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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Four-year long-path monitoring of ambient aerosol extinction at a central European urban site: dependence on relative humidity" *by* A. Skupin et al.

Anonymous Referee #1

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The authors present in their study the ambient aerosol extinction coefficient measured by a long-path spectrometer system over a period of four years at Leipzig, Germany. Out of these four years, 143 days with a pronounced diurnal relative humidity (RH) cycle were selected to discuss the annual variation of the ambient extinction enhancement factor. In addition, case studies and a trajectory analysis were performed and discussed. The main results were compared to the ambient extinction coefficient estimated from AERONET observations (with the planetary boundary layer height given by a numerical weather prediction model) and to the extinction coefficient calculated using the measured particle size distribution (for a few days).

1 General comments

Although I have no doubts on the high technical quality of the performed measurements, I have strong doubts on the validity of the main statements and its underlying assumptions. As already mentioned at the quick-review stage of this manuscript, the main concern is that for the retrieval of the enhancement factor different atmospheric processes that cause a change in particle light extinction are mixed into one parameter. The authors have selected days with a pronounced RH cycle and used an empirical parametrization to fit their data. As nicely shown in their case studies (Fig. 5 and 10) a decrease in RH was often coincident with a decrease in particle light extinction, which of course can be partially due to hygroscopic growth. However, the diurnal cycle also causes a change in PBL height and thus a dilution of the aerosol concentration which directly influences the measured light extinction. In addition, local sources must largely have affected the measurements, i.e. a major highway runs below the line of sight of the instrument, which must have have had an influence on the measurements, e.g. with diurnal variations during rush hours. Despite these major issues no satisfactory discussion can be found in the manuscript.

During days with a high variability in air temperature, the diurnal cycle of aerosol (optical) properties will also be influenced by partitioning processes e.g. of ammonium nitrate (see e.g. Morgan et al., 2010) or semi-volatile organics (see e.g. Donahue et al., 2006). These factors and the course of the PBL will clearly influence the curvature of the recorded and selected humidograms (and thus the apparent hygroscopicity parameter γ as discussed here). To retrieve reliable enhancement factors, the authors have to relate and normalize their extinction measurements to a second independent measurement (e.g. using the particle size distribution or the in-situ particle light extinction coefficient) or at least introduce an appropriate dilution factor.

In its current state, the given parametrization is highly questionable and thus not very useful to the reader and scientific community. The authors have to thoroughly revise

their method (and manuscript) to prove the validity of their method, which is unfortunately not given at the current state. This includes a substantial improvement of their method, result and discussion section. It is for the reason that I suggest major revision of the manuscript.

2 Specific comments

There are further major concerns (besides the major one described above) which should be carefully regarded. The following comments are given in arbitrary order.

- Page 12585, Line 22-25: There is actually a high number of publications on that topic (incl. very recent ones). Therefore, the authors should conduct a more thorough review and discussion of the literature; at the very least more recent results from Melpitz should be discussed given its vicinity to the sample station used during this campaign (Zieger et al., 2014). Zieger et al. (2014) measured the scattering enhancement directly during the winter months of 2009, which overlaps with the measurements discussed here. Their enhancement factors were significantly higher (median of 2.78 at 85 % and 550 nm) than the values presented here. These observations, although made using different techniques, can be directly compared since the RH-related scattering enhancement is larger than the absorption enhancement, and the scattering coefficient exceeds largely the absorption coefficient. Therefore I strongly encourage the authors to have a second look at this work and discuss potential agreement/differences.
- Page 12587, Line 2: Unfortunately, the influence of sea spray can not be regarded as low at this site (Spindler et al., 2010) and it also affects the optical properties (incl. hysteresis effects, see Zieger et al., 2014). This sentence is also in contradiction with the authors statement made below (page 12593, line 16-18:

"*The largest value of 3.5 was observed for northerly air flows with the comparably largest influence of marine particles (at comparably low levels of pollution advection from the Baltic Sea and Scandinavia).*"). Please revise and discuss appropriately.

- Eq. (3) and Eq. (4): It is not clear, if Eq. (3) is only used for the low RH range (RH$< 70\%$), while Eq. (4) is used for the range above 70 % RH throughout their analysis (see statement on page 12588, line 14). If so, then it has to be clearly described and discussed. In this case, many of the statements in the result section (incl. the given parametrization and the figures) need to be revised to avoid this ambiguity (γ would be the parameter for the low and intermediate RH range and the c-values representative for the high RH range).
- The factor of 0.3 in Eq. (5) is probably referring to the dry reference RH of 30%. However, all the following results are later given at 0 %. Does this assumption have an effect? In addition, if entering the coefficients given below, the results would be $\gamma = 0.4413$ and not 0.4364. Please clarify.
- Sect. 3.3: How exactly were these 143 days out of the four years of data selected? What criteria were applied and how many days were neglected? The fitting procedure is described (and maybe performed?) in a careless way. As it reads now, both Equations 3 and 4 were fitted separately to the recorded data, however, if the mean values of c_1 and c_2 are then inserted into Eq. 5 a value of $\gamma = 0.2732$ is retrieved, while the second fit gave $\gamma = 0.464$ as stated in Fig. 6, which is almost a factor of two different. Why?
  Ignoring for a moment all the major limitation mentioned here: Would it not be totally sufficient to just use Eq. 3 (with γ and the intercept as the only free parameters)? The separation as derived by Haenel (1984) probably can't be made since the measurements were not performed in an controlled environment. Haenel (1984) is an empirical parametrization and many other parameterizations were

used later on within the literature. Therefore I would suggest to only use one parametrization (i.e. Eq. 3).

- Sect. 3.4: How many days backwards in time were the trajectories being used? What criteria led to exactly eight clusters? Has the residence time within the PBL (as the main source region of aerosols) being considered for the analysis?
- Page 12592, Line 2 and Fig. 7: Please add to the figure (for the ambient values) the mean RH for each sector.
- Page 12591, Line 5: Were the mean values of c_1 and c_2 from the entire campaign or for each cluster separately being taken? Would it give the same results if the mean cluster values of γ (Fig. 9) was used?
- Page 12593 and Fig. 8: It is surprising that the pattern of the enhancement factor changes when going from 80 % to 95 % RH. This is somehow counterintuitive given the monotonic increasing function shown in Fig. 6. Are these the same datasets or why for example is suddenly sector 6 at 95 % RH below sector 7 and 5, while it showed larger values than the two at 80 %? If I use the γ-values given in Fig. 9, the result for the enhancement factors are much different than presented in Fig. 8. I could imagine that the authors used the c-values to derive Fig. 8, however these values should be consistent with the results using the γ-values. This probably relates to the fact that the coefficients given in Fig. 6 are not consistent or that the coefficients are valid for different RH-ranges. Please clarify.
- Page 12591, Line 24: Are the 18 000 single observations identical with the 143 selected days? What is the time step for each observation?
- Were any seasonal trends or monthly patterns in the enhancement factors observed? This discussion would be interesting, since partitioning effects, differ-

ences in aerosol emissions and the PBL development probably caused a clear seasonal variation.

- Page Page 12593, Line 1-3: This statement is too speculative. Are the authors really sure that a regulation introduced in 2011 already shows an effect the year later? What exactly has been regulated?
- Sect. 5.3 (Comparison to in-situ measurements): As a kind of validation, the authors present a 5-day comparison (as a timeline) to Mie calculations using the measured particle size distribution. However, this is described in inadequate detail and more needs to be added here.
  - With what kind of instrument has the particle number distribution been measured? What was its upper size limit?
  - How has the coarse mode (above 1 micron) in the Mie calculations been treated?
  - It is not clear how long exactly the in-situ measurements were performed. Please clarify.
  - Please show a scatter plot of the entire comparison of the (dry) extinction coefficient and discuss the degree of agreement (incl. regression line and statistical parameter). A nice looking example as a time series is not enough to judge on the overall performance.
  - Why were the results not directly compared to the long-term records of (dry) optical properties measured in situ at the Melpitz site, which is close to Leipzig and run by the same institute (as I believe)? This comparison would definitely help to strengthen the message of this work and partially clear out the strong doubts brought up within this review.
- Sect. 5.3 (Comparison to AERONET):

  - It is not clear why the differences in wavelengths has not been corrected for. Please use the Angstrom law (Eq. 1) and transfer the AERONET measurements to 550 nm. Secondly, the reviewer wants to see a scatter plot with a linear regression line and statistical values. Figure 11 is to the reviewer's opinion not sufficient to show a direct comparison.
  - What is the average ratio (mean and SD) of the AERONET and SAEMS ambient extinction coefficient exactly? Can it be fully explained by particles above the PBL?
  - Why was the PBL height retrieved from the lidar not being used or (in another way) how does the PBL height given by the model compare to the continuous lidar measurements?

- Sect. 3.6: The spectral dependency of the extinction coefficient shown in Fig. 13 clearly indicate a decreasing Angstrom exponent with increasing RH, however the discussion of the Angstrom exponent using two pairs (390/440 nm and 390/881 nm) is not very convincing.
  How did the in-situ/AERONET comparison look for the 390 and 881 nm?
  The 390 and 440 nm are influenced by the absorption of NO_2, which might be relevant when considering that the instrument measured across a large highway. How was this corrected for? Could there also be a calibration or technical (temperature dependent?) issue of the red channel? The results as presented now are largely based on small variations of the 881 nm measurement where the relative uncertainties are higher. I would suggest to use a numerical fit to determine the Angstrom exponent and repeat/improve the discussion.

- Page 12596, Line 25: Why were the following two years not included?

- Page 12597, Line 5: I would soften the discussion on non-hygroscopic coarse particles here, since hygroscopic sea spray particle can't be fully excluded (see comment above).

- Page 12586, Line 21: It is here (and further down) often referred to the PhD thesis of the main author ("The full set of analysis results can be found in Skupin (2014)."), also for critical points ("More case studies and more details to the parameterization efforts can be found in Skupin (2014)", line 18, page 12591). Unfortunately, this thesis is written in German and thus not accessible to the majority of the scientific community. Please list all needed information to the reader in the revised manuscript and state in the reference list that this is a thesis written in German.

- Page 12585, line 18: The wording "manipulation" is not appropriate here since it implies a certain willful intention and the authors should bear in mind that all measurement techniques in aerosol science have certain drawbacks. I suggest to replace it with "introduction of certain potential measurement artifacts".

- In general, the authors should tone down their language. Statements like "*manipulation*" (see comment above), "*corroborates the usefulness*" (page 12595, line 5), "*corroborates the high quality and reliability of our long-term observations*" (page 12591, line 17), "*year-by-year differences are also obvious*" (page 12592, line 27), "*nicely shows*" (page 12595, line 8), "*obviously do not grow*" (page 12592, line 6) are often empty and subjective statements without any statistical backbone. Real numbers would be more useful.

- There are a lot of figures in the current manuscript and there is some space for improvement.

  - Figure 3: This figure could be merged with Fig. 10, where one example RH time line is already shown.
  - Figure 4: This figure can be omitted. Not much is learned here and the numbers can be given in the text.

- Figure 5: Please add the confidence intervals to the fit parameters in panel c and f. As mentioned above, I believe it is fully sufficient to just use the γ-parametrization as a one-parameter fit for the humidograms. Otherwise the authors should justify why the c_1 and c_2 are needed.
- Figure 6: Please reduce the fit-coefficients (SD) to their significant digits. Why is Eq. 5 not fulfilled here (see comment above)?
- Figure 7 and 9 could be merged into one since they are related as a result of trajectory analysis. The bar plots (panel c of Fig. 7) could be omitted, not much is learned here and a sentence in the text would be sufficient.

- For RH $\rightarrow$ 100 % the enhancement factor goes towards infinity (Eq. 3 and 4), but the authors show in Figure 13 the extinction coefficient for it (red curve). Please clarify.

3 Technical corrections

- Please add the respective wavelengths to all the figures where needed.
- Figure 9: Please replace "extinction-enhancement-describing parameter" by "hygroscopic exponent" to be consistent with the text.
- Table 1: Please replace 'Norge', 'Suisse' and 'anthropogen' by its correct English words. Also add the wavelengths to the literature values.

References

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