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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Estimation of aerosol water and chemical composition from AERONET at Cabauw, the Netherlands" *by* A. J. van Beelen et al.

Anonymous Referee #2

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Van Beelen et al. propose a site-specific model that estimates the columnar aerosol composition and water aerosol water content using AERONET Sun photometer data. A minimization algorithm is used to retrieve the composition and concentration for the main aerosol components. The model is compared to a two week data set of aerosol composition that was recorded within the IMPACT 2008 campaign at Cabauw, The Netherlands. Reasonable agreement is found when comparing columnar and campaign averaged values, however diurnal variations were not captured. This paper presents a very ambitious model goal and the idea sounds appealing. However, I have strong doubts on several technical details and the performance of this model.

Two main arguments have brought me to this conclusion:

1. The authors claim that their model has been validated. However this has not been done in a satisfactorily manner since only a comparison to ground based measurements is shown in a very cursory way. Mainly time series and campaign averages (plus standard deviations) are reported. In addition, only selected in-situ measurements were used for the comparison, while other aerosol parameters that were measured at the site (also within monitoring networks) were not used. A correct validation should include scatter plots of all the data, the uncertainties of model and measurements, and mathematical statements (e.g. using linear regressions, the results could also be summarized in a table). The manuscript would benefit, if the aerosol water uptake (one of the main quantity discussed here!) and the aerosol size distribution measurements would be included in this comparison, since they have been performed during this period and are available (e.g. from ebas.nilu.no).

2. The model is restricted to coarse mode free aerosols, since dust and sea salt were omitted within this study (Page 15198, line 3). Although the authors state that sea salt has not been observed at ground, this is highly uncertain at a place like Cabauw which is located approx. 50 km from the ocean. Also layers above the ground (included in the columnar AERONET data) can be effected by coarse mode particles and/or sea salt can be found in the fine mode. The authors state that the model cannot retrieve values of the complex refractive index (real part) below 1.4 and mark AERONET retrieved values below 1.4 as "suspect". However, aerosol particles with a hygroscopic growth factor of $GF = D_{\mathrm{wet}}/D_{\mathrm{dry}} = 1.5$ (or larger) already have a real part of the refractive index below 1.4 (if the dry refractive index e.g. 1.54 and homogeneously mixed particles are assumed). One should also keep in mind that sea spray aerosol can be transported for long distances, can be found in the fine mode and may only be observed in upper layers. The authors have excluded the second half of the impact campaign, where

sea salt and dust events were reported for this site (Mensah et al., 2012). To undermine this statement, a detailed trajectory analysis and all the data points of the second half of the IMPACT campaign have to be added to the analysis.

The manuscript has to be substantially revised, with more data and model analysis to be added, in order to convince the reader on the model validity and its scientific benefit. In its current stage, it does not fulfil the quality standards of *Atmospheric Chemistry and Physics*.

Detailed comments:

- Page 15192, Line 20 (abstract): "Water volume fraction is highly variable depending on composition, up to $>$ 0.5 at 70-80% and $<$ 0.1 at 40% relative humidity." This sentence does not make sense. Here, it is just said that the water volume fraction is depending on the relative humidity (and not on the composition), which is obvious.
- Page 15193, Line 17: Which satellite product derives refractive index? The aerosol size i.e. is also only indirectly derived (e.g. via the Angstroem exponent).
- Page 15193, Line 18: All other derived components like size or SSA are effected by aerosol hygroscopicity. Please precise.
- Page 15193, Line 21: Can the authors add current literature on this aspect (hygroscopicity and model validation), which is the main motivation of this study?
- Page 15193, Line 27: " ... the ratio of scattering of aerosol ..." Please add real physical expressions (I believe Jeong et al. looked at particle light scattering coefficients?).

- Page 15194, Line 14: " ... is validated with detailed measurements of aerosol properties (including chemical composition) ..." Well, this is only partly true. The model has not been validated against aerosol size distribution, aerosol optical or hygroscopicity in situ measurements, although data exists for this time period May 2008 (Source: database at ebas.nilu.no).
- Page 15195, Line 20: Table 1: Is a mass mixing ratio of black carbon in the coarse mode really needed?
- Page 15196: The water uptake by aerosol particles can be precisely measured (as has been done also during the IMPACT campaign) by using H-TDMA instruments (Hygroscopic Tandem Differential Mobility Analyzer). To compare the input values to real measurements, it would help if you could add the resulting hygroscopic growth factors ($GF = D_{\mathsf{wet}}/D_{\mathsf{dry}}$) of the input components on Table 1.
- Page 15196, Line 2: Why are sea salt (NaCl) and mentioned dust mentioned here, but are not found in Table 1? Have they been included in the model or not?
- Page 15196, Line 12: Please rephrase this sentence: You have neglected the Kelvin term because of the particle size and not because of the model runtime (which is not a scientific argument).
- Page 15197, Line 4: Why has the Angstroem exponent been excluded from the optical properties (also an AERONET product and easily be determined by the Mie calculations)? What about fine and coarse mode AOT?
- Page 15197: Please state the investigated AERONET wavelengths here.
- Page 15197, Line 20, Table 3: It is not clear to the reviewer, if the geometric standard deviations of the individual components have been varied or were fixed (if so, they have to be reported in Tab. 3 with references).

- Page 15198, Line 3: The influence of sea salt and dust cannot be excluded, especially for a site like Cabauw. In May 2008, both mineral dust (23 May) and sea salt (17-20 May) were transported to the site (Mensah et al., 2012). A point measurement is not sufficient to exclude dust or sea salt, since columnar AERONET data is then used for the entire model. Excluding half of the IMPACT observation period for the model validation gives therefore a bitter smack to the entire model evaluation (see comment above). A detailed trajectory analysis (needed for different elevations) would be helpful here, to really exclude lofted dust sea salt layers. In addition, the sea salt can also be substantially included in the fine mode (see e.g., de Leeuw et al., 2011).
- Page 15198, Line 19: Again, why is the Angstroem exponent not used?
- Page 15199, Line 1: Please quantify "relatively accurate"
- Page 15199, Line 4: The 15% uncertainty is valid for the range of 0.1 to 7 micron and is increasing for the distribution edges. Table 2 however states a 15% error for the volume distribution in the entire 22 bins. Please clarify on the exact errors which were used.
- Page 15200, Line 11: " ... the Angstroem exponent was generally well above 1, indicating the absence of a significant coarse mode fraction." I disagree. On May 4 and May 11 (and additionally maybe May 2 and May 13, afternoon) the Angstroem exponent is clearly below 1 and this could be an indicator for (maybe lofted) layers of coarse particles which might be missed by the ground based measurements.
- Page 15200, Line 21: What is the R^2? I would expect a clear correlation since the refractive index at high RH should approach that of water.
- Page 15200, Sect. 2.2.2: The model has only been compared to chemical composition data, but a comparison with HTDMA hygroscopicity measurements (Uni-

versity of Helsinki) is missing and also a comparison with ground based size distribution and optical measurements (SSA, Angstroem exponent) has not been done. Please clarify.

- Page 15201, Line 11: What is the measurement uncertainty of the AMS?
- Page 15201, Line 17: The inlet at Cabauw has a PM_{10} size cut, followed by a drier, therefore essentially measuring approx. PM_5 (or less). Is this relevant? And how are the losses of the in situ measured parameters treated?
- Page 15202, Line 4: "Our model cannot simulate these values at the observed columnar RH with the current choice of aerosol compounds." Here I would argue that this is exactly the missing sea salt (which can be in the fine mode), with a high hygroscopicity and therefore a high water uptake with a resulting low refractive index (which approaches the one of water at high RH).
- Page 15202, Line 13: Are these suspect values by chance periods with low Angstroem exponents?
- Page 15202, Line 13: "...removes a lot of data points that seem to be good." This is not a very scientific statement. Please quantify and report the differences (with respect to the model agreement) for level 1.5 and level 2.0, separately. A table would be sufficient.
- Page 15202, Line 16, Table 5: "Correlations" is not the correct term, "squared correlation coefficient" would be a more suitable one. This "excellent agreement" is here valid for the extensive parameter AOT, but how does the model compare to AERONET with respect to the volume size distribution (volume, mean effective radius) which is also retrieved? Is the agreement also excellent for fine and coarse mode AOD also retrieved by AERONET? R^2 may not be the entire truth, e.g. are there any offsets or slopes in this comparison?

- Page 15202, Line 19, Figure 4, 5, and 6: The comparison has to be quantified. Just showing time series and mean values is not sufficient. This should be done by showing scatter plots (with linear regression lines and uncertainties). It could be done for the daily and hourly values separately. In addition, I would recommend the authors to discuss one golden day in detail in a separate section. This will help the reader to see the benefits and restrictions of the model with respect to the observations.

- Page 15202, Line 15202: I clearly doubt this assumption of a well-mixed PBL at Cabauw. Different model studies and measurement have actually shown elevated layers for May 2008 (e.g. the later cited Morgan et al., 2010; Aan de Burgh et al., 2012). It is also commonly observed in lidar measurements (e.g. Mattis et al, 2008 observed in 43% within the regular measurements pollution above the continental PBL). This statement here has to be quantified. What are the shapes of the lidar profiles for the two weeks? Maybe the profiles can be shown for one example day, which is later discussed in detail.

- Page 15203, Line 10: "This layer will rapidly mix with the atmosphere above when heated by the sun, leading to a reduction in the aerosol concentration near the surface without changing the total column aerosol burden." I again doubt this statement. The change in the temperature profile during the course of the day will also change the aerosol columnar aerosol burden, e.g. due to portioning effects. It is actually correctly stated in the following sentence. The authors have shown here that the assumption of a 2 km well-mixed PBL is probably not valid at this site.

- Page 15203, Line 15: "More abundant road traffic and photochemical production of secondary aerosol during daytime may be the reason why the computed (column average) dry mass increases in the afternoon." But this should be observed in the measurements? I would change the argumentation here, e.g. by stating

that the computed (column average) dry mass increases in the afternoon because certain aerosol effects have not correctly been implemented in the model.

- Page 15205, Line 4: "Discrepancies from this behavior (e.g. at RRI = 1.41 in Fig. 8) are associated with the effects of water uptake from ambient RH: at very high relative humidity the aerosol can still contain a significant fraction of organics at a relatively low RRI, while this is not possible at somewhat lower RH." I don't understand this sentence and the artefact seen in Fig. 8 at RRI=1.41. The real part of the refractive index of organic and inorganic compounds are very similar, so I would assume this behaviour to be model artefact or should there really be a physical explanation? If yes, please precise this sentence.

- Page 15205, Line 13: I thought the SSA is also used?

- Page 15205, Line 24: "Validated" is definitely not the correct term here. The model has been "compared" and has not been validated, as it e.g. failed to retrieve the diurnal variations. Only daily mean values (or even campaign means) were more or less reproduced. In addition, other important aerosol parameters, like aerosol size distribution, hygroscopicity or optical measurements measured in situ at Cabauw were not compared to the model results, so the "validation" is not even complete.

- Page 15206, line 26: Please replace "hydrophobic" by "non-hygroscopic", which is the more suitable term.

- Page 15207, Line 16: Please add the R^2-value at its first appearance (Page 15200, Line 21).

- Page 15207, 3rd point: The importance of the AERONET RRI and its high uncertainty should motivate to show the comparison for the level 1.5 and level 2.0 data separately (at least in one table).

- The conclusion and discussion part have to be separated in one discussion part and a short and precise separate conclusion, which is missing so far.
- Table 1: How are coarse and fine mode defined in terms of particle diameter?
- Table 5: If possible, please also add the other AERONET retrieved and calculated values. If the slope differed from 1 or an off-set was determined, this would be the place to mention it.
- Fig. 1: Has the columnar temperature been included as an a priori information as well?
- Fig. 2: "The altitude weighted average ..." How was the altitude included in the average RH? Please add this shortly to the manuscript.
- Fig. 3: Have the authors tried to color code the "suspect" values with other parameter (e.g. Angstroem exponent, SSA, etc) to find other explanations on why the model fails here?
- Fig. 4 to Fig. 6 could be combined to show the time series of observation and model. However, it is necessary, to show scatter plot (for daily and hourly averages separately) with linear regression lines to quantify the comparison.
- Fig. 7: Could the authors show (at least within the reply letter) the water fraction vs. the mean observed RH? Does it follow typical hygroscopic growth factor curves measured by the HTDMA at Cabauw?
- The title would be more specific, if "Sun photometer measurements" or just "data" would be added behind the word AERONET.

References:

- Aan de Brugh, J. , Henzing, J., Schaap, M., Morgan, W., van Heerwaarden, C., Weijers, E., Coe, H., and Krol, M.: Modelling the partitioning of ammonium nitrate in the 20 convective boundary layer, Atmos. Chem. Phys., 12, 3005–3023, doi:10.5194/acp-12-3005-2012, 2012.
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