Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-73-AC2, 2018

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

David Patoulias et al.

spyros@chemeng.upatras.gr

Received and published: 2 July 2018

1. *The manuscript describeσ 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-day 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.*

There is a misunderstanding regarding the duration of the simulation period. It is 34

days (from June 5 to July 8, 2012) and not 4. We clarify in the revised manuscript that the simulation period was 34 days.

General comments:

2. *I have a number of questions concerning how the model was setup 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).*

We have followed the recommendation of the reviewer and added more details about the VBS approach and its implementation in PMCAMx-UF. The current work focuses on the effect of the formation of semivolatile organic aerosol on particle number concentrations. The role of chemical aging reactions but also LVOC and ELVOC formation will be the topic of a forthcoming publication. This is now explained in the revised manuscript, both in the Model Description and in Conclusions sections.

3. *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.*

Please note that as the simulation period is more than a month (34 days) and is not short, the discussion of the details of the model performance is justified. The first reviewer has actually recommended some additional analysis about the performance of the model in Hyytiala. We now stress in the conclusions the new insights about the effects of semivolatile organic compounds on aerosol number. The increase of N100 concentrations and the decrease of N10 concentrations are significant insights. The fact that better simulation of these organic compounds closes the gap between observations and predictions is also an important conclusion.

Specific/minor comments:

4. *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.*

We have replaced the corresponding statements with quantitative information about the model performance in the revised paper.

5. *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.*

We decided to focus on SVOCs in the present work. The complex role of LVOCs and ELVOCs is investigated in a forthcoming manuscript. Please see also our response to Comment 2.

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

The word "diameter" has been added.

7. *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 percent of N10 and 75 percent 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.

We followed the suggestion of the reviewer and removed "quite well".

8. *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.*

We have rephrased this sentence. Organics dominate the growth in a lot of environments, but sulfuric acid and ammonia play an important role too in sulfur rich areas.

9. *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?*

The version of PMCAMx-UF used by Fountoukis et al. (2012) did not consider condensation of organic species. We have deleted the word "ultrafine".

10. *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.*

One of the major points of the present work is that organic condensation plays a much more complex role than simply helping in the UF particle growth. It increases the condensational and coagulation sinks thus reducing nucleation rates and increasing coagulation rates. Given the complexity and the nonlinearity of these interactions the net effect of organic condensation on particle number concentrations is by no means obvious. We conclude here, that in most areas this process actually leads to reductions in total particle number concentrations during this photochemically active period something rather unexpected. We have added a brief discussion of these points to further motivate our work.

11. *Line 120-121: "The lowest boundary is at 3.75 × 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.*

The aerosol size distribution is described with 41 size sections with the lowest boundary at 3.75 × 10^{-25} kg dry aerosol mass per particle. That corresponds to 0.8 nm dry diameter. The density can be calculated and updated continuously as a function of the composition of the particles in each bin. Each successive boundary has double the mass of the previous one. The use of mass as a variable is convenient for coagulation simulations, because it is conserved and also allows the direct transformation of the number to the mass distribution (Tzivion et al., 1987; 1989).

12. *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?*

The assumed cluster size is consistent with its composition (Napari et al., 2002).

13. *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?

The particle emissions were based on the pan-European anthropogenic particle number emission inventory (Denier van der Gon et al., 2009; Kulmala et al., 2011) and the carbonaceous aerosol inventory (Kulmala et al., 2011) developed during the EUCAARI project. The resulting number/mass inventory includes both number emissions and consistent size-resolved composition for particles over the size range of 10 nm to 10 μm. The international shipping, industrial, domestic, agricultural and traffic emission sources were included in the anthropogenic inventory (Denier van der Gon et al., 2009; Kulmala et al., 2011). The natural emissions include both particulate matter and gases and combine three different data sets: emissions from ecosystems based on the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2006), marine emissions based on the model of O'Dowd et al. (2008), and wildfire emissions (Sofiev et al., 2008a, b). This information has been added to the paper.

14. *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 simplification. 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.*

The PMCAMx-UF use the bulk equilibrium approach (the most computationally efficient approach) to simulate of inorganic aerosol growth. At each time step the amount of nitric acid and hydrochloric acid transferred between the gas and aerosol phases is determined by applying the aerosol thermodynamic equilibrium model ISORROPIA (Nenes et al., 1998). This amount is then distributed over the aerosol size sections by using weighting factors for each size section based on their effective surface area (Pandis et al., 1993). This treatment ensures that the appropriate amount is transferred to the accumulation mode, however it cannot describe accurately any potential transfer of these acids to the nucleation mode. This is now described in the revised paper.

15. *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?*

We have used the same gas phase mechanism (SAPRC) and the stoichiometric yields of Murphy et al. (2009). These stoichiometric yields are described in detail in the corresponding supplementary information of Murphy et al. (2009) (Table S2). A reference to this has been added. However, in this work, we have not used the next generation reactions of the semivolatile and intermediate volatility organic including functionalization and fragmentation reactions.

16. *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?

The initial conditions affect the predictions for a period similar to the average residence time of the pollutants in the modeling domain. Given that this is regional simulation, this period is significantly shorter than the lifetime of the particles in the atmosphere. In other words, the particles leave the modeling domain due to advection, before they are removed by precipitation or dry deposition. We have tested this, and 2 days are indeed sufficient for the model to "forget" the initial conditions and for emissions and chemistry to take over. The initial concentrations are relatively low and are now mentioned in the Supplementary Information.

17. *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.*

This is a valid point. A table with the boundary conditions used has been added to the SI. The effect of these boundary conditions on the predicted number concentrations is discussed in a new sensitivity analysis section (see Comment 2 of Reviewer 1).

18. *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?*

We have rephrased this sentence following the recommendation of the reviewer.

19. *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 substantially to the initial growth of particles below 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.*

The situation is also more complex because the LVOCs and ELVOCs also condense on the accumulation mode increasing this way the condensational and coagulation sinks. These effects tend to reduce the particle number concentrations and lead to the opposite direction compared to the faster growth of the freshly formed particles. This complexity is the reason that we did not include all these results in the present work and instead discuss them in a forthcoming publication.

20. *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.*

The factor of 2 is used as a useful indicator for the comparison of particle number observations to simulated results. It has been reported in previous publications and therefore it is also use here. Additional metrics (normalized mean bias and error) have also been added to give a better picture of the performance of the model.

21. *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 frequency of 90 and 10 percent respectively if you only consider 4 days?*

Please note that this is a misunderstanding. The simulated period is 34 days, which

allows us to draw some conclusions about the nucleation frequency. Please see also our response to Comment 1.

22. *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.*

We have followed the suggestion of both reviewers (see also Comment 6 of Reviewer 1) and added a section comparing the model predictions for PM1 composition with the corresponding measurements. Overall, the model reproduces the observations of inorganic aerosol components (sulfate, nitrate, ammonium) reasonably well (e.g., errors in the average concentrations of less than 0.5 μ g m^{-3} in the Italian sites), but it tends to underpredict the organic aerosol concentrations. For example, the OA in San Pietro Capofiume is underpredicted by 40 percent. This underprediction of the organics is the major reason for the underprediction of the condensational sink shown in Figure 7. Based on previous work with the sister model PMCAMx in Europe, the chemical aging processes, that are not simulated in this version of PMCAMx-UF, should be able to explain a significant fraction of the missing OA. The role of these processes, as explained elsewhere, is the topic of a follow-up publication that is currently under preparation.

References

Denier van der Gon, H. A. C., Visschedijk, A. J. H., Johansson, C., Hedberg Larsson, E., Harrison, R., and Beddows, D.: Size resolved pan European anthropogenic particle number inventory, EUCAARI Deliverable report D141 (available on request from EUCAARI project office), TNO, the Netherlands, 2009.

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, Environ. Sci. Technol., 40, 2635–2643, 2006.

Fountoukis, C., Riipinen, I., Denier van der Gon, H. A. C., Charalampidis, P. E., Pilinis, C., Wiedensohler, A., O'Dowd, C., Putaud, J. P., Moerman, M., and Pandis, S. N.: Simulating ultrafine particle formation in Europe using a regional CTM: contribution of primary emissions versus secondary formation to aerosol number concentrations, Atmos. Chem. Phys., 12, 8663-8677, 2012.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181–3210, 2006.

Kulmala, M., Asmi, A., Lappalainen, H. K., Baltensperger, U., Brenguier, J. L., Facchini, M. C., Hansson, H. C., Hov, O'Dowd, C. D., Pöschl, U., Wiedensohler, A., Boers, R., Boucher, O., De Leeuw, G., Denier Van Der Gon, H. A. C., Feichter, J., Krejci, R., Laj, P., Lihavainen, H., Lohmann, U., McFiggans, G., Mentel, T., Pilinis, C., Riipinen, I., Schulz, M., Stohl, A., Swietlicki, E., Vignati, E., Alves, C., Amann, M., Ammann, M., Arabas, S., Artaxo, P., Baars, H., Beddows, D. C. S., Bergström, R., Beukes, J. P., Bilde, M., Burkhart, J. F., Canonaco, F., Clegg, S. L., Coe, H., Crumeyrolle, S., D'Anna, B., Decesari, S., Gilardoni, S., Fischer, M., Fjaeraa, A. M., Fountoukis, C., George, C., Gomes, L., Halloran, P., Hamburger, T., Harrison, R. M., Herrmann, H., Hoffmann, T., Hoose, C., Hu, M., Hyvärinen, A., Hõrrak, U., Iinuma, Y., Iversen, T., Josipovic, M., Kanakidou, M., Kiendler-Scharr, A., Kirkevåg, A., Kiss, G., Klimont, Z., Kolmonen, P., Komppula, M., Kristjánsson, J. E., Laakso, L., Laaksonen, A., Labonnote, L., Lanz, V. A., Lehtinen, K. E. J., Rizzo, L. V., Makkonen, R., Manninen, H. E., McMeeking, G.,

Merikanto, J., Minikin, A., Mirme, S., Morgan, W. T., Nemitz, E., O'Donnell, D., Panwar, T. S., Pawlowska, H., Petzold, A., Pienaar, J. J., Pio, C., Plass-Duelmer, C., Prévôt, A. S. H., Pryor, S., Reddington, C. L., Roberts, G., Rosenfeld, D., Schwarz, J., Seland, O., et al.: General overview: European Integrated project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI)-integrating aerosol research from nano to global scales, Atmos. Chem. Phys., 11, 13061–130143, 2011.

Murphy, B. N. and Pandis, S. N.: Simulating the formation of semivolatile primary and secondary organic aerosol in a regional chemical transport model, Environ. Sci. Technol., 43, 4722– 4728, 2009.

Nenes, A., Pandis, S. N., and Pilinis, C.: ISORROPIA: a new thermodynamic equilibrium model for multiphase multicomponent inorganic aerosols, Aquat. Geochem., 4, 123–152, 1998. Odum, J. R., Hoffman, T., Bowman, F., Collins, D., Flagan, R. C., Seinfeld, J. H.: Gas/particle partitioning and secondary organic aerosol yields. Environ. Sci. Technol., 30, 2580–2585, 1996.

Pandis, S. N., Wexler, A. S., and Seinfeld, J. H.: Secondary organic aerosol formation and transport. 2. Predicting the ambient secondary organic aerosol size distribution, Atmos. Environ., 27A, 2403–2416, 1993.

Sofiev, M., Vankevich, R., Lanne, M., Koskinen, J., and Kukkonen, J.: On integration of a Fire Assimilation System and a chemical transport model for near-real-time monitoring of the impact of wild-land fires on atmospheric composition and air quality, Modelling, Monitoring and Management of Forest Fires, WIT Trans. Ecol. Envir., 119, 343–351, 2008a.

Sofiev, M., Lanne, M., Vankevich, R., Prank, M., Karppinen, A., and Kukkonen, J.: Impact of wild-land fires on European air quality in 2006–2008, Modelling, Monitoring and Management of Forest Fires, WIT Trans. Ecol. Envir., 119, 353–361, 2008b.

Tzivion, S., Feingold, G., and Levin, Z.: An efficient numerical solution to the stochastic collection equation, J. Atmos. Sci., 44, 3139–3149, 1987.

Tzivion, S., Feingold, G., and Levin, Z.: The evolution of raindrop spectra. Part II: collisional collection/breakup and evaporation in a rain shaft, Journal of the Atmospheric Sciences, 46, 3312–3327, 1989.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-73, 2018.