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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Size distributions of non-volatile particle residuals (D_p<800 nm) at a rural site in Germany and relation to airmass origin" *by* C. Engler et al.

C. Engler et al.

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1 Specific comments

1. "The average ratio..."
   As advised by the referee, we analyzed the ratio between the total particle number concentrations measured downstream and upstream the thermodenuder in more detail. The following text and Figure 4 have been added to the manuscript (Section 3.3): "Figure 4 shows daily averages of this ratio for the entire duration of the measurement campaign. Different lower cut-off sizes for the calculation of the total particle concentration were used. For the interval 3–800 nm (Figure 4a),

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it can be seen that on individual days, up to 10 times more particles were detected downstream the thermodenuder than upstream the thermodenuder. This is apparently the result of the nucleation of new particles in the cooling section of the thermodenuder. It shows that under certain circumstances, the volatilized particle material is not transferred quickly enough onto the walls of the cooling section, so that the generated vapors nucleation into new particles. Figure 4b shows the same concentration ratio, however, with 5 nm as a lower threshold. This limits the occasions of concentration ratios $>$ 1 dramatically, and shows that the newly nucleated particles are predominantly smaller than 5 nm. The average concentration ratios downstream and upstream the thermodenuder is within 0.8 and 1.2 in almost all cases, confirming the statement that almost "every ambient particle has a non-volatile core". When selecting 10 nm as a lower threshold in the calculations, concentration ratios $>$ 1 disappear altogether. Now, ratios between 0.5 and 1.0 are observed. The values below 1.0 can mainly be explained by non-conditioned particles larger that 10 nm, which fall below the lower size cur of 10 nm after thermo-conditioning. A conclusion of Figure 4 is that the effects of the nucleation inside the thermodenuder are of minor importance to the overall discussion of particle size distributions as long as only particles $>$ 5 nm are considered."
Eliminating the periods of nucleation inside TD has no visible effect on the size distributions shown in the second part of the paper.

2. "Following on from this..."
From the reviewer's statement we read that he/she is interested in knowing about the relationships between occasions of nucleation in the thermodenuder and environmental variables, including the aerosol itself. Indeed the nucleation inside the thermodenuder (mainly limited to particles of $<$ 5 nm in size) is a very sporadic phenomenon, and this is why it could be indicative for certain, exceptionally occurring properties of the aerosol measured. We had made a correlation analysis

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between occasions of nucleation in the thermodenuder and a number of parameters like ambient temperature, relative humidity, time of day, total particle volume concentration $< 1\,\mu$m, etc., but no such obvious correlation existed. Inspired by the reviewer's comments, we have now also considered correlations between nucleation inside the thermodenuder and further integral aerosol properties. One idea was to look at the relationship towards organic carbon concentrations. It may be hypothesized that certain higher molecular organic compounds have a potential to nucleate or recondense more easily as a result of their lower vapor pressure. The relation between the number ratio TD/non-conditioned and the concentration of particulate organic carbon has been displayed, which is available from daily filter samples of PM_1, $PM_{2.5}$, and PM_{10} at Melpitz (cf., Spindler et al., 2004). We see the OC mass metric as a valid indicator for the potential of an aerosol sample to cause nucleation in the thermodenuder, since a) the upper size of particles before entering the thermodenuder is $10\,\mu$m (PM_{10} Andersen inlet), and b) it is the mass of evaporated material which leads to proportional concentrations of supersaturated vapors that govern nucleation rates. However, no clear tendency could be observed. It is true that, e.g., for $PM_{2.5}$, number ratios TD/non-conditioned > 2 are associated with higher average OC concentrations than for ratios < 2. However, the relationship is not easy to define, especially when looking at the data for PM_1 and PM_{10}. Nucleation in the thermodenuder also occurs for days with relatively low OC concentration. The pictures do not change significantly when the total PM mass (i.e., all chemical compounds) are examined. Our conclusion is that there is a positive correlation between nucleation inside the thermodenuder (number ratios downstream/upstream the TD > 2) and high values of OC concentration, but this correlation is not straightforward to analyze in terms of correlation coefficients, or a threshold criterion.

3. "The authors should expand on how the summation method works..."
   If total particle number is conserved inside the thermodenuder (In fact, the sum-

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mation method is only applicable for this assumption, with the justification of this assumption being demonstrated above.), the summation method will produce the following results: In case of unimodal size distributions both upstream and downstream the TD, the degree of external particle mixture will be limited. This "average" case features predominantly particles of the "less volatile" type, i.e., those that contain significant volatile material, but also a non-volatile core. Consequently, the diameter shrinking factor will be relatively low (i.e., particles collapse to lower diameters), and depend relatively weakly on particle diameter. (See cluster 1 in the first or cluster 3 in the second cluster analysis as an example.) A unimodal size distribution upstream and a bimodal particle size distribution downstream the TD indicates a significant external mixture in the aerosol entering the TD. The smaller particle mode exiting the TD represents the number fraction of partially volatile particles of the original single mode, while the larger particle mode exiting the TD represents the entirely non-volatile particle. Since the size range of entirely non-volatile particles is concentrated on the size range above 80 nm (the range of diesel soot emissions, and with increasing contributions of crustal material with increasing particle size), the shrinking factor will be on average higher (i.e., particles shrink less), and also depends more significantly on particle size. (See cluster 4,5 in the first or cluster 5 in the second cluster analysis as an example.)

4. "It would also be helpful and informative..."
   As shown above, increase in number concentration through nucleation inside the thermodenuder is limited to the size interval smaller than 10 nm, mainly smaller than 5 nm. Therefore, the summation method is expected to be insensitive towards this kind of nucleation for particles larger than 10 nm.

5. "I agree with the first reviewer..."
   As recommended by the referee, a selection of quantitative multimodal lognormal size distribution parameters was added for all ambient and non-volatile size distri-

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butions. The parameters included the number concentration, geometric standard deviation and mean geometric diameter for each of the three lognormal modes accumulation, Aitken, and nucleation mode. The lognormal modes were fitted using a Levenberg Marquardt least squares fitting routine, which was also used to fit size distributions in an earlier paper (Birmili et al., 2001).

2 Technical comments

1. "P5508 1st sentence. EC/OC analyzers..."
   In the first sentence, "black carbon" has been replaced by "elemental carbon".

2. "If I understand correctly..."
   We agree that the term "ambient", as used in the previous manuscript, is a source of confusion. For clarity, we have now denoted particle samples downstream the thermodenuder as "non-volatile", or "conditioned", whereas we refer to particle samples upstream the thermodenuder as "non-conditioned". In fact, the "non-conditioned" particle samples are exposed to a relative humidity of about 5% in the DMA sheath air, so that the particles' state cannot be denoted "ambient" any more. Accordingly, the term "ambient" has been replaced by "non-conditioned" throughout the text.

References

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