in the aqueous phase. Line 27 page 25, I believe "emphasis" should be "emphasizes" in this sentence. English is generally okay although it could be improved in some places. Please translate from French into English all labels in the plots in supplementary 2. In the table in supplementary 1 please change "substitut" with "substitute".

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