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Comment on acp-2021-601

Anonymous Referee #2

Referee comment on "Understanding aerosol composition in a tropical inter-Andean valley impacted by agro-industrial and urban emissions" by Lady Mateus-Fontecha et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-601-RC2, 2021

The manuscript by Mateus-Fontecha and coworkers describes the results of an intensive field study to characterize the PM2.5 burden in a major economic region of Colombia, the Cauca River Valley (CRV), both in terms of total burden and of their sources, in particular sugarcane processing. The presented work relies on the analysis of 24 h filters, and both the major components are reported (following the IMPROVE protocol), and important additional information on possibly source profiles is gathered by the additional analysis of metal and organic markers (specifically primary BB tracers, PAHs, and alkanes). This is then complemented by a Principle Component Analysis (PCA) of the measured variables, with mixed results.

Overall this is an interesting study addressing two important subjects, rural/suburban air quality in developing countries and the contribution of sugarcane harvesting and processing to the overall biomass burning (BB) emission burden. But, perhaps unsurprisingly, the low time resolution of the measurements, lack of ancillary measurements to further characterize meteorological/source regimes and uncertainties in the variables reported severely limit the interpretability of the results. Hence while the PM2.5 speciated data presented here from a very understudies region of the worlds is a valuable datapoint for future studies, most of the attempts at source identification and apportionment, specifically for sugarcane emissions, is inconclusive. Additional analysis is likely to lead to better constrains from the current data (some suggestions are given below), but overall I think it is unlikely that a full source characterization will be viable with the methods and analysis tools being used. Therefore, should the authors decide to resubmit to ACP, this is a pretty ideal candidate for the "Measurement Report" category: novel enough to warrant publication in ACP, but without the type of scientific findings we expect for a full ACP paper.

Major comments:

- While the data and methods are presented quite well, the manuscript seems unfocused in the introduction. As the abstract makes pretty clear, this is first and foremost an observational report from a rural/suburban area with some AG burning thrown in. So I would expect a discussion of similar studies both in South America as well as other rural areas. Instead, the intro is focused on sugarcane burning, which might be one motivation for this study but is certainly not its main goal nor result. So a reorganization of the intro would I think make clearer what this effort is about and also help shorten the overall length.
- The paper clearly shows that there is plenty of primary aerosol in the CRV, both from fossil fuel (FF) combustion and agricultural burning (BB). However, the EC/OC ratios for these two types of sources are quite different (also b/c of some fraction of brown carbon getting assigned to EC in the sunset instrument). So using a simple regression to differentiate primary and secondary OC in this case is likely not very accurate, as the authors concede. A multivariate analysis is often superior in separating the different contributions, but the PCA analysis shown later does not really seem to be providing a meaningful distinction. So assuming a better multivariate analysis is not available, it might be better to try to predict primary OC based on a simple linear model that uses e.g. levoglucosan or K+ (which as a non-volatile tracer is likely a better choice) as a predictor for primary BBOM, and the sum of the lower alkanes as a predictor for primary OM from FF. As a boundary condition, we know that for most types of primary BBOA, levoglucosan is 3-6% of the total OA, so 5-8% of OM (see e.g. Jolleys et al 2015 and Sullivan et al 2019). This approach will likely underestimate secondary OM, but it will possibly give us more insight on what conditions actually lead to these primary components being maximized.
- In that context, if the filtered extracts were still available, the authors could consider running a 14C analysis on the OM fraction, which would separate the FF contribution from everything else and hence also provide much better constrains on the sugarcane emissions, the main interest of the authors.
- The values currently used for the OM to OC conversion are reasonable, and clearly contribute to a decent mass closure (which I think should be better documented by e.g. showing a timeseries of the mass closure for each filter). However, I am not following the reasoning behind some of the values discussed. For primary BB emissions, in his recent review, Andreae (2019) used 1.6, which is a number that is roughly consistent with the results from other recent primary BB studies (e.g. Hodshire et al, 2019). BBOA can oxidize quite quickly, so secondary BBOA can indeed exhibit much higher OA:OC ratios, but that's not relevant in that context. Likewise, levoglucosan is an excellent tracer for primary BB, and hence does not belong into a discussion of secondary OM/OC. Importantly, references for the 2.1 value used for secondary OM are completely missing.
- I am puzzled by the discussion of particle acidity. It is obviously always problematic to infer acidity without taking into account the gas phase, but having said that, a Cation:Anion ratio of ~0.8 is in most cases indicative of a fairly acidic aerosol (e.g. not that different from the SE US, where pH~1 was reported by Guo et al, 2015). And as the authors write, the NH4:SO4 ratio suggest that the fine aerosol might be even more acidic (Cation:Anion ratio of ~0.6) and that seasalt and dust are probably biasing the bulk ratio high. This has a few important implications that I think should be discussed at greater length:

- If the aerosol is this acidic. nitrate is mostly going to partition to the gas phase, which is essentially what the data shows (although as mentioned below, some volatilization might play a role here). So nitrate from both NOx emissions from primary combustion processes is not going to be detected, and therefore there is no point in interpreting NO3/SO4 ratios as indicative of any particular source. Furthermore, as discussed later in the PCA section, a significant fraction of nitrate seems to be associated with dust, so it is likely that there is no secondary NH4NO3 in this dataset at all. If so, the mass closure might improve by assuming all nitrate to be Ca(NO3)2 and not NH4NO3
- But more importantly, given that both agriculture and BB are large sources of NH3(g), this is a very surprising result and I would encourage the authors to try to understand how it comes about. Given the overall composition, a fairly large source of SO2/H2SO4 would be needed to sustain such an imbalance (e.g. like the large SO2 emissions from coal fired plants in the SE US). But that does not seem to be the case here. Alternatively, the marine aerosol coming off the Walker Circulation might be quite acidic (e.g Nault et al, 2021), but that would imply that most of the sulfate is of marine origin, which seems unlikely.

- Related to the previous point, I wonder if there are published MSA/SO4 (or SO4/seasalt) ratios for the coastal aereas in Colombia that could be used to address one of the larger open questions in this study, namely how much background aerosol from the ocean (and also the mountains when the katabatic winds kick in) contributes to the air quality in the CRV.
- In its current form, the PCA analysis does not really contribute much to our understanding of the data, especially since the factors are not really discussed in the context of the rich marker analysis introduced before. But regardless how it is presented, while the factors for FF combustion make some intuitive sense, that's not the case for the others. E.g. having all the secondary and marine aerosols in one factor (factor 2) probably mostly reflects that all of these come from the same wind direction and have no strong correlations with other factor. Likewise, I was surprised to see levoglucosan in the road dust factor and Cl in one of the dust factors, but not associated with MSA/Na. To be clear, multivariate analysis is often messy, so some oddities are normal, but overall this analysis seems unfinished and tacked on. As the other reviewer already mentioned, this could at least partially be due to PCA not being the best tool to analyze this type of data, especially given how many low S/N tracers are included in the input matrix. But regardless of the choice of method, the whole point of such an analysis is to simplify the trends in the data, and it clearly fails at that. So I would suggest either eliminating it completely, and instead spend more time discussing how to combine the different findings from the marker analysis (which is currently missing), or try to find a new solution, either with PCA or other techniques (e.g. PMF) that is more suitable. In the end, the dataset might just be too flat to get good factors out of it, so the marker discussion approach seems more promising.

Minor/technical comments:

- All the abstract level numbers seem to be at least 1-2 digits over their actual significance, consider revising
- All Figures (except maybe Figure 3): please increase the font of the axis by at least 30-50%, very hard to read
- A dust fraction of 9% in PM2.5 is quite high, and would suggest that PM10 is quite a bit larger than PM2.5, this should probably be mentioned in the discussion of inventories vs measurements
- Semivolatile components of PM, such as ammonium nitrate and SVOA can easily evaporate from filters, biasing the fractional and overall composition measurement (see e.g. Heim et al, 2020 for a recent example). The sampling site seems to have been fair enough removed from primary sources that this is probably a minor concern, but it is a common filter artifact that should be mentioned.
- Given how stable the RH was during sampling (which should probably be better emphasized when discussing this), there is nothing wrong with estimating a constant particulate water contribution with E-AIM, although it might be simpler and more comparable to just use speciated kappa values instead (e.g. Peters et al 2007, Brock et al 2016).
- I am not too familiar with the CPI measure, but I wonder if BB emission could lead to e.g. a bias towards non-FF emissions, please discuss.
- L44-L47: One large emission source that remains unmentioned here but is brought in later are FF emissions from often unregulated agricultural heavy machinery (L96), it could be mentioned here as well.
- L54: This statement seems to be a gross exaggeration, and is also not supported by the reference provided. Biomass burning as a whole is indeed one of the largest sources of particles by mass worldwide, but the estimates for the contribution of agricultural fires are all over the place. This is to a large extent due to fact that non-wildfires BB sources are much less studied, and hence the current work is a welcome addition to the literature, but this needs to be qualified by a lot or rephrased.
- L60-62: If I follow, there is an important distinction to be made here: most AG burning is to clean out fields post-harvest. Sugarcane is burned as part of an expedited harvesting practice (although it might also be used post-harvest - this is not clear from the manuscript). This matters ultimately in terms of possible mitigation practices, so would suggest clarifying
- L67: Not sure how that reference is relevant. Also, you already mentioned AG burning field studies in L57-59, and those were not out of Europe/North America
- L84: I think "center" makes more sense here than "centroid"
- L102: The source for the non-sugarcane emission inventories should be mentioned here as well, not just in the table
- L117: I think you mean "attribution", not "identification" (which has already happened)
- L154: Source for the fire events?
- L212: "non-combustion"
- L218: same comment as before
- L507: "zero", not "cero"
- Figure 2: Please specify what the red points in the right side figures are. I assume they are the upper 10% outliers, but that's not explained. Also, I would strongly suggest to show the average direction as a function of time of the day in the right side plots as well, since the afternoon switch in wind direction is key to interpret the results.
- Figure S1: Pleas use English abbreviations in the X-Axis. Also, indicate the source of this information
- Figure S2: Same comment about the X-Axis. Also please consider making the legends larger, it's extremely hard to read atm. Also please add the source of these measurements
- Figure S4: Legend for line+symbol trace missing

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