Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2021-930-RC1, 2021

Comment on acp-2021-930

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Referee comment on "Cellulose in atmospheric particulate matter at rural and urban sites across France and Switzerland" by Adam Brighty et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-930-RC1, 2021

Review of Brighty et al., "Cellulose in atmospheric particulate matter"

The submitted paper constitutes a fine research work about a seldom reported topic: "Cellulose in atmospheric particulate matter".

The general appearance is excellent, there are clear intentions, interesting conclusions, and an intention to deliver a "new standard" in this field is glaring. In fact, the delivered data is one of three of the larger data sets obtained for the occurrence of atmospheric cellulose so far. However, the treatment of the past literature and the presentation of data leaves to be improved.

Historically the first large data set originated from the CARBOSOL Project – with data from 6 – regional to remote background sites in a west-east transect from the Azores to Hungary, spanning a two year period, and published in a JGR series of papers overviewed by Legrand and Puxbaum (JGR 212; 2007; https://doi.org/10.1029/2006JD008271), and for cellulose reported by Sanchez-Ochoa et al. (JGR 212; 2007) – cited in the submission.

Second is the AQUELLA data set, from urban and regional sites in Austria. It comprises a large data set from several local and regional projects in Austria. The results were given in Reports to the Country Governments, however not published in scientific literature, except for following 10 sites: - 4 sites in Vienna, 3 sites in Graz and surrounding, and 3 sites in Salzburg and surrounding, with data over a year – these data are reported in detail in Alexandre Caseiro´s doctoral thesis (2008) – cited in the submission.

The third larger data set arrives now in the current submission, with data from 9 sites in France and Switzerland, over time spans of around two years.

There are also reported atmospheric cellulose data from shorter studies, including the primary paper on cellulose in the atmospheric aerosol (Kunit&Puxbaum 1996), and about the occurrence in fine particles (Puxbaum&Tenze-Kunit 2003). Followed by papers from measurement campaigns with aerosol-mass-spectroscopic instrumentation designed to find more conveniently instrumentally accessible markers for plant debris or vegetative detritus (two papers from Yttri et al., cited in the submission, and papers from campaigns of the Paul Scherrer Institute – not cited in the submitted text (e.g. Lanz et al., EST 2008 - https://doi.org/10.1021/es0707207 ; Daellenbach et al., ACP 2017 - https://doi.org/10.5194/acp-17-13265-2017).

A clever presentation and comparison of recent data with earlier ones is presented in the (cited) Bozetti et al., EST 2016 paper, which seems to be a sort of precursor of the current submission. It is recommended to the current authors to think of a presentation for comparing cellulose data from different studies as shown in the Bozetti paper / or in another overview type graph or table.

Overlooked has been a quite important paper from the Aveiro Group about the Indoor-occurrence of particulate cellulose: Cerqueira et al. Atmos.Env. 2010 - doi:10.1016/j.atmosenv.2009.11.043 .

And – there is a report about cellulose in Beijing aerosol determined with the Kunit-Puxbaum assay: Yi DING, et al., Study on the Vegetative Detritus Contribution to Beijing Urban $PM_{2.5}$ Using Cellulose as a Marker[J]. *Rock and Mineral Analysis*, 2013, 32(5): 738-746 (no doi given, access via Google scholar).

I absolutely recommend publishing the paper, however after a thorough revision including following improvements and corrections:

- In the introduction various aspects of aerosol characterization are mentioned, of which most are only weakly related to the topic of determining an insoluble component of the organic aerosol. The background to understand the composition of insoluble organic particles and the contribution of vegetative detritus to the atmospheric aerosol dates back to the times of Glen Cass, Monica Mazurek, Lynn Hildeman, Berdt Simoneit, and Wolfgang Rogge, who was the thesis candidate and paper lead author. The primary point of the Rogge et al., Atmos. Env. 1993 - https://doi.org/10.1016/0960-1686(93)90257-Y paper for the cellulose issue was the clear statement that in the investigated case of LA aerosol, more than 50% of the organic material was insoluble in water and common solvents. And they proposed markers obtained from the "soluble" part to draw conclusions about insolubles, e.g. plant waxes for vegetative detritus – Rogge et al. EST 1993 -

https://doi.org/10.1021/es00049a008 . The vegetative detritus marker in the Rogge et al paper, however was going back to Simoneit and Mazurek`s paper in Atmos. Env. 1982 - https://doi.org/10.1016/0004-6981(82)90284-0 . The search for primary biological particles was getting directed towards insoluble bio-polymeric material already by Matthias-Maser&Jaenicke, continued for cellulose containing particles by Kunit and Puxbaum.

- The treatment of the insoluble particles in the manuscript should disentangle the bacteria/fungal spores story versus the plant fragments story – while for the determination of primary "idividua" a range of possibilities is available, as is most of the literature about PBOP, for the plant fragments only a few groups are currently involved (see above).

- A) Time sequence of citations:
  Please sort the citations in text chronologically - by the year of appearance, then the primary information should get credit.
  B) Unclear citation sequences: e.g. line 60:
  "In the majority of studies, at most 20% of the OM can be speciated and quantified at the molecular level (Michoud et al., 2021; Alfarra et al., 2007)" Actually, the sentence is sort of textbook knowledge, now what is the reason, to cite these two papers here? Did they increase the per cent output of OM?
  Why we should think of the unability for GC-MS or aerosol-AMS techniques to find more of the soluble OC part, when the study is directed to the insolubles?

- Detailed request for responses:

Line 24: "novel HPLC-PAD method": The "HPLC-PAD" method appears in Samake et al., 2019 in Supplement 2; in Borlaza et al., 2020, and now in Brighty et al. It was used in a likely different modification in Daellenbach et al., 2017 (https://doi.org/10.5194/acp-17-13265-2017) and could go back in the HPLC-PAD part to the Iinuma et al., 2009 method, so the expression "a new method" should be reconsidered.

Line 47-49: What actually had been "deeply improved"?

Line 55-57: Primary citation on the EC/OC content of aerosols would be Novakov/Hansen (Designers of the Aethalometer) and Birch&Carey (Designers of the Sunset Instrument). I miss in this respect the important parameter "Brown Carbon", which came accidentally today over my desk: Solomon et al. 2021 (https://doi.org/

10.3390/metrology1020010) – BrC another GC-MS wise not accessible component of the organic aerosol.

The citations in the text are certainly given with a respective idea – this is however not obvious for the reader –

Line 71-73: "such particles": After experiments of Mathias-Maser&Jaenicke, and from Kunit and Puxbaum, we know already, that PBOP are at least 2 differently emitted and behaving particle types, so thus the reference to "such particles" is unclear. See my general comment above.

Line 75-76: "solid airborne particles derived from biological organisms, including microorganisms and fragments of biological materials such as plant debris and animal dander" (Fuzzi et al., 2006; Després et al., 2012).

You use a direct quotation and 2 citations – so who of the two stated the sentence?

Line 83-85: Which of the published emission estimates differentiated between viable particles and plant matter?

Line 101: "Cellulose is used as a molecular marker in order to quantify the total ambient concentrations of plant debris (Sánchez-Ochoa et al., 2007; Butler and Bailey, 1973)": Butler and Baily are a plant physiology textbook and for sure never stated, that cellulose might be used as marker in atmospheric studies.

Line 104: What is meant by an "insufficient ambient condition"?

Line 114: There is a misprint: the delignification step for plant particles was first described by Kunit and Puxbaum 1996, following and down-scaling a method of Gould et al., 1984,

for delignifying agricultural residues.

Line 117-123: I have tried to find the "stark discrepancies" – in my opinion, this argument is a result of a sloppy reading past literature – by checking Sanchez-Ochoa, and Caseiro data I do not see such stark discrepancies and therefore recommend to include the larger past data sets into a comparison table or graph – and the differences will clear out. E.g. The authors mixed up the absolute annual concentration trend – and the relative concentration related to OC. They neglected important characteristics of site differences – e.g. for the CARBOSOL project the differences in site characteristics, see May et al. Tellus 61B, 464-472, 2009. In fact, the overview of the present data, together with earlier published ones allows to offer an overview about communalities and differences, and increase the outcomes of scientific goals of the authors, to understand the atmospheric behavior and fate of plant debris.

Line 125-126: Is here meant, that more data in addition to the current ones are needed, or is this an appraisal of the data given in this article?

Line 134-135: I agree, that you have a very fine and for several reasons important data set. I recommend adding, that you have the chance for PM2.5/PM10 inter comparison, which is really a very important contribution, and the bi-annual data set (which had been also available in Carbosol, but with far lower time resolution).

Chapter 3:

Why the intercomparison with earlier data is performed at the start of the chapter, and not at the end after showing your data?

Could you think of a graphic intercomparison – including the elevational differences of the sites? The elevation of sites ranges from near zero to 3000 m. From remote – some 1000 km out in the Atlantic – to urban.

While I agree that local influences are actually very important, how can the relatively high absolute concentrations at the 3000 (SBO) and 1400 m (PDD) level can be explained?

There might be an overviewed summer source for cellulose at low and mid alpine levels: Grass mowing – hey drying (see EMEP/EEA air pollutant emission inventory guidebook 2019 chapter 11C, NFR Other Sources and Sinks: Natural Grassland and Other Vegetation) – Alpine meadows undergo a 2-3x cut per season (graph below from p.16,

/b11.C Other Sources and Sinks; Activities 110401-110404.

A comment about correlations: If you have a set of spurious sources (in addition to one major source) why should you find then a correlation of the spurious with one of the other known tracers? Cellulose obviously is supplied from many small sources of a very large reservoir.

Is there a reason for fully neglecting the possibility of a biomass combustion contribution – an emission factor / relationships to smoke mass are found in TU Wien wood combustion studies. In Schmidl et al., Atmos. Env. 42, 126-141, 2008; 0.08% w/w in a mixed sample of beech and spruce wood smoke was identified.