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Interactive comment on "To what extent can aerosol water explain the discrepancy between model calculated and gravimetric PM_{10} and $PM_{2.5}$?" *by* S. G. Tsyro

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Firstly, I'd like to thank the referees for their valuable comments to the work on estimating the importance of aerosol water presented in the submitted manuscript. Since many of the comments/questions in both Referee Comments are concerned with rather similar issues, I shall adderess them in the same Author Comments text.

1. I agree with the referee that the conclusion about 'better' agreement of calculated mean PM concentrations when aerosol water is added with measurements is rather obvious. On the other hand, the improvement of temporal correlations of wet PM10 and PM2.5 with observations is a more significant result. It was pointed out by the

referee that Conclusions in the manuscript should highlight those results. This will be done in the revised manuscript. Also conclusions in general will be strengthen, as suggested.

2. Aerodynamic vs. actual sizes. In the model, the actual size of particles, and not their aerodynamic diameters, are used when allocating particles to size modes, and also when calculating PM10 and PM2.5 concentrations. This is certainly one of the uncertainties in comparison of model calculations with measurements. The inaccuracy due to using actual sizes in the model is reduced to some degree due to decrease of particle density as particles undergo deliquescence at the ambient conditions. (In the extreme cases of a large soluble aerosol fraction and at high realative humidities the aerosol density approaches the density of water (1000 kg/m3), which is a density used to derive the aerodynamic diameter).

In the model, particle size distribution is described with four monodisperse modes, using mean diameters in the size modes. In the calculations, the annual mean diameter varies between 0.3 and 0.75 mkm in the accumulation model and between 4 and 6.5 mkm in the coarse mode across Europe. According to rough estimates, the difference between actual and aerodynamic diameter varies ca. between 5 and 20% for PM2.5 and 15 and 30% for coarse PM, depending on the aerosol chemical composition and ambient relative humidity.

It can be pointed out that the further model development will affect the density of modelled aerosols: 1) inclusion of secondary OC and water associated with OC; 2) implementation of wind blown dust, which increases the particle density.

Finally, major uncertainties in calculated aerosol size distribution is still related to uncertainties in the size distribution of primary particles, in particular anthropogenic PM2.5 and PM10.

3. Water soluble organics can indeed contribute to particle water content. Organic carbon is one of the most uncertain aerosol components in the model. Presently, only

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primary anthropogenic organic aerosols are included in the EMEP aerosol model, for which the chemical speciation is not available. The parameterisation for secondary OA has been developed and tested last years and are intended to be implemented in the aerosol model in 2005. However, as it was fairly pointed out by J. Putaud, due to considerable uncertainties in calculating both primary and especially secondary OA and determining its chemical composition and water content, it'll be difficult to accurately calculate aerosol water associated with organic aerosol fraction. On the other hand, the contribution to aerosol water due to organic aerosols is expected to be within 16-20% (Pandis, November 2004, personal communication).

4. The amount of non-C atoms in OC varies depending on the chemical speciation of organic aerosol and, as it was fairly pointed out by the referee, poorly known. Therefore, it was decided to consider two cases when estimating the contribution of aerosol water in the unidentified PM mass: (1) when OC mass was represented by the mass of C atoms and the unaccounted PM mass was said to be partly due to non-C atoms and partly due to water (to avoid introducing an additional uncertainty due to conversion OC to OM); and (2) when a rough attempt was made to convert OC mass to the total mass of organic matter (OM).

5. As it was pointed out, the artefacts in filter measurements of PM can be considerable and can result in drawing erroneous conclusions from comparison between model results and measurements. Loss or gain of semi-volatile components, ammonium nitrate and organic aerosols, on the filter will affect aerosol water content. For EMEP data, 'quality classes' for measurement sites and flagging system indicateing the quality of the individual measurements is available and taken in to account when analysing the results of comparison of model calculations with observations.

As suggested, a shift from wet to dry PM concentration measurements at the EMEP sites can be considered as a possible way to reconcile model results with measurements. However, before deciding on recommending that, tests are needed to investigate how concentrations of other semi-volatile aerosol compounds (nitrates) will be

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affected by the reduction of relative humidity.

6. Recognised caveats to model estimates of particle water, presented in the paper, are that there is no accurate verification of the modelled aerosol water as no appropriate data was available to the author. However, the author intend to continue work on further testing and verification of model calculations of aerosol water with measurements as new appropriate data becomes available. Therefore, measurements at Ispra, containing PM10 and PM2.5 mass at 50% and 20% relative humidity and their chemical compositions, are certainly very valuable data for evaluating the model results. Unfortunately, it was not feasible to perform model calculations for 2002 at the time of paper preparation as no meteorology and emission data for 2002 were available yet. However, the author intends to make model calculations for 2002 (and later years as input data become available) and compare model results of PM mass and composition and water content with Ispra measurements. It'll also be very valuable to verify the calculations of PM water with the thermodynamic module, implemented in the EMEP aerosol model, useing the measured PM chemical composition, as recommened by J.-P. Putaud.

The Specific Comments:

p. 6028, line 29 and p. 6033, line 18: Agree, the phrasing is incorrect. It also contradicts other sentences in the manuscript saying that depending on the ambient relative humidity, particles can either loose or gain water under conditioning. The phrase will be changed.

p. 6032, line 11: Yes, impresise phrasing. The meaning was of course that in the model, secondary inorganic aerosols and sea salt represent the soluble aerosol fraction, while organic aerosol is presently assumed to be insoluble. More comments to OC are given in (3) above.

p. 6033, line 18: Good points; the sentence will be edited.

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p. 6034, line 24: 'Verified' will be changed with 'compared with measurements'.

p. 6037, line 19: Redundant phrase will be removed.

p. 6039, line 1: In the case discussed here, OC was not converted to organic matter. Therefore, the negative values of unaccounted mass cannot be explained by this reason.

p. 6039, line 14: Well spotted! Unfortunately inconsistent results from different model runs were includede in Fig. 3 and Fig. 4. Therefore, the figures did not show that model calculated fine OC compared better with measurements than coarse OC. The corrected Fig. 3 will be submitted. Furthermore, a discussion on uncertainties both in EC measurements as well as in model EC calculations could be interesting, but as it was pointed out by the referee, not needed here.

p. 6040, line 28: Agree, the statement will be re-phrased.

p. 6041, line 13-18: I'll re-write and stengthen this conclusion, as suggested.

p. 6041, line 19-22: What I meant to say here was that measurement artefacts and conditions of sample storage, transportation etc. can vary at the same site and as well as between sites. This will probably effect the results of comparison between modelled aerosol water and the unacounted PM mass in measurements. I'll re-think this point and try to come up with a better agruments.

p. 6043, line 15-16: Here, the evaluation of model results for dry PM and PM including water are compared. A better explanation will be given in the revised manuscript.

p. 6044, line 5-7: I agree that there is an inconsistency. I'll exclude model comparison with AIRBASE PM measurements from Table 3.

p. 6044, line 25-26: I do agree with the referee that OC mass should be converted to OM mass when deriving the "identified" chemical PM mass. As it was discussed above, the conversion factor is variable and mostly unknown. In this work, it was decided to

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show OC in ug(C) when presenting PM chemical composition, while it was explained that the unaccounted PM mass includes also non-C atoms from OM.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 6025, 2004.