

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-518

Anonymous Referee #2

Referee comment on "Insights into tropical cloud chemistry in Réunion (Indian Ocean): results from the BIO-MAÏDO campaign" by Pamela A. Dominutti et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-518-RC2>, 2021

The manuscript presents and discusses results from chemical and physical characterization of clouds at Reunion Island. The study is impressively extensive with regards to the many chemical parameters measured in one study. The manuscript is very descriptive but the results are novel enough to justify publication as not many studies exist, especially in this kind of environment. The discussion is at times quite superficial though and does not lead to clear conclusions. Hence one wonders if some parts could possibly be omitted. Quite a few items should be clarified and potential artifacts excluded before publication of the manuscript.

Major points

The authors see a substantial amount of non-sea salt sulfate. Given that Reunion Island has active volcanoes, it immediately comes to mind if there is volcanic outgassing. This seems quite obvious as possible source and the total lack of discussion of this is surprising. Related to this the back trajectory discussion and figure only going back a few hours is a little surprising? What is the rationale to not look back further and more at regional transport. Both these things might be related and could/should be better discussed.

The experimental section lacks critical details, if this is a clear description of the collector and how the size cut was determined or a clear discussion on blank values (both organics and metals as the authors used an aluminum collector). The blank discussion is a must! For all compounds even the gas phase ones.

The authors tackle a very challenging task of measuring H₂O₂ and iron speciation in cloud samples. Given that both species are highly reactive, it is critical to specify how long the samples were sitting before being aliquoted and worked up. See e.g. Siefert et al., 1998

for measurements at 10 minutes. Given the reactivity, even long collection times will lead to reactivity in the sampling bottle. This is a little acknowledged in the discussion but it is unclear how long this was. Depending on the time delay that whole section could be not informative when the samples were sitting too long to say anything on the concentrations in clouds and the current text says this a little with the disclaimer in it. Therefore may be that section can be omitted as the experiment might not allow for any clear statement (and you have a lot of other interesting high quality observations).

Statistics are being used but they need to be described in the experimental section. For the correlations it is critical to say what is statistically significant and what not and at what confidence level. This is never specified and often only r^2 values are given which have no direct meaning while the discussion is qualitative "strong correlation". The PLS method needs to be clearly described. The whole PLS discussion is not very clear, neither how PLS was performed (experimental?), nor the results. This is very obscure actually. Also unclear is if PLS does fine with non normal distribution of variables and when the variables are not independent such as LWC and chemical concentrations. I do not say anything is wrong, it just need explanation and may be evaluation of this really adds anything to the manuscript?

The discussion of the partitioning makes one wonder about analytics. Terpenes are really hard to measure by grab and analyze methods. Could the discussion be clearer on how well the analytics did perform and if there could be realistic error bars on these measurements. Again there is also a concern for storage of the samples and transport? (if not analyzed at Reunion) and potential artifacts.

While I recognize that this manuscript is not a review paper, the results could however be put better in context. There is a substantial literature that is being missed on many of the chemical parameters discussed, on partitioning (going back to the 1980s) and on marine cloud observations. Too often Puy de Dome or source apportionment in metropolitan France seems to be the primary reference in discussions and while the authors might be most familiar with this, it is not necessarily the most appropriate references for context or insights. Overall the referencing could also be improved to justify methods (e.g. cloud collector or HPLC-PAD method) as the authors cite their papers but not where the collector is described in detail or the method but just papers where they use the device/method. The actual primary source would be most useful.

Minor

Experimental:

Given the presence of sulfur and aldehydes, would you know if HMSA shows as formaldehyde or not with your analytical method? There is a question if you have reactive sulfur (SO₂) that some of it could be in adducts and then if you still determine formaldehyde as formaldehyde or not, idem for sulfate. This will impact both your carbonyls and your sulfate values.

A clear description of sample conservation (fridge, freezer, bactericide) is missing

The authors mention in the ferrozine method description that they used aspartic acid. This seems highly unusual as iron is typically reduced by ascorbic acid? Is aspartic acid a common reducing agent?

Observations:

One misses a discussion of pH? And context to recent studies (e.g. Pye et al., ACP 2020)

Many other studies exist in marine environments. See airborne cloud observations by Sorooshian and others which have organic acids, carbonyls, discussion of chemistry (see current ACPD paper by Stahl et al., 2021 and references therein <https://acp.copernicus.org/preprints/acp-2021-403/>) or a recent study by Boris et al., 2018 which has many of the species that are covered here at a coastal site or Hatchings et al., 2009 has cloud VOC data, just some examples of actual relevant observations). These are just some examples, there are many more missed observational studies.

As for partitioning discussion, there were substantial discussion on small molecular weight organics and their partitioning in fog all the way back to the 1980s, see e.g. Winiwarter et al., 1994 and many papers... to the present day. see Stieger et al., 2021. Overall this discussion is quite superficial in the present manuscript. Other authors looked even at droplet size resolved differences.

details

L35 "As expected, our findings show the presence of compounds of marine origin in cloud water samples (e.g., chloride, sodium) demonstrating ocean–cloud exchange" this is a non statement, as any cloud water will have Cl and Na,. maybe say something on the ratio but not a sentence that does not say anything. Overall the abstract is lacking quantitative

information.

L45 "Additionally, several VOCs (oxygenated and low-soluble VOCs) were analysed in both gas and aqueous phases." But what was the outcome, quantitative information is missing here.

L64 how do clouds impact homogeneous gas phase chemistry? Consider reformulating

L70 What is the rationale here for the late 1990s.? this is a little unfair to some of the early studies who looked at organic matter in clouds... carbonyls, organic acids and even VOCs and higher organics were studied way before by people like Capel, Munger, Collett, Fuzzi and others (see also early EU funded large studies at Great Dunn Fell, Kleiner Feldberg or Po Valley.... Including papers on Henry's law).

The statement on the non targeted compounds, there are some (semi-)quantitative papers out there using chromatographic separations by Decesari or Herckes while for mass spectrometry and besides your work, there are others too who used this like Mazzoleni (<https://doi.org/10.1021/es903409k>)

Also geographically Southern Hemisphere, there is work in Namibia and other locations.

L86" "near urban conglomerates"? does not sound right? Consider reformulating

L185 Typo in sulfate SO₄²⁻ not -2

L268 and others: Deff may be written D_{eff} with eff as subscript

L288 and other locations correlations please state what is significant and what not and at what level

L313 +- 44.0 please keep decimals consistent

L340 "contrarily" sounds odd starting the sentence with an adverb, consider reformulating

L356 even though.... Consider reformulating

357" what does "is found to be dominant" mean?

L370 If you keep this discussion then the issue of storage and possible artifact from reactivity before you measure needs to be front and center and not just some detail at the end

L478 AA_ contribution

L480 cloudS

L488 AA_ distribution

L512 are all your OVOCs carbonyls?

L517 and other locations. What are "highly marine" clouds at PUY?

L522 OH radical: please use center dot symbol

L539 I suggest you say low solubility and VOCs (no " ' " when plural)

L541 suggest you say " even THOUGH these compounds..."

L541 what does "Sanitary" mean? Do you mean that they have a potential health effect? Adverse effect on environmental or human health?

L552 suggest you cut one decimal in the numbers idem lines 562/563

L563 " in his review" suggest to use "their" review this was more than one author

L675 what is a "cadastre"?

L688: "which could suggest the influence of dust sources (Samaké et al., 2019b)." but how does Ca look in these samples, given what you say about Ca, does this here really make sense?

L689-91 "Strong correlations are also observed between polyols (inositol, sorbitol, arabitol and mannitol) with nitrate and potassium, suggesting the contribution from biomass burning sources (Li et al., 2003). Interestingly, levoglucosan, a well-known biomass burning tracer, does not show any correlation with any of these ions." 1) what is a strong correlation? 2) nitrate is not a biomass burning tracer and 3) many studies showed that levoglucosan and K⁺ are not necessarily well correlated as K can have other sources while levoglucosan can vary by a factor of up to 10 depending on the fuel burnt. The latter is why I mentioned that French source apportionment studies are not necessarily relevant for what is happening at La Reunion, the biomass burning seen at La Reunion is likely not a fireplace like in the Alps.

L733 "However, our results depict even higher supersaturation of terpenoids, suggesting their importance in the aqueous phase chemistry in highly impacted tropical areas." What is this statement based on?

On figures:

Figure 4: hard to see the difference in shades and impossible to read the % numbers in the pie chart and for sure there should be less digits

Figure 5: again hard to see the differences in shading and what is the rationale for the color? As there are anhydrous, there are polyols, there are saccharides... but all are mixes?

Figure 6: hard to read the number in the pie diagram also too many digits. Same thing what is the rationale for the color coding?

Figure 7: left panel/ why just lines with dots? Right panel: right pie chart cannot read too

small and what are light acids?

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