

Atmos. Chem. Phys. Discuss., referee comment RC1  
<https://doi.org/10.5194/acp-2021-516-RC1>, 2021  
© Author(s) 2021. This work is distributed under  
the Creative Commons Attribution 4.0 License.

## Comment on acp-2021-516

Anonymous Referee #1

---

Referee comment on "Chemically speciated mass size distribution, particle density, shape and origin of non-refractory PM<sub>1</sub> measured at a rural background site in central Europe" by Petra Pokorná et al., Atmos. Chem. Phys. Discuss.,  
<https://doi.org/10.5194/acp-2021-516-RC1>, 2021

---

Review to „Chemically speciated mass size distribution, particle effective density and origin of non-refractory PM<sub>1</sub> measured at a rural background site in Central “ by P. Pokorna et al.

This manuscript reports on two one-month field measurements conducted in summer and winter, respectively. This study is the first of its kind in the Czech republic. The results are used to infer general particle properties, the origin of the aerosol particles, and their effective density of the particles.

The fact that this study is the first in the Czech republic makes the data set interesting, but on the other hand, Czech Republic is in the middle of Europe, so one would not expect to see large differences in chemical composition and particle origin compared to neighboring countries where many studies like this (using ACSM and AMS instrument) have been already conducted.

Furthermore, the results are not presented in a clear and concise way. There is no clear concept in this manuscript, no “story line”. The analyses are done one by one, without connecting them, and many times the order of the analyses is confusing to the reader. The overall findings are not clearly summarized and highlighted. Some weaknesses are found in the discussion of the effective density.

I therefore recommend major revisions according to my comments below

### Major overall comments

### 1) Effective density

The authors use two different equations to calculate the effective density. The first is taken from DeCarlo et al. (2004). Here it should be mentioned that DeCarlo et al. give three different possible definitions of the effective density. This should be commented.

The second definition used here relies on the measured composition of the particles. Thus, this represents the "real" density of the particle material, in DeCarlo this is denoted with "rho\_m". This is not an effective density. In fact, using DeCarlo's equation 45, one can infer the Shape factor from measuring rho\_eff and rho\_m. Thus, I think here is some general lack of understanding what the measured quantities mean.

### 2) Structure of the manuscript

As I mentioned above, there is no clear story line in the manuscript. It more reads like a measurement report.

For example I suggest to discuss the results from the clustered trajectory analysis before the single events. The presentation should progress from a general overview (Fig 2) to the general results of air mass origin (Fig 4) to the specific events (Fig 3 + Fig 5).

Furthermore, the definition of the events needs to be made clear. I also suggest moving a few figures from the appendix to the main text (see details below). Tables, in contrast, may preferably go into the appendix.

### 3) PMF of particle number size distributions

I am not sure about the PMF results. Factors obtained by PMF have to be checked whether they are physically meaningful. I don't see how this has been done here. The presented factors do not look like ambient aerosol number size distributions. This needs to be justified and better explained.

## **Specific comments**

Lines 138-139:

Is this only the sulfate CE? What CE values were used for the others?

Lines 150 - 153:

I don't understand in the first approach how you calculated  $D_m$ . Why use  $1.5 \text{ g/cm}^3$ ? Where does this come from? Why not calculating  $dV$  from  $dN$  (using  $D_m$ ), and then comparing the main mode of MPSS and AMS and adjusting the density (thereby changing  $D_{va}$  to  $D_m$  with Equ.1) until the position of the main modes match?

Line 167:

Is the organic density from Turpin and Lim appropriate for your conditions?

Lines 184 ff (Section 2.2.4.1):

I don't understand what was chosen here. What was the intention? To find out episodes with highest number concentration? Why do you need PMF for that? Why not taking the time series of the total number concentration and select based on a threshold or based on probability density function?

Lines 231-232:

Why are you using a constant density and not the density derived from AMS?

Lines 243-239:

Shouldn't the transmission effects be taken into account by the CE correction? As far as I understood, the CE correction was based on comparison of AMS data to filter data. So the same method as applied here. So, why is there a difference? This also refers to my question on the CE values for the other species above.

Lines 240-241:

Yes, the constant density is certainly a limitation. So why not use the density inferred from the chemical composition? Or otherwise: Why presenting two closures? For volume closure, you convert AMS mass to volume using the measured density, for mass closure, you convert the MPSS volume to mass using a constant density of 0.5. What additional insights do you expect from the mass closure if it is clear that the assumed density is a simplification?

Lines 254-256:

Are the CE estimation and the mass closure also affected from this  $\text{NH}_4\text{NO}_3$  loss? I would think so.

Table 2:

Why do you calculate the NR-PM1 share? Why not taking AMS +eBC as the "total PM1" reference? I think we would learn more from a "share on PM1".

Line 306 (caption Fig 2):

Again, why not taking the measured density?

Line 308:

What were the exact selection criteria? The explanation given in 2.2.4 is not clear. Additionally I think it would be helpful to indicate the selected events in Fig 2.

Line 311 ff, Figs A6, A7, and Section 2.2.3:

It is not clear how the trajectories were calculated. In Section 2.2.3 it is said „500 m“. In Fig A6 and A7 it appears that 100, 500, and 1500 m were used.

Trajectory analysis requires more information on variability. Either initialize the calculate at least every hour during the selected events (some events last more than 12 hours, a time during which the air mass origin may change), or use the "ensemble" mode where HYSPLIT varies the initial conditions. This allows for a better estimation on the spread and the variability of the air mass movements

Line 330:

What is f44f60? Furthermore, f44 and f60 have not been introduced up to here.

Lines 335 ff:

Please give a short explanation what f43 and f44 are. Not every reader is an AMS user. The paragraph needs references (e.g. to Ng et al., 2010, for f43 and f44), but also later when MOOA and LV-OOA are mentioned (e.g. to Jimenez 2009, Crippa 2013 etc).

Lines 347 ff:

I am surprised by the low BB content in the rural winter data. Can you comment on lifetime and aging of f60? See Cubison et al. (2011), Hennigan et al (2011) and Milic et al. (2017)

Fig 4:

The bars for chloride in winter look strange. Were there many data gaps or data below the detection limit? Please explain.

Fig. 4:

Please add total PM1, eBC and total particle number to Fig 4.

Lines 395-396:

The episodes need to be defined earlier (see comment above asking for the selection criteria), and this would include also the split of W6 episode.

Table 3:

Caption should read "Mode diameter of mass distributions"

Lines 440-442 and Fig 5:

This finding is interesting and deserves more discussion. The correlation between organic particle size and f44 is a new result. Is the correlation for summer significant? Do you expect a linear relationship? Have there been other studies doing this?

Lines 449 ff (Section 3.5):

Are the episodes here the same as S1-10 and W1-13?

Lines 453-454:

PMF: How did you decide what is the most physically meaningful result? The whole PMF procedure need more explanation. Is it common to apply PMF to PNSD? Are there references?

What are "two-sided size bins"? Each bin has two sides. Do you mean "the first two bins and the last two bins"? And did you downweigh them because of low particle numbers in those bins?

Fig A10:

The lines represent the percentages, not a fitted lognormal distribution to the total PNSD. Wouldn't a meaningful factor look like a lognormal distribution? I think that the idea of PMF is that you add up the individual contributions (of different particle sources) to the total observed particle population. Similar to in AMS PMF, where the individual factors have to correspond to existing mass spectra (of reference particles or other observed

particle types). So here I would assume that the individual factors should look like size distributions as well. Some of the factors do not look like "typical" size distributions. But it may well be that I am wrong, so please explain and comment.

Line 463 ff:

Here it becomes clear that the "high particle number concentration episodes" are not the same as S1-10 and W1-13. So W1-W8 from Table 4 are not the same as W1-W8 from Table A1? This is indeed confusing to the reader.

Line 481 ff:

The "episodes of high mass concentration" are the same as those from Table A1, as I guess now.

Table 4 vs Table 5:

Why did you use only one method for the effective density in Table 4 but both methods for Table 5?

Fig A5 and A13:

I suggest moving Fig A13 and Fig A5 to the main text. There too many important figures in the Appendix.

Fig A13:

How does the plot look when you include the densities from Equ (1)?

Fig A14:

Move also Fig A14 to main text. Rather shift tables into the appendix (the reader likes to

see figures not tables). Which equation was used? (it is missing in the caption). Furthermore, it seems tha the fit to nitrate for summer do not really match the data points

Extrapolating the organic fraction would reach from  $\rho = 1.2$ . at 100% org to  $\rho = 1.77$  for 0% organics. That fits very well to the "real" density. I therefore suggest to expand the y-axis and extend the linear fits.

Lines 512 – 518:

The differences between Equ 1 and 2 for the density is basically the shape factor (see DeCarlo).

Therefore, from comparison between (1) and (2) you can infer the shape of the particles. I think that's important piece of information you can retrieve here,

Summary and Conclusions:

This is only a summary. You repeat the findings that you listed in the individual sections of the paper. But are there any conclusions? I think that the density results in Figs A13 and A14 are interesting enough to discuss them further. As I said, Equ (2) yields the "real" density ( $\rho_m$  in DeCarlo), while Equ (1) (which is Equ 44 in DeCarlo 2004) yields the effective density. If you include Equ [45] from deCarlo, you can infer the shape factor from the measured parameters.

### **Technical comments**

Line 103: "1" is missing in "16.7 l min<sup>-1</sup>"

Line 105: "0.1-l min" -> "0.1 l min<sup>-1</sup>"



Line 105 – 108: Only the IE calibration is performed in BFSP mode, the other two don't require BFSP. Performing an IE calibration only at the beginning of the campaign is not best practice. Typically it's recommended at minimum once per week ([http://cires1.colorado.edu/jimenez-group/wiki/index.php/Field\\_ToF-AMS\\_Operation#Standard\\_Field\\_Calibration\\_procedures](http://cires1.colorado.edu/jimenez-group/wiki/index.php/Field_ToF-AMS_Operation#Standard_Field_Calibration_procedures)), but at least a second IE calibration should have been performed after the campaign

Fig A2: It is easier to compare if %-scales are the same

Line 242: Ammonium (ammonia is the gas NH<sub>3</sub>)

Fig 1: Right plot axis labels:  $\mu\text{m}$  ->  $\mu\text{g}$

Line 148: The data are recorded a function of particle time-of-flight (PToF). 10 nm – 7000 nm is just an extrapolation of the size calibration curve to the PToF. It is not the actual size range (as you mention), because the aerodynamic lens does not transmit particles over this size range. But please delete this size range here because it is not real. A related question: which type of aerodynamic lens was used in this C-ToF-AMS?

Line 148: correct "Squirrely"

Line 150: "he" -> "the"

## References

Crippa, M., DeCarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., Nicolas, J. B., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J.-L., Prévôt, A. S. H., and Baltensperger, U.: Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris, *Atmos. Chem. Phys.*, 13, 961-981, doi:10.5194/acp-13-961-2013, 2013.

Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune,

W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A., and Jimenez, J. L.: Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, *Atmos. Chem. Phys.*, 11, 12049–12064, <https://doi.org/10.5194/acp-11-12049-2011>, 2011.

Hennigan, C. J., Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., Sullivan, A. P., McMeeking, G. R., Coe, H., Wold, C. E., Hao, W.-M., Gilman, J. B., Kuster, W. C., de Gouw, J., Schichtel, B. A., Collett Jr., J. L., Kreidenweis, S. M., and Robinson, A. L.: Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber, *Atmos. Chem. Phys.*, 11, 7669–7686, <https://doi.org/10.5194/acp-11-7669-2011>, 2011.

Jimenez, J.L., M.R. Canagaratna, N.M. Donahue, A.S.H. Prevot, Q. Zhang, J.H. Kroll, P.F. DeCarlo, J.D. Allan, H. Coe, N.L. Ng, A.C. Aiken, K.D. Docherty, I.M. Ulbrich, A.P. Grieshop, A.L. Robinson, J. Duplissy, J. D. Smith, K.R. Wilson, V.A. Lanz, C. Hueglin, Y.L. Sun, J. Tian, A. Laaksonen, T. Raatikainen, J. Rautiainen, P. Vaattovaara, M. Ehn, M. Kulmala, J.M. Tomlinson, D.R. Collins, M.J. Cubison, E.J. Dunlea, J.A. Huffman, T.B. Onasch, M.R. Alfarra, P.I. Williams, K. Bower, Y. Kondo, J. Schneider, F. Drewnick, S. Borrmann, S. Weimer, K. Demerjian, D. Salcedo, L. Cottrell, R. Griffin, A. Takami, T. Miyoshi, S. Hatakeyama, A. Shimono, J.Y. Sun, Y.M. Zhang, K. Dzepina, J.R. Kimmel, D. Sueper, J.T. Jayne, S.C. Herndon, A.M. Trimborn, L.R. Williams, E.C. Wood, C.E. Kolb, A.M. Middlebrook, U. Baltensperger, and D.R. Worsnop, Evolution of Organic Aerosols in the Atmosphere, *Science*, 326, 1525-1529, doi: 10.1126/science.1180353, 2009.

Milic, A., Mallet, M. D., Cravigan, L. T., Alroe, J., Ristovski, Z. D., Selleck, P., Lawson, S. J., Ward, J., Desservettaz, M. J., Paton-Walsh, C., Williams, L. R., Keywood, M. D., and Miljevic, B.: Biomass burning and biogenic aerosols in northern Australia during the SAFIRED campaign, *Atmos. Chem. Phys.*, 17, 3945–3961, <https://doi.org/10.5194/acp-17-3945-2017>, 2017.

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prévôt, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, *Atmos. Chem. Phys.*, 10, 4625–4641, <https://doi.org/10.5194/acp-10-4625-2010>, 2010.