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Atmospheric
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Interactive comment on "Particle number size distributions in urban air before and after volatilisation" *by* W. Birmili et al.

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Reply to the comments of Anonymous Referee No. 3

Abstract, Line 1, 16: The text of the abstract seems to imply that the thermodenuder was utilized for the entire size range, while it was really only used for a portion, correct?. This is slightly misleading to those scanning through.

Reply: The issue was clarified by adding the sentence "Size distributions below 0.8 μm were also measured downstream of a thermodenuder, allowing to retrieve the volume fraction of non-volatile compounds."

Page 9174, Line 18-20: The introduction to the volatility analysis is brief. This is somewhat acceptable, but using Schmid et al. 2002 as the only reference point for volatility

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analysis in general is a bit strange. The technique of discriminating aerosols by their volatility had been in use for many years before 2002, for example.

Reply: According to the Referee's suggestion, we have added three more references, stated in the following modified text: "Previous research has been particularly directed towards differentiating between, for instance, sulphuric acid, neutralised sulphate, sodium chloride, and elemental carbon (Clarke, 1991; Smith and O'Dowd, 1996; Kreidenweis et al., 1998; Schmid et al., 2002)."

Page 9175, Line 24-25: "allow conclusions on the non-volatile sub-fraction in the sub-μm, which is broadly associated with soot." I do not disagree with the comment that the non-volatile aerosol sub-fraction in this size range may be dominated by soot in many sampling locations, certainly in an urban area, but I feel it needs to be admitted for completeness of thought here that there are other possibilities. Mineral dust ... can be an important fraction in many locations, and biological aerosols can also contribute a significant amount of material even at sub-micron sizes. I suggest adding a sentence here with this admission, or changing the wording so as to imply less firmly that soot is the only contributor.

Fine, we added the following statement: "In the sub-μm range, this fraction is broadly associated with soot, although other particle types, such as mineral dust or biological particles are admitted to contribute to the non-volatile fraction as well."

Page 9177, Line 1-3: "The temperature of 300°C was selected with the aim of evaporating the overwhelming fraction of inorganic ions (particularly ammonium sulfate and nitrate, although not sodium chloride) as well as organic carbon from the particulate phase." Could reference be given for this (for both the inorganic and organic ions)? Or is this inarguably true, for example?

Ammonium nitrate and ammonium sulphate are reported to have volatilisation temperatures of 75 and ca. 202°C (Pinnick et al., 1987; Johnson et al., 2004). In Engler et al. (2007) we provided an overview of known volatilisation temperatures from the literature. As a conclusion, we modified the sentence as follows:

The temperature of 300°C was selected with the aim of evaporating the overwhelming fraction of inorganic ions (particularly ammonium sulfate and nitrate, although not sodium chloride (see, e.g., Table 1 in Engler et al., 2007) as well as organic carbon from the particle phase.

Pinnick, R. G., Jennings, S. G., and Fernandez, G.: Volatility of aerosols in the arid southwestern United States, J. Atmos. Sci., 44, 562–576, 1987.

Johnson, G. R., Ristovski, Z., and Morawska, L.: Method for measuring the hygroscopic behaviour of lower volatility fractions in an internally mixed aerosol, J. Aerosol Sci., 35, 443–455, 2004.

Engler, C., Rose, D., Wehner, B., Wiedensohler, A., Brueggemann, E., Gnauk, T., Spindler, G., Tuch, T., and Birmili,W.: Size distributions of non-volatile particle residuals (Dp $<$ 800 nm) at a rural site in Germany and relation to air mass origin, Atmos. Chem. Phys., 7, 5785–5802, 2007.

Page 9177, Line 11-17: Particles less than 6 nm are shown to nucleate in the thermodenuder after heating. This is fascinating. Has this been shown before? If so can a reference be provided for comparison. If not, a suggestion along these lines is appropriate. Can you give an estimate for how much of an error this effect would introduce to the total number & volume/mass of the post-thermodenuder ratio?

During our research we have observed this effect previously, when examining rural background aerosol at Melpitz in the Leipzig area (Engler et al., 2007) Here, it affected mainly particle diameters below 6 nm. The highest degree of this effect, however, was observed when examining urban aerosol in the megacity of Beijing, China. There, nucleated particles up 20 nm exited the thermodenuder. Our intuitive interpretation of these observations was that the nucleation rate (and subsequent growth rate by condensation and coagulation) of particles at the exit of the thermodenuder is related to the amount of evaporated particle material, and therefore high when dealing with high total mass concentrations. A detailed analysis of the Melpitz data, however, yielded no conclusive (not even monotonous) relationship of the number of nucleated particles, for instance, with total particle mass concentration or the mass concentration of organic aerosol (i.e. prime candidates for species that could evaporate and then re-nucleate). Although it would be desirable to exploit the number of nucleated particles as an additional property of the observed aerosol, we have so far not obtained any conclusive theory why particles nucleate during particular episodes, and not during others. At the current stage of knowledge, we need to treat it as an interfering artefact. Presently, similar size distribution measurements with and without thermodenuder are going on at multiple sites in Germany in conjunction with soot measurements (MAAP). This more comprehensive data set will hopefully allow more substantial conclusions on the issue.

The error in the number ratio (N with thermodenuder/N without thermodenuder) was estimated from the Melpitz data as follows (cf. Fig. 4 in Engler et al., 2007): When considering particles downstream of the thermodenuder down to 3 nm, a ratio of up to 60 was observed (should be 1 at maximum without nucleation). Down to 5 nm ratios up to 2. When truncating of the post-thermodenuder size distribution at 10 nm, errors in the number ratio vanished. For the present article we see very similar results, which are summarised in Figure 2.

This new information was accordingly incorporated in the modified text: “It is noteworthy that at certain times, new particles are observed to nucleate at the exit of the thermodenuder due to the cooling of vapours that have not been completely absorbed by the tube walls. This leads to ratios in the number concentration downstream/upstream the TD bigger than 1. This effect, which was found at a rural observation site as well during an earlier experiment (Fig. 4 in Engler et al., 2007), can lead to an overestimation of this number concentration ratio up to 100.”

The volume ratio effect is, however, more difficult to assess, since we cannot separate evaporation from re-condensation in the comparison of size distributions before and after the thermodenuder. (In the case of nucleation, we can.)

Page 9178, Line 20-22: Are these diffusional losses published or discussed anywhere? If so, can a citation be given here. How large are these losses? Are the graphs reported in the paper shown after correcting for these losses (if so clearly state)? What about other loss mechanisms such as thermophoresis?

These losses have not been published explicitely. As a consequence of your remark we added a new sentence: “A sample aerosol is subject to enhanced particle losses. One can think, e.g., of diffusional as well as thermophoretic losses, which are both a function of particle size. Prior to the field experiment, the particle loss across the TD was determined in the laboratory using monodisperse and spherical silver particles (solid at 300°C), and by measuring the particle counts upstream and downstream of the TD. The penetration of solid particles through the heated thermodenuder in the warm state is 0.34 at 3 nm, 0.66 at 10 nm and 0.85 at diameters bigger than 100 nm. All particle number size distributions downstream of the thermodenuder were corrected accordingly.”

Page 9178, Line 24: Do you have any idea what the estimated uncertainty on this chosen value of 1.7 g/cm3 for density would be? How confident are you in this number?

Thank you for this hint. Accordingly, we added two sentences as follows: “Pitz et al. (2008b) obtained this particular value by matching TDMPS and APS size distributions in the overlap region 800-900 nm in mobility diameter. The value is also within the uncertainty range of the effective density that reconciles TDMPS/APS volume size distributions with a gravimetric $PM_{2.5}$ measurement (1.5–1.8 g cm^{-3}; Pitz et al., 2008a).”

Page 9180, Line 8: The 20-l buffer volume used - wouldn’t this contribute to significant additional particle losses to the walls of the volume?

It is true that the buffer volume contributes to additional particle losses. The losses in the buffer volume in Augsburg were not explicitely determined. The following sentence is added to the text: “The particle penetration through the Augsburg buffer volume was not measured directly, but only with a comparable device in the laboratory. The particle penetration was 0.45 at 10 nm, 0.93 at 54 nm and roughly unity at particle diameters bigger than 100 nm. Due to the uncertainty in determining the losses, we refrained from applying these corrections to the measurement data.”

Page 9183, Line 11: “The remarkable correlation...” I agree that this is an interesting correlation. The use of the word ’correlation’ seems to imply that some R2 value should be given. I immediately looked for it out of interest.

Here, the text was rewritten, and the value of R^2 added accordingly: “In much contrast to the 7 nm particles, coarse particles (2000 nm) show a concentration maximum in summer, with concentration being higher by approximately 50% compared to winter. In Fig. 4 there is a positive correlation between coarse particle concentrations and temperature (R^2=0.5). These observations suggest an increased probability of particle re-suspension from agricultural lands and roads under the rather dry conditions in summer.”

Page 9185, Line 25-26: Do you really mean that “thermal conditioning kept the total particle number constant”? I’m assuming that you mean something more like: “while thermal conditioning was taking place the total particle number concentration was assumed to be constant” or something similar. As written the thermal conditioning is seemingly performing an action on the ambient particle concentration.

This passage was reformulated as follows: “An essential result was that that the total particle number remained virtually unchanged after passage through the thermodenuder (Fig. 2), i.e. it seems that within the accuracy of the measurement, every particle has a core that is non-volatile at 300°C.”

Page 9187, Line 24-25: This conclusion about the maximum of non-volatile material being observed in autumn is very interesting. Can the authors, even if presumed, state a reason or guess as to why these trends exist? Of if they are implied within the *manuscript, can they be reinforced in this section?*

It seems that in the autumn season, the highest particle number concentrations were observed during the morning rush hours. As the traffic density is not expected to drastically vary throughout the year, the underlying reasons are, most likely, meteorological. We reformulated the text accordingly: "When differentiating the data after season, the maximum of non-volatile material (SF∼0.7) was observed during autumn (September-November). A likely explanation was that during our measurements, the absolute number concentrations during the morning peak hours (06:00–09:00) were the highest during the autumn period: The autumn number concentrations at 80 nm were, for instance, 10% higher than during winter (December-february), 25% higher than in summer (June-August), and 28% higher than in spring (March-May). The concentrations measured during the the morning peak hours are expected to be the most strongly influenced by traffic sources, contributing non-volatile diesel soot particles."

Page 9189, Line 17: Type - "It is worth to note" Should be either: "It is worthy to note" or "It is worth noting" etc.

Thank you for this stylistic advice. We corrected the corresponding sentences.

Page 9181, Line 22: "tend to lie" is ambiguous and vague

This was rewritten as "...range in the lower scale..."

Page 9189, Line 20: What do you mean by "equivalent" here? Portion, fraction . . . ?

We replaced equivalent by "unit amount".

Page 9190, Line 22: "particulate volume" should be "particulate volume concentration" This also should be corrected in Figure 11.

Thank you, these issues were corrected.

Page 9193, Line 13: Again, is this number of 69% after correction due to diffusion losses within the thermodenuder? It needs to be clearly stated here either yes or no.

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The use of the correction is now confirmed in the text — see above.

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