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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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Review of manuscript ACPD-2004-0124 To what extent can aerosol water explain the discrepancy between model calculated and gravimetric PM10 and PM2.5? by S. G. Tsyro

General comments:

This work - as clearly reflected by its title - deals with the amount of water contributing to the particulate matter (PM) mass determined according to the Reference Method EN12341. This is a very relevant question, within the scope of ACP and beyond, since PM limit value could well be exceeded in some parts of the EU just because ofĚ water bound to particles collected on filters equilibrated at 50% RH and 20 °C for 48 hrs (recommended conditions for gravimetric measurements). This paper addresses

the question from the modeling view-point, and represents clearly an original contribution. However, the conclusions should be made more clear and focused (and shorter). For instance, the EMEP modeled PM mass concentrations are generally smaller than measured PM mass concentrations, and this is all right, since PM sources are known to be lacking in the current version of the EMEP model. Obviously, adding a new component (water), the "agreement will be better" (sic). But this conclusion is weak, compared to what is explained in the text body (that correlations between modeled and measured PM mass increase - at most sites - when modeled PM includes water). Actually, looking at correlations is certainly more founded than comparing PM concentrations values, as I'm not sure (I should certainly find this in previous papers) that the EMEP model calculates PM10 and PM2.5 with 10 and 2.5 representing aerodynamic diameters, as selected by PM sampling heads. An important assumption regarding the organic carbon (OC) hydrophobic character is made. It should at least be discussed, since OC accounts for a large fraction of PM at many sites, and several works showed that a significant fraction of OC is actually water soluble (WS). Let's mention here that modeling the WSOC concentration is certainly a very difficult task, and that WSOC is not measured in any of the EMEP network station for now. Information about WSOC concentrations at the EMEP network stations will therefore still be lacking for some time. The amount of non-C atoms consisting organic matter (OM) is also poorly known. However, does it make sense to consider the unaccounted PM mass calculated without including any conversion factor to assess the organic matter (OM) mass concentration from the organic carbon (OC) mass concentration and to compare it with anything else? The abstract and conclusion report on such a comparison with modeled waterĚ When determining what fraction of the unaccounted gravimetric mass could be particle bound water at the sites where the whole PM chemistry is known, it would also be perhaps more appropriate to apply the equilibrium module to the measured PM chemical composition, rather than to modeled concentrations, which would lead to stronger conclusions. Finally, it should be kept in mind that what is collected on filters used for gravimetric analysis may be quite different from the ambient particulate mat-

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ter, which is supposed to be reproduced by the model. Several positive and negative artifacts have been clearly identified and can affect the collected PM mass at least as significantly as particle-bound water. Practical solutions to avoid theses artifacts are being developed, but are not all available yet. At least, the amount particle-bound water instead can be limited by equilibrating filters at $<$20% RH. More specific points are addressed below.

Specific comments:

p. 6028, line 9 and everywhere else: Putaud et al., A European aerosol phenomenology - 2 was published in 2004. p. 6028, line 29: the sentence "However, equilibration of filters does not remove all particle-bound water". is not correct. This equilibration not only cannot remove all the particle-bound water, but can add up some. p. 6032, line 11: several works have shown that a significant fraction of OC is also water soluble (e.g. Putaud et al., ACP, 4, 1-14, 2004.). p. 6033, line 18: again, the phrasing "filter conditioning does not remove all water associated with particles" is not correct. The equilibration is not aimed at doing so, and cannot do it. p. 6033, line 18: at least TEOMs do not use only heating for removing water. Furthermore, RH is lowered to ca. 30%, which is not completely dry yet. p. 6034, line 24: I wouldn't use the word "verified". p. 6037, line 19: the statement "In most of Europe, the fraction of residual water in PM10 is 20-30%" appears already at line 15. p. 6039, line 1: negative unaccounted mass can also be due to overestimated carbon mass - to - molecular mass ratio for organic matter. p. 6039, line 14: It is difficult to see that "model fine OC compares better with measurements than OC in PM10". Furthermore, comparing modeled and measured EC asks for a deep discussion on the uncertainties in EC measurements. However, it is not needed here, as both OC and EC are considered 100% hydrophobic. p. 6040, line 28: "eliminating the unaccounted part of PM2.5 due to non-C atoms in organic particles" by using an arbitrary OC - to - OM conversion factor seems a bit ambitious. Doing this, we just try to account for them. p. 6041, line 13-18: this conclusion should be stronger. Aerosol particles collected on a filter exposed at 50% RH at 20°C

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for 48 hrs certainly contain water, which is usually not measured independently - we do not need any model to say this. This model work should be able to give a more definitive answer. p. 6041, line 19-22: please specify how “artefacts in particle sampling” or “different conditions of filters transportation, storage and handling” can affect the unaccounted mass. I believe that any loss would affect equally the gravimetric mass and chemical mass. p. 6043, line 15-16: please clarify “As expected, the spatial correlation between modelled and measured PM10 and PM2.5 has not improved”. Compared to what ? p. 6044, line 5-7: the statement “comparison of calculated wet PM concentrations with the corrected PM mass from automated instruments is not physically justified and can give dubious results” is fully founded, and I was about to make this comment at the beginning of this section, when I thought that correcting “by a relevant factor to produce results equivalent to those that would have been achieved by using the reference method” was considered to be an acceptable method by the author. If it is not the case, I do not understand why this comparison is shown anyway. p. 6044, line 25-26: it does not make sense to assess the “the unaccounted mass in measured PM10 and PM2.5 concentrations” if there is no attempt of assessing the non C atom content of organic matter, as suggested by the legend “OC” in Fig. 3.

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