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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The size-composition distribution of atmospheric nanoparticles over Europe" *by* David Patoulias et al.

Anonymous Referee #2

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Review of the manuscript titled "The size-composition distribution of atmospheric nanoparticles over Europe". The manuscript describe the new features of the PMCAMx-UF, which now considers condensation of organic compounds using the VBS approach. The new version of PMCAMx-UF was used to simulate the particle number concentrations over Europe for a 4-days time period during the PEGASOS campaign in 2012. The model results are compared against observations from 16 ground based stations and vertical profiles observations with a Zeppelin over the Po Valley. The model was run with our without secondary organic aerosol (SOA) formation in order to evaluate the impact of SOA formation on the sub-micron particle number concentrations.

General comments I have a number of questions concerning how the model was setup

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which need to be addressed. At least you need to describe in more details the new features of PMCAMx-UF for the reader. Especially the assumptions behind the VBS approach and how it is implemented is only briefly described and need a more detailed description. I am also a bit skeptical to why you did not consider LVOC and ELVOC since only these type of compounds can contribute to the initial growth of new sub 3 nm particles (see e.g. Tröstl et al., 2016).

I think you need to explain more clearly what it new/novel with this study and not just what is the new features of PMCAMx-UF? Generally I think the overall results in the figures 4,6,7,8,9 looks good but when you read the results section this information is somewhat lost in all details about the model performance at single stations and locations. Since you only look at a short time period I am not sure that it is worth to go into details and speculate too much about possible reasons for the model bias at single locations.

After you have improved the manuscript concerning these general points and also have addressed my specific comments given below and the other reviewers concerns I am open to serve as review for the manuscript a second time.

Specific/minor comments:

In a number of places you write vague statements of the type “quite good”. Please try to avoid such unspecific statements. I have given a few specific examples below.

Line 20-21 in abstract. Why do you only consider SVOC and not ELVOCs and LVOCs? Several recent studies show that ELVOC and LVOC are formed e.g. by peroxy radical autoxidation.

Line 24 in abstract. Particles larger than 100 nm in diameter I presume. Please clarify that it is diameter you refer to.

Line 27-28 in abstract. It is not easy to understand exactly what you mean with “The model performed quite well compared to the Zeppelin measurements, reproducing

more than 85% of N10 and 75% of the N100 data, within a factor of 2." I would also remove "quite well" from the sentence and explain more in detail how the model agrees with the observations.

Line 49-50: "Under some conditions, growth of new particles has been attributed to the condensation of organic species" I think this statement is a bit misleading since many studies show that the particles growth rates often are dominated by condensation of organic species.

Line 80-81: "These problems were caused mainly by insufficient organic vapor condensation (Fountoukis et al., 2012), as the model did not explicitly include SOA condensation on ultrafine particles.". Does this mean that PMCAMx-UF already before considered condensation of organic species but not on the sub 100 nm in diameter particles?

Line 97-99: "Our hypothesis is that simulation of the corresponding interactions improves the ability of CTMs to reproduce ambient observations of the aerosol number distribution." What do you mean with "corresponding interactions"? It is not a very bold hypothesis to state that the model performance will improve if we include condensation of organic compounds since several studies before this has shown that organic compounds dominate the UF particle growth at many locations around the world.

Line 120-121: "The lowest boundary is at 3.75 $\times$ 10$-$25 kg of dry aerosol mass per particle." Do you mean that the model has fixed particle mass size bins but not exactly fixed diameter size bins? E.g. The single particle volume and diameter changes depending on the chemical composition (density) of the particles? I think that you usually have fixed dry particle diameters and single particle volumes but let the single particle mass in each size bin change depending on the chemical composition.

L136-138: "The critical nucleus is assumed to consist of roughly two molecules of sulfuric acid and two molecules of ammonia (Napari et al., 2002)." Does this correspond to an initial dry particle diameter of roughly 0.8 nm?

L170-173: You specify the sources of anthropogenic gas emissions but not the primary particle sources. How did you estimate the primary particle emissions from the different sources. What particle emission size distribution and chemical composition did you use/assume? How were the gas and primary particle emissions from ships estimated? Did you consider natural primary particle emissions from the ocean and land surfaces?

L186-190: "Semi-volatile nitric acid and hydrochloric acid in DMAN partition to particles (as nitrate and chloride, respectively) in the accumulation mode range. This simplification dramatically reduces the computational burden, and is not problematic for accuracy since ultrafine particle growth is governed by low volatility compounds." Yes, this is indeed a simplifications. Is the partitioning of nitric acid and hydrochloric acid reversible and depend on the temperature, RH and the particle acidity? I.e. Does the model include a thermodynamics model? How can you state that it is not problematic for the accuracy if you have not evaluated the model performance against a model which explicitly simulates the reversible partitioning of nitric acid and hydrochloric acid onto all particle sizes? Also the partitioning of these vapors onto the accumulation mode will influence the condensation and coagulation sinks and if this is not correctly described in the model the growth and lifetime of the UF particles will also be affected.

Line 198-199: "The SOA yields used in the updated version of PMCAMx-UF are based on the NOx-dependent stoichiometric yields of Murphy at al. (2009)." Please explain this in more detail. Do you use different yields for each VOC from the gas-phase mechanism? Is it exactly the same VOC as in the study by Murthy et al. (2009)? If not you should specify what yields you used for each VOC and what C* they enter into the VBS. Is the VBS approach you use considering consecutive oxidation steps leading to functionalization and fragmentation?

L216-218: "The first two days of each simulation were excluded from the analysis to minimize the effect of the initial conditions on the results." This is not much considering that the lifetime of accumulation mode particles can be around one week in the atmosphere. I think also after 2-days your model results will still be influence considerably

by the initial conditions. By the way what was the initial particle concentrations and chemical composition? Did you use observations to assign the initial conditions?

L218-220: “Constant very low values have been used for the boundary conditions so that the predicted particle number concentrations over Europe are determined for all practical purposes by the emissions and corresponding processes simulated by the model.” Aa a reader you want to know exactly what the boundary conditions was and not just that the values were low.

L259-260: “The spatial distributions of Ntot and N10 are quite similar, while the distributions of N50 and N100 are quite different both when compared against Ntot and from each other.” Try to avoid using unspecific terms like “quite similar” and “quite different”. What does this really mean?

L274-275: “The condensation of organics was predicted to decrease the total number concentration Ntot over most continental Europe.” I think this can partly be explained by the fact that you do not consider contribution of LVOC and ELVOC to the particle growth. With these vapors included the newly formed particles would also grow by condensation of organics. With the SVOCs that you consider I doubt that they contribute substantailly to the initial growth of particles below $\sim$5 nm in diameter. I think this should be discussed with proper references to recent studies on LVOC and ELVOC contribution to the growth of new particles.

L304-307: Why did you decide to present the fraction of modeled particle number concentrations that are within a factor of 2 of the observed concentrations? IS this factor of 2 the approximate uncertainty in the observations? To me it is very hard to understand if the agreement between the model and observations are good or not.

L331-343: Since the study was conducted for a very limited time period, only 4 days, I think it is hard to draw any conclusions about the bias in the nucleation frequency. How can you get a nucleation frequencey of 90 and 10 % respectively if you only consider 4 days?

L369-373: “This overprediction is probably due to our assumptions about the chemical aging of the biogenic SOA. The detailed evaluation of PMCAMx PM1 mass and composition predictions during the PEGASOS campaigns and the sensitivity of the model to chemical aging parameterizations are presented in detail in forthcoming publications.” What assumption? I don’t think you have described this in the method section. I don’t think it is too much to ask to also compare the modeled and measured PM1 chemical composition of organics, nitrate, sulfate and ammonia for the stations where this data exists. This would add value to this study and make the model results more trustworthy.

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