Response to Referee #1

1. In this paper, the authors apply the PMCAMx-UF air quality model to a European domain to assess its ability to simulate nanoparticles over the domain. They suggest the model performs favourably, with the results generally within a factor of 2. They also assessed the simulated impact of organics, finding it leads to a large increase in N100 particles in parts of Europe. They also found using VBS improved model performance. In general, this work appears to be well done, though is rather limited in its scope of model evaluation, the core of the study.

We do appreciate the positive assessment of our work. We have made several changes in the revised text in an effort to improve it and avoid any misunderstandings. These changes are described below following each comment of the reviewer (in italics).

2. In a model application and evaluation such as this, it is important to provide some idea of what is driving the model. Is it the emissions of nanoparticles (which is a rather uncertain quantity, particularly the appropriate size distribution to be used given the model resolution: how is the very near field dynamics of traffic emissions treated?)? Is it boundary conditions? Is it nucleation, and if so, from emissions within the domain or from boundary conditions? (Note: there is rather little discussion of boundary conditions or emissions: they should discuss both in more detail and provide a spatial distribution of emissions by size. They can use NTotal, N10, N50 and N100, though as noted below, I would use N10-50, N50-100, N>100). Even if just for a one-week simulation, they should provide the results of four additional simulations: Halving the BCs on all PM, halving the BCs on species that might react to form condensable species, Halving the emissions. (They need not use changes of one half, but something where the response would be seen if it is important). In the end, the article should address, very precisely, why the simulated levels are what they are, by size. For now, there is a bit of that for organics.

We have followed the suggestion of the reviewer and quantified the sensitivity of the model predictions to the boundary conditions and emissions. We performed eight additional simulations with: (i) 50% reduction of PM boundary conditions, (ii) 50% reduction of the boundary conditions for all gases, (iii) 50% reduction of just the SO_2 boundary conditions, (iv) set the SO_2

at the boundaries equal to zero, (v) 50% reduction of PM emissions at all sizes, (vi) 50% reduction of the emissions of all gases, (vii) 50% reduction of just the SO_2 emissions, and (viii) set the SO_2 emissions equal to zero. The effect of these changes on the particle number distribution was quantified. Summarizing the effect of the changes in the boundary conditions by 50% was less than 5% for all cases, showing that the boundary conditions were not a major driver of the simulation. On the other hand, the emissions of sulfur dioxide, other vapors and particles had a major effect with changes of 10-35% for a corresponding 50% emission changes. Setting the sulfur dioxide emissions to zero resulted in changes of 40-70% in the concentrations in the different particle size ranges showing its importance for new particle formation and growth during this photochemically active period. The results of this sensitivity analysis are now discussed in a new sensitivity analysis section.

3. It is interesting that their simulated results are spatially more uniform than might be expected. Looking at Fig. 5, the simulated results are typically about 2500-10000. The observations go rather

lower. This requires more discussion. It also appears as though the results at Hyytalia are dominated by boundary conditions that are fixed in time… Is this true? If not, an interesting pseudo-steady state appears to be at work that should be explained. On the other hand, the simulation shows more variability than the observations in Fig. 8. Again, rather more discussions is warranted as this is the focus of the paper.

The comparison of the model predictions with the observed values in Figure 4 for the 16 sites suggests that the model does a good job in capturing the observed variability in all size ranges. There is no evidence that the model fails to capture the observations at the low concentration levels. This is now mentioned in the revised paper.

Indeed, the model predictions at the station at Hyytiala are affected more than most other sites by the boundary conditions due to its location and the prevailing meteorology. A discussion of the sensitivity of the corresponding predictions and the average diurnal profiles for this station has been added. Also reasons for the discrepancies between observations and predictions for this important site are analyzed in additional detail.

4. The title should be changed. This article is not focused on nanoparticles over Europe, but the simulation of nanoparticles over Europe. It also has almost nothing on the actual composition (they have a small piece on sensitivity to SOA formation). Much more information and analysis is necessary to have the more general title. I would propose “Spatial distribution of simulated nanoparticles over Europe”.

We agree with the suggestion of the reviewer and we have added the word “simulation” to the title of the paper.

5. The comparison of results to the flight data is remarkable. They really do need to show what is contributing to the results, particularly how the bump at 800 m exists given the vertical diffusion found in most air quality models. The bump at 800 m is very interesting and really understanding it is key. Given the model’s ability to capture this, I was surprised there was no discussion of it. They could take the analyses done to assess the processes leading to their simulated levels discussed above and use that.

This is a good point, but unfortunately the explanation for the bump at the 800 m is rather mundane. There were few measurements at this altitude in a few flights in days with relatively high particle number concentrations. These created the apparent bump in the measurements. The model captured these high concentration periods so it predicted the same bump for the average concentration profile. We now explain in the revised paper that the average profile is the result of averaging of measurements and predictions from different flights and simulations. There were relatively fewer measurements in altitudes above 600 m. The number of samples at different altitudes changed for each flight creating additional variability in the measured profiles.

6. The manuscript also does not provide any information on how well the model captures aerosol composition. If the model is within a factor of 2 on total number, but off by a factor of 2 on OC or sulphate mass, this has important implications, particularly if the differences are in different directions.

We have followed the suggestion of the reviewer and added a section comparing the model predictions for PM_1 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 μg 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%. 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.

7. I think it would be better to show their results by size groups, e.g., N<10, N10-50, N50-100 and N>100. This would better demonstrate the variability in the different sizes, and if, for example, one size range is much more uniform than the others.

We have followed the suggestion of the reviewer and added selected results in the Supplementary Information using the suggested size distribution ranges. We would prefer to keep though the current size ranges in the main paper for consistency with previous studies (Fountoukis et al., 2012; Baranizadeh et al., 2016).

8. It appears that WRF is applied without nudging, but is simply reinitialized every three days/ Why? To what degree does the reinitialization impact the system? How does the performance degrade after multiple days?

We have tested the performance of WRF with different types of initialization and nudging. The three-day reinitialization has been chosen because of its simplicity and the fact that the corresponding WRF predictions remain consistent with all the measurements. The measurements are pre-processed by the WPS package, which provides each atmospheric and static field with fidelity appropriate to the chosen grid resolution of the model. The performance of WRF for

Europe against observed meteorological variables has been the topic of several recent studies (Jimenez-Guerrero et al., 2008; de Meij et al., 2009; Im et al., 2010; Argueso et al., 2011; Garcia-Diez et al., 2012) showing good performance. A brief discussion of this point has been added to the paper.

9. In summary, the submitted manuscript is a good start on what can be a nice contribution to the literature, though it is currently too limited in what they have done and what they explain. The authors should provide a more extensive analysis on what processes drive their simulations. At a minimum, they should: 1. Provide a set of calculations showing how the model responds to changes in emissions and boundary conditions, and the role of sulfate nucleation, and the origin of the SO2 (BC or emissions inside). 2. Provide some information on how well the composition is captured is also needed. Without such further information it is difficult to say whether the model results are reasonable or not. 3. Provide more detailed information on the model application, including vertical cell spacing, overall performance for more species. How well does WRF capture the meteorology? 4. Change the title to include "simulation" as the article does not really focus on the distribution of nanoparticles (as observed).

We have done our best to address the comments of the referee. More specifically, the results of eight sensitivity simulations are now described in a new sensitivity analysis section (please see response to Comment 2). A brief evaluation of the performance of PMCAMx-UF in reproducing the PM composition observations has been added (please see response to Comment 6). We have also added in the Supplementary Information a table with the vertical levels of the model and a brief justification of our choice for the WRF reinitialization (response to Comment 8). The title has been changed to clarify that this is a modeling study (response to Comment 4).

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Response to Referee #2

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% 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.

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 % 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 PM_1 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 μg 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%. 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.

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Simulation of ~~T~~the size-composition distribution of atmospheric nanoparticles over Europe

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Abstract

PMCAMx-UF, a three-dimensional chemical transport model focusing on the simulation of the ultrafine particle size distribution and composition has been extended with the addition of the volatility basis set (VBS) approach for the simulation of organic aerosol (OA). The model was applied in Europe to quantify the effect of secondary semi-volatile organic vapors on particle number concentrations. The model predictions were evaluated against field observations collected during the PEGASOS-2012 campaign. The measurements included both ground and airborne measurements, from stations across Europe and a Zeppelin measuring above Po-Valley. The ground level concentrations of particles with diameter larger than 100 nm (N_{100}) were reproduced with a daily normalized mean error of 40% and a daily normalized mean bias of -20%. PMCAMx-UF tended to overestimate the concentration of particles with diameter larger than 10 nm (N_{10}) with a daily normalized mean bias of 75%. ~~The model performed quite well compared to the Zeppelin measurements, reproducing more than 85% of the N_{10} and 75% of the N_{100} data, within a factor of 2.~~ The model was able to reproduce within a factor of two 85% of the N_{10} and 75% of the N_{100} ~~the observations (~~Zeppelin measurements above ground~~) for more than 85% (N_{10}) and 75% (N_{100}), within a factor of 2~~. The condensation of organics led to an increase (50-

120%) of the N_{100} concentration mainly in central and northern Europe, while the N_{10} concentration decreased by 10-30%. Including the VBS in the PMCAMx-UF improved its ability to simulate aerosol number concentration compared to simulations neglecting organic condensation on ultrafine particles.

1. Introduction

New particles are introduced in the atmosphere by two major processes; direct emission from multiple sources and nucleation from low volatility vapors. Nucleation and subsequent growth of new particles have been observed in a variety of environments worldwide (Kulmala et al., 2004), representing a significant source of aerosol number. Fresh particles formed by nucleation can either be lost through coagulation with pre-existing larger particles or grow through condensation of vapors (e.g. sulfuric acid, ammonia, organics, and nitric acid) to larger sizes (Adams and Seinfeld, 2002) and become cloud condensation nuclei (CCN), thereby increasing the cloud droplet number concentration (Adams and Seinfeld, 2002). Thus, nucleation and subsequent growth by condensation can be an important source of CCN (Makkonen et al., 2009; Merikanto et al., 2009; Pierce and Adams, 2009; Wang and Penner, 2009; Yu and Luo, 2009).

Considerable uncertainty arises from the partial understanding of the identity of the species involved in the growth of these nuclei (Kulmala et al., 2004; Kerminen et al., 2012). Field measurements (Eisele and McMurry, 1997; Weber et al., 1998, 1999) and model simulations (Kulmala et al., 2000; Pirjola and Kulmala, 2001; Anttila and Kerminen, 2003) indicated that the condensation of sulfuric acid alone is often not sufficient to justify the observed growth rates of fresh particles (Riipinen et al., 2011). Organics dominate particle ~~the~~ growth in a lot of environments, but sulfuric acid and ammonia also play an important role ~~too~~ in sulfur rich areas (Stanier et al., 2004; Yue et al., 2010). ~~U~~G~~nder some conditions, g~~rowth of new particles has been attributed to the condensation of organic species (Kulmala et al., 1998; Anttila and Kerminen, 2003; Kerminen et al., 2000), heterogeneous reactions (Zhang and Wexler, 2002), or ion-enhanced condensation (Laakso et al., 2002).

Secondary organic aerosol (SOA) comprises a major mass fraction (20-90%) of sub-micrometer particulate matter in many locations around the globe (Jimenez et al., 2009). Even though organic aerosol (OA) has been the subject of numerous studies (Hallquist et al., 2009), its chemical composition remains uncertain, making it one of the least understood components of atmospheric aerosols, due to the large number of different atmospheric organic compounds (Goldstein and Galbally, 2007).

Atmospheric OA composition continuously evolves with time as a result of various chemical reactions (Kanakidou et al., 2005). The semi-volatile products which are produced from the gas-phase oxidation of volatile organic compounds (VOCs) can afterwards condense to the particulate phase. The volatility bases set (VBS) framework describes the volatility distribution of OA compounds (Donahue et al., 2006) using logarithmically spaced bins of the effective saturation concentration, C^* (in μg m^{-3}) at 298 K, to classify atmospheric organic species. This framework has been tested in three-dimensional regional (3-D) chemical transport models (CTMs), and appears to perform well for simulations of aerosol mass distributions (Gaydos et al., 2007; Karydis et al., 2007; Murphy et al., 2009; Tsimpidi et al., 2010; Fountoukis et al., 2011, 2014).

A new 3-D CTM, PMCAMx-UF, with detailed aerosol microphysics was developed by Jung et al. (2010), and has been used for simulations over the US and Europe (Fountoukis et al., 2012; Baranizadeh et al., 2016). For the US domain, the first comparison of the model and the measurements in Pittsburgh was encouraging; this evaluation focused on the frequency, timing, and strength of nucleation events (Jung et al., 2010). Applications in Europe compared model predictions against size distribution measurements from seven sites (Fountoukis et al., 2012). The model was capable of reproducing more than 70% of the hourly number concentrations of particles larger than 10 nm (N_{10}) within a factor of 2. However, the concentration of particles larger than 100 nm (N_{100}, the number of particles that can act as CCN) was underpredicted by 50%. Even at sites where the sulfate to OA mass ratio was high (e.g., Melpitz), the nanoparticle growth rates was underpredicted, but with smaller errors as compared with sites with relatively less sulfate. 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. Based on observations from two background sites, Riipinen et al. (2011) estimated that roughly half of the condensed organic mass should contribute to nanoparticle growth in order to explain the observed aerosol growth rates.

Patoulias et al. (2015) developed a new aerosol dynamic model, DMANx (Dynamic Model for Aerosol Nucleation), that simulates aerosol size/composition distribution, and includes the condensation of organic vapors on nanoparticles using the VBS framework. Simulations were performed for the sites of Hyytiälä (Finland) and Finokalia (Greece); two locations with different organic sources. Patoulias et al. (2015) investigated the effect of condensation of organics and chemical aging reactions of SOA precursors on ultrafine particle growth and particle number concentration during a typical springtime nucleation event in both locations. At the Finokalia site, the simulations suggested that the organics play a complementary role in new particle growth, contributing 45% to the total mass of new particles. Condensation of organics increased the N_{100} by 13% at Finokalia, and 25% at Hyytiälä during a typical spring day with nucleation.

The overall objective of this work is to examine the effect of the condensation of secondary organic vapors (products of the oxidation of VOCs and of the intermediate volatility organic compounds; IVOCs) on particle number concentrations. Our hypothesis is that simulation of the corresponding interactions improves the ability of CTMs to reproduce ambient observations of the aerosol number distribution. Organic condensation can play a much more complex role than simply helping in the ultrafine 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 extended the 3-D CTM PMCAMx-UF (Fountoukis et al., 2012; Jung et al., 2010), which originally assumed that ultrafine particles can grow only by condensation of sulfuric acid and ammonia as well as by coagulation. The updated version of PMCAMx-UF includes the condensation of organic vapors on ultrafine particles using the VBS framework. We evaluated the model by comparing its predictions to surface-based high-time-resolution measurements from 16 stations in Europe and airborne measurements from the PEGASOS Zeppelin campaign over the Po Valley, in Italy. ~~One of the major points of the present work is that organic condensation plays a much more complex role than simply helping in the ultrafine 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. In most areas this process actually lead to reductions in total particle number concentrations during this photochemically active period something rather unexpected.~~

2. Model description

PMCAMx-UF is a three-dimensional CTM that simulates the aerosol number size distribution, in addition to the mass/composition size distribution (Jung et al., 2010; Fountoukis et al., 2012). PMCAMx-UF is based on the framework of PMCAMx (Gaydos et al., 2007; Karydis et al., 2007), describing the processes of horizontal and vertical advection, emissions, horizontal and vertical dispersion, wet and dry deposition, aqueous and aerosol phase chemistry, as well as aerosol dynamics. For the simulation of aerosol microphysics, PMCAMx-UF uses the updated DMANx model of Patoulias et al. (2015), which simulates the processes of coagulation, condensation/evaporation and nucleation, assuming an internally mixed aerosol. DMANx uses the two-moment aerosol sectional (TOMAS) algorithm (Adams and Seinfeld, 2002; Jung et al., 2006). A key feature of TOMAS is its ability to track two independent moments of the aerosol size distribution for each size bin; the aerosol number and mass concentration.

~~The aerosol size distribution is discretized into 41 sections covering the diameter range from approximately 0.8 nm to 10 μm. The lowest boundary is at 3.75 × 10^{-25} kg of dry aerosol mass per particle. Each successive boundary has twice the mass of the previous one.~~ 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 approximately to a dry diameter of ~~to~~ 0.8 nm~~m dry diameter~~. The particle density in each bin is~~can be~~ calculated and updated continuously as a function of the corresponding composition~~ of the particles in each bin~~. Each successive boundary has double the mass of the previous one to facilitate the simulation of coagulation~~. 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).

~~The~~ The particle components modeled include sulfate, ammonium, nitrate, sodium, chloride, crustal material, water (H_2O), elemental carbon (EC), primary organic aerosol (POA) and four SOA components. The TOMAS algorithm simulates the evaporation, condensation of sulfuric acid (H_2SO_4), ammonia (NH_3) and organics, independently.

2.1 Nucleation parameterizations

PMCAMx-UF has the option of using a number of nucleation treatments (Fountoukis et al., 2012; Baranizadeh et al., 2016). In this work, the nucleation rate was calculated using a scaled ternary nucleation parameterization based on the original expressions of Napari et al. (2002) and the binary parameterization of Vehkamäki et al. (2002), if the NH_3 concentration is below a threshold value of 0.01 ppt. The original NH_3-H_2SO_4-H_2O parameterization had predicted successfully the presence or lack of nucleation events (Gaydos et al., 2005) in sulfur rich environments. However, it overpredicted ultrafine number concentrations during nucleation events (Fountoukis et al., 2012; Jung et al., 2008, 2010), and thus a scaling factor of 10^{-6} was applied to the nucleation rate following the suggestions of Fountoukis et al. (2012). The critical nucleus is assumed to consist of roughly two molecules of sulfuric acid and two molecules of ammonia consistent with its assumed size (Napari et al., 2002).

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

2.2 Gas-phase chemistry

The gas phase chemistry mechanism in PMCAMx-UF was updated in this work to the SAPRC chemical mechanism (Carter, 2000; Environ, 2003), which includes 211 reactions of 56 gases and 18 free radicals. The SAPRC version used here includes five lumped alkanes (ALK1-5), two lumped olefins (OLE1-2), two lumped aromatics (ARO1-2), isoprene (ISOP), a lumped monoterpene (TERP) and a lumped sesquiterpene species (SESQ). OLE1 contains all the terminal alkenes, while OLE2 represents all the internal and cyclic alkenes. All lumped VOCs with the exception of ALK1-3 are considered as SOA precursors (Lane et al., 2008a, b; Tsimpidi et al., 2010).

2.3 Coagulation

Coagulation of particles in the atmosphere is an important sink of aerosol number, but is also a mechanism by which freshly nucleated particles grow to larger sizes (Adams and Seinfeld, 2002). The TOMAS algorithm is used for the simulation of coagulation. Following Adams and Seinfeld (2002), TOMAS assumes that the particles coagulate via Brownian diffusion and the effects of gravitational settling and turbulence are neglected.

2.4 Particle number/mass emissions

~~The EUCAARI (European Integrated project on Aerosol, Cloud, Climate, and Air Quality Interactions) Pan-European anthropogenic particle number emission inventory (Kulmala et al., 2011) was used in this study.~~ 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 (European Integrated project on Aerosol, Cloud, Climate, and Air Quality Interactions) 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. Hourly gridded anthropogenic and biogenic emissions included both gases and primary particulate matter. 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). ~~Three different datasets were combined in order to produce the biogenic gridded emissions for the model. Emissions from ecosystems were estimated by MEGAN (model of emissions of gases and aerosols from nature; Guenther et al., 2006).~~ MEGAN uses as inputs the plant functional type, the leaf area index, various chemical species emission factors and weather data provided by the weather research and forecasting model (WRF) ~~–~~(Skamarock et al., 2005). Since sea surface covers a considerable portion of the domain, the marine aerosol emission model developed by O'Dowd et al. (2008) was also used. Wind speed fields from WRF and chlorophyll-a concentrations were used as inputs of the marine aerosol model. VOCs were speciated based on the approach proposed by Visschedijk et al. (2007). Anthropogenic gas emissions included land emissions from the GEMS (global and regional Earth-system monitoring using satellite and in-situ data) dataset (Visschedijk et al., 2007)~~, as well as international shipping emissions~~. I~~The i~~nternational shipping, industrial, domestic, agricultural, and traffic aerosol emission sources were included in the anthropogenic inventory (Denier van der Gon et al., 2009; Kulmala et al., 2011). ~~Industrial, domestic, agricultural and traffic emission sources were included in the anthropogenic inventory.~~

2.5 Condensation/Evaporation

Condensation of gas-phase species to existing aerosol particles is an important source of aerosol mass and a means by which small particles grow to CCN sizes. The TOMAS algorithm was used for the simulation of condensation/evaporation of sulfuric acid, ammonia and organic vapors, using the wet diameters of the particles (Gaydos et al., 2005).

Sulfuric acid is assumed to be in pseudo-steady state in DMANx. This pseudo steady-state approximation (PSSA) for sulfuric acid proposed by Pierce and Adams (2009) increases the computational speed with a small loss in accuracy. Jung et al. (2010) evaluated the performance of PSSA for sulfuric acid in DMAN against a 4th order Runge-Kutta algorithm and showed that PSSA was accurate and computationally efficient. Condensation of ammonia was simulated following the approach described by Jung et al. (2006). Ammonia condensation on the ultrafine particles ends when sulfate is fully neutralized to ammonium sulfate.

N~~Semi-volatile n~~itric ~~acid ~~and hydrochloric acid partition to particles in the accumulation and coarse modes in DMAN as nitrate and chloride, respectively~~ partition to particles (as nitrate and chloride, respectively) in the accumulation mode range~~. This partitioning is ~~The PMCAMx-UF ~~simulated using~~e~~ 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 distribution~~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 larger particles~~accumulation mode~~;~~,~~ however it cannot describe accurately any potential transfer of these acids to the nucleation mode. This simplification dramatically reduces the computational burden with a minimal loss of ,~~, and is not problematic for ~~accuracy, since ultrafine particle growth is governed by low-~~ ~~volatility compounds.

2.6 Secondary organic aerosol formation

Gas-phase oxidation of VOCs produces semi-volatile products that can then condense to the particle phase.~~ The VBS framework used in PMCAMx-UF (Donahue et al., 2006) describes the volatility distribution of the OA compounds.~~ The VBS framework (Donahue et al., 2006) used in PMCAMx-UF describes the ~~complete ~~volatility distribution~~range~~ of OA compounds using logarithmically spaced bins, characterized by an effective saturation concentration, C^* (in µg m^{-3}). SOA components partition between the aerosol and gas phases, and can be formed from anthropogenic ~~SOA ~~(aSOA) and biogenic~~ SOA~~ (bSOA) precursors. SOA partitioning was simulated using 4 volatility bins ($1 - 10^3$ μg m^{-3} at 298 K). We assume an average molecular weight of 200 g mol^{-1} for SOA, and an effective enthalpy of vaporization of 30 kJ mol^{-1} (Pathak et al., 2007; Stanier et al., 2007). The partitioning of OA between the gas and particulate phases is simulated dynamically (Patoulias et al., 2015).

The SOA yields used in the updated version of PMCAMx-UF are based on the NO_x-dependent ~~stoichiometric~~ yields of Murphy at al. (2009). The current work focuses on the effect of the formation of semi-volatile organic aerosol on particle number concentrations. ~~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). However, in this work, we have not used the next generation reactions of the semivolatile and intermediate volatility organic including functionalization and fragmentation reactions. The current work focuses on the effect of the formation of semivolatile organic aerosol on particle number concentrations.~~ The role of later generation reactions (known as chemical aging) and ~~reactions but~~ also the formation of low volatility (LVOC) and extremely low-volatility organic compound (ELVOC) formation (Ehn et al., 2014; Tröstl et al., 2016)~~.~~ will be the topic of future work. ~~a forthcoming publication. The partitioning of OA between the gas and particulate phases was calculated dynamically (Patoulias et al., 2015)~~.~~).~~

2.7 Meteorological input fields

Meteorological inputs to PMCAMx-UF included horizontal wind components, vertical diffusivity, temperature, pressure, water vapor, clouds and rainfall. The meteorological model WRF (Skamarock et al., 2005) was used to create the above inputs. WRF was driven by geographical and dynamic meteorological data (historical data generated by the Global Forecast System). Each layer of PMCAMx-UF was aligned with the layers used in WRF. The WRF simulation was periodically re-initialized (every 3 days) with observed conditions to ensure accuracy in the corresponding fields that were used as inputs in PMCAMx-UF, for 34 days from June 5 to July 8, 2012. The three-day re-initialization has been chosen because of its simplicity and the fact that the corresponding WRF predictions remain consistent with all the measurements. The measurements are pre-processed by the WPS (WRF Preprocessing System) package, which provides each atmospheric and static field with fidelity appropriate to the chosen grid resolution of the model. The performance of WRF for Europe against observed meteorological variables has been the topic of several ~~recent~~ studies (Jimenez-Guerrero et al., 2008; de Meij et al., 2009; Im et al., 2010; Argueso et al., 2011; Garcia-Diez et al., 2012) with all of them showing ~~presenting~~ good performance.

3. Model Application and Measurements

The PMCAMx-UF modeling domain in this application covered a 5400 × 5832 km^2 region in Europe (Fig. 1), with 150 cells in the x- and 162 cells in the y- direction, with a 36 × 36 km grid resolution and 14 vertical layers (the height of each layer can be found in the Supplementary Information, Table S1) extending up to approximately 7.5~~6~~ km ~~(Fig. 1)~~. PMCAMx-UF was set to perform simulations on a rotated polar stereographic map projection.

The first two days of each simulation were excluded from the analysis to minimize the effect of the initial conditions on the results. 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 a regional simulation, this period is significantly shorter than the lifetime of the particles in the atmosphere. Based on our tests ~~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~~ two~~2~~ days are indeed sufficient for the model to “forget” the initial conditions and for emissions and chemistry to take over. The initial concentrations used are ~~relatively~~ low to further decrease their impact on the results (Supplementary Information, Table S2).

Constant very low values have been used for the boundary conditions (Table S2) 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~~. The boundary conditions used are shown in Table S2~~. The effect of these boundary conditions on the predicted number concentrations is discussed in a subsequent section~~scussed below~~.

An intensive field campaign took place in Europe, as part of the Pan-European-Gas-AeroSOl-climate-interaction Study (PEGASOS) project, for 34 days from June 5 to July 8, 2012. Measurements of aerosol size distribution from the Aerosols, Clouds, and Trace gases Research Infra-Structure Network (ACTRIS), Chemistry-Aerosol Mediterranean Experiment (ChArMEx) and the German Ultrafine Aerosol Network (GUAN) network are also available for the same period. The model results were compared against measurements in ground sites (Fig. 1): Birkenes (Norway), Hyytiala (Finland), Aspvreten (Sweden), Vavihill (Sweden), K-Puszta (Hungary), Ispra (Italy), San Pietro Capofiume (Italy), Corsica (France), Patras (Greece), Finokalia (Greece), Thessaloniki (Greece), Mace Head (Ireland), Hohenpeissenberg (Germany), Melpitz (Germany), Waldhof (Germany) and Schneefernerhaus (Germany). The measurements are available in the European Supersites for Atmospheric Aerosol Research (EUSAAR), ChArMEx (charmex.lsce.ipsl.fr) and EBAS databases (ebas.nilu.no). Particle size distribution measurements at all sites were made using either a Differential Mobility Particle Sizer (DMPS) or a Scanning Mobility Particle Sizer (SMPS). Information about all stations can be found in the Supplementary Information (SI, section S1).

The airborne measurements acquired by a Zeppelin were part of the PEGASOS project over the Po Valley in Italy.~~, for 34 days during June 5 to July 8, 2012. ~~The Po Valley region is situated between the Alps in the north and the Apennines Mountains in the south–southwest. The mountains surround the valley on three sides and strongly modify both the local and regional air flow patterns in the area (Sogacheva et al., 2007). High levels of pollutants are often observed in the region due to the industrial, agricultural, and other anthropogenic emissions. In addition, the emissions from ship traffic on the Adriatic Sea (Hamed et al., 2007) and long-range transport from central-eastern Europe are possible sources of pollutants in the region (Sogacheva et al., 2007). A scanning mobility particle sizer (SMPS) was used to measure the number size distribution of particles in the size range of 10 to 430 nm.

4. Results

4.1 Base Case simulation

Figure 2 shows the base case PMCAMx-UF predictions of ground level average number concentration for all particles (N_{tot}) and for particles with diameters above 10 nm (N_{10}), 50 nm (N_{50}), and 100 nm (N_{100}), d~~d~~uring June 5 to July 8, 2012 (34 days). The N_{50} and N_{100} concentrations are often used as proxies for CCN-related aerosol number concentrations

(Fountoukis et al., 2012). The N_{10} can be directly compared against the differential mobility particle sizer (DMPS) or SMPS measurements. On a domain average basis, the model predicted for the ground level N_{tot} = 6500 cm^{-3}, N_{10} = 3800 cm^{-3}, N_{50}= 1550 cm^{-3} and N_{100} = 520 cm^{-3} during the simulated period. ~~The spatial distributions of N_{tot} and N_{10} are quite similar, while the distributions of N_{50} and N_{100} are quite different both when compared against N_{tot} and from each other.~~ ~~The spatial distributions of N_{tot} and N_{10} present their highest and lowest values for the same locations in the domain, while the distributions of N_{50} and N_{100} present high dissimilarities both when compared against N_{tot} and to each other.~~ High N_{tot} and N_{10} are predicted in areas with frequent nucleation events and also areas with high primary particle number emissions. Average N_{tot} concentrations exceeding 20,000 cm^{-3} were predicted over Bulgaria, Bosnia, southern Romania, Turkey, Germany, Poland, Holland, Portugal, northern Spain, eastern UK, northern Italy, and central Russia. On the other hand, ~~the~~ N_{50} and N_{100} are also affected by secondary particulate matter production. ~~Highest N_{tot} concentration exceeding 20,000 cm^{-3} were predicted over Bulgaria, Bosnia, southern Romania, Turkey, Germany, Poland, Holland, Portugal, northern Spain, eastern UK, northern Italy, and central Russia.~~ T~~In contrast, t~~he highest N_{50} and N_{100} concentrations are predicted over the Mediterranean, mainly in areas near southern Spain, southern Italy and Greece.

An additional simulation, without taking into account the condensation of organics was also performed. The average fractional increase of N_x, f_{Nx}~~–~~, due to the condensation of organic species is defined as:

$$f_{Nx} = \frac{N_x(\text{with organics}) - N_x(\text{without organics})}{N_x(\text{without organics})} \qquad (4~~3~~.1~~2~~)$$

where x ~~x~~ is 10, 50, 100 nm or total.

Predictions of f_{Nx} ~~–~~are shown in Fig. 3. The average fractional changes are -0.02, -0.05, 0.15 and 0.33 for the N_{tot}, N_{10}, N_{50} and N_{100}, respectively. The condensation of organics was predicted to decrease the total number concentration N_{tot} over most continental Europe. The largest decrease was approximately 50%. This rather counterintuitive result is due to the increase of both the condensation and coagulation sinks as SOA is formed. These effects dominated over the faster growth of fresh nuclei or other nanoparticles to larger sizes that tend to slow down their coagulation rate and increase their lifetime. In the other extreme an increase of N_{tot} of approximately 60% was predicted over the eastern UK. In this area organic condensation does lead to higher number concentrations. The predicted N_{10} also decreased between 15-30%, due to organic condensation over most of Europe. The minimum value of f_{N10} was about -0.30 over Serbia, while the maximum f_{N10} was about 0.35 over eastern UK. On the other hand, the condensation of organics increased the N_{50} over the whole domain. The increase was 40-80% over Scandinavia and northern Russia. The condensation of semi-volatile organic vapors results in an increase of N_{100} by 70-150% over northern Scandinavia and northwestern Russia according to PMCAMx-UF.

The absolute increase in particle number concentration (ΔN_x) due to the organic condensation is defined as:

$$\Delta N_x = N_x\ (\text{with organics}) - N_x\ (\text{without organics})$$

\- (4~~3~~.2~~3~~)

where x is 10, 50, 100 nm or total.

~~The~~ N_{tot} decreased over Turkey, central and Eastern Europe, and Balkans by 2000 to 5000 cm^{-3} while it increased over the eastern UK by roughly 3000 cm^{-3} (Fig. S1 in~~, -~~Supplementary Information~~, SI~~). The highest reduction of N_{tot} was approximately 15000 cm^{-3} over Hungary and central Turkey. The predicted ΔN_{10} over central Europe was in the range of -1000 to -3000 cm^{-3}. The maximum reduction of N_{10} was equal to 3600 cm^{-3} over Hungary while its maximum increase was 6500 cm^{-3} over eastern UK. The N_{50} increased due to the condensation of organics~~s species~~ over Italy, central Russia, Holland, Ukraine, eastern Mediterranean, the coast of Algeria and Spain by 500 - 2000 cm^{-3}. N_{100} increases from 300 to 800 cm^{-3} over the Mediterranean and south Russia. The maximum N_{100} increase was about 2000 cm^{-3} over Malta and southern Italy. The corresponding changes of the concentrations of

~~Figure S2 shows the PMCAMx-UF with organics condensation predictions of ground level average number concentration for~~ particles with diameters between 10 nm and 50 nm (N_{10-50}) and ~~, and particles with diameters~~ between 50 nm and 100 nm (N_{10-50}) are shown in Figure S2.

~~. Also, the absolute increase in particle number concentration ΔN_{10-50} and ΔN_{50-100} due to the organic condensation for 34 days during June 5 to July 8, 2012 are displayed.~~

4.2 Evaluation of extended PMCAMx-UF

The predicted daily average concentrations of particles larger than 10, 50 and 100 nm~~,~~ are compared to the corresponding observations in all ground stations in Fig. 4. Around 65% of the observed N_{10} observations were reproduced within a factor of 2 by PMCAMx-UF, with the model tending to overestimate the corresponding concentrations. The model performed even better for N_{50} reproducing 80% of the measurements within a factor of 2. PMCAMx-UF presented a tendency to underestimate the N_{100}, levels but still reproduced 70% of the data, within a factor of 2. The model does a good job in capturing the observed variability in all size ranges and also appears to reproduce the observations at the low concentration levels.

The prediction skill metrics of PMCAMx-UF, when compared against the daily average measurements from the 16 stations, are summarized in Tables 1-3. The average normalized mean error (NME) for N_{10} was 90% and the normalized mean bias (NMB) was 75%. The N_{10} was overestimated in most locations with the exception of Hyytiala, San Pietro Capofiume, and Hohenpeissenberg. The normalized mean bias was less than 30% in K-Puszta, Melpitz and Patras. The model really overpredicted N_{10} (NMB>100%) in several stations in Northern Europe (Aspvreten, Birkenes, Vavihill), some coastal locations (Corsica and Mace Head), two German sites (Waldhod and Schneefernerhaus) and the Thessaloniki site in northern Greece. The overall NMB and NME for N_{50} were 25% and 50%, respectively. The N_{50} NMB was less than 50% in 14 stations, with only Aspvreten and Thessaloniki being exceptions. In these 14 stations the corresponding error was less than 70%. Finally, the N_{100} was underpredicted in all stations with the exception of two Greek sites (Thessaloniki and Finokalia). However, this underprediction was less than 30% in 9 out of the 14 sites. Overall, the NMB for N_{100} was -20% and the NME for N_{100} was 40% for the simulation with organics.

Figures 5 and ~~Figures ~~S3~~2~~-S5~~4~~ show measured and predicted average diurnal profiles of N_{10}.

-In Hyytiala, Patras and Hohenpeissenberg, the observed diurnal profiles of N_{10} were flat, and the predicted diurnal profiles of N_{10} were close to the observations. In Melpitz and San Pietro Capofiume, the observed and predicted N_{10} increased at noon due to nucleation. In K-Puszta, Ispra, Birkenes, Aspvreten, Vavihill, Thessaloniki, Schneefernerhaus, Finokalia, Corsica and Waldhof, the model overpredicted N_{10}.

One of the potential explanations for the overprediction of N_{10} is the corresponding overprediction in the frequency of nucleation. Figure 6 shows the predicted and measured nucleation frequency for the 16 stations during the~~June 5 to July 8, 2012~~ ~~(~~34 simulation days~~)~~. The criteria proposed by Dal Maso et al. (2005) were used for the categorization of a day as a nucleation event. The nucleation frequency was defined as the ratio of the number of days characterized as nucleation events to the total number of days.

The observed nucleation frequency varied dramatically in the 16 sites from over 90% in San Pietro Capofiume to less than 10% in Patras. PMCAMx-UF reproduced this wide range (Fig. 6) with the predicted nucleation frequency being within 20% of the observed one in 12 out of the 16 stations. The model tends to overpredict nucleation frequency with the most significant errors in two coastal stations in the Mediterranean (Corsica and Patras) and two stations in Scandinavia (Birkenes and Aspreveten). This suggests that overpredicted nucleation frequency can explain part of the N_{10} overprediction in at least three (Corsica, Birkenes and Aspreveten) out of the eight stations.

The overprediction of N_{10} could be also due to the low surface area of the particles resulting in lower condensation and coagulation rates. The capability of the existing aerosol population to remove vapors and freshly formed particles can be described by the condensational sinks (CS) (Dal Maso et al., 2005). The model undepredicted the measured the condensational sink in most of the sites. In Corsica the model overpredicted the condensation sink, while in Thessaloniki, Birkenes and Aspreveten the model is in good agreement with the measurements (Fig. 7). Summarizing, the errors in N_{10} are caused by the high predicted nucleation rate at Aspvreten, Birkenes, Schneefernerhaus, Thessaloniki and Vavihill and they are, at least partially, due to low predicted condensation sink at Ispra, K-Puszta, Mace Head and Melpitz. At Corsica, the overprediction of N_{10} is due to errors in both the predicted nucleation rates and the condensation sink.

The average diurnal profiles of N_{100} for all sites are shown in Fig. 8 and Figures S~~5~~6-S~~7~~8. The model reproduced satisfactorily the average observed of N_{100} in the Mediterranean (Corsica, San Pietro Capofiume, Patra and Finokalia) with the exceptions of Thessaloniki, where PMCAMx-UF overestimated N_{100} for the most hours of the day.

In northern Europe, the predicted N_{100} was in general below the observed N_{100}. The maximum underprediction of N_{100} was observed in Hyytiala, Mace Head, and Melpitz. This indicated that the concentration of large particles was lower than observed, and therefore the condensation sink was also lower (Fig. 7). This underprediction is probably due to a combination of lower primary particles emissions and lower growth rates of the particles. The PMCAMx-UF predictions for Hyytiala and Mace Head are also quite sensitive to the boundary conditions used.

Underestimation of the corresponding values could contribute to the N_{100} underpredictions in these locations. The low prediction of organic aerosol is causing the underprediction of N_{100} in Patras and San Pietro Capofiume.

~~The comparison of the model predictions to the observed values in diurnal profiles for the 16 sites suggests that the model does a good job in capturing the observed variability in all size ranges. There is no evidence that the model fails to capture the observations at the low concentration levels.~~

~~The model predictions at the station at Hyytiala are affected more than most other sites by the boundary conditions due to its location and the prevailing meteorology. Its flat diurnal profile is not the result of new nucleated particles that either could not reach diameters higher than 10 nm or collided to bigger ones leading to no apparent peak during the midday hours. Maybe by adding condensation of LVOCs and ELVOCs on particles, would aid the increase of size regarding the freshly nucleated particles . Also, at Hyytiala, the model underpredicted the~~ ~~N_{100}~~ ~~mainly during the midday hours, implying the need of improvement of either the size distribution of the emissions, and/or number of pre-existing particles (condensation sink), and/or the addition of chemical aging of semi-volatile, and/or the effect of extremely low volatility organic vapors in the model.~~

4.3 Comparison to aerosol composition ~~mass~~ measurements

The PMCAMx-UF predictions can be evaluated during that period using available PM_1 measurements from Aerosol Mass Spectrometers in 4 stations (~~;~~ Bologna and San Pietro Capofiume in Italy as well as Finokalia and Patras in ~~(~~Greece) and filter $PM_{2.5}$ measurements from 12 additional stations in Europe ~~),~~ ~~Bologna and San Pietro Capofiume (Italy)~~ (~~the location of stations are shown in~~ Table S3).

~~These are summarized in Table S4. Overall,~~In Italy and Greece, 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 μg m^{-3} in the Italian sites), but it tends to underpredict the organic aerosol concentrations (Table S4). For example, the OA in San Pietro Capofiume is underpredicted by 40%. This underprediction of the organics is the major reason for the underprediction of the condensational sink shown in Figure 7 and is probably due to our assumptions about the chemical aging of the anthropogenic~~biogenic~~ SOA. Based on previous work with the sister model PMCAMx (Fountoukis et al., 2011; 2014) 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,~~ the detailed evaluation of PMCAMx PM$_1$ mass and composition predictions during the PEGASOS campaigns and the sensitivity of the model to chemical aging parameterizations are the main topics of on-going work~~a follow-up publication that is currently under preparation~~.

~~The ability of PMCAMx-UF to reproduce the submicrometer aerosol composition during this period was similar to that of PMCAMx over the same domain both at the ground and aloft (Fountoukis et al., 2011). For example, the model reproduced the average mass concentrations of the major inorganic PM$_1$ components within 20-30% in the Po Valley stations, but tended to overpredict the organic aerosol concentrations.~~

~~This overprediction is probably due to our assumptions about the chemical aging of the biogenic SOA. The detailed evaluation of PMCAMx PM$_1$ 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.~~

~~Additionally, the model was compared to measured PM$_{2.5}$ mass concentration from filters from different European countries (Table S5).~~For the rest of Europe we have used ~~The~~ measurements ~~are~~ available in the European Supersites for Atmospheric Aerosol Research (EUSAAR) and EBAS databases (ebas.nilu.no) for~~. We have~~ ~~selected~~ stations that had available data~~lable filter measurements~~ for more than 15 days during the simulation period. ~~5 June - 8 July.~~ Concerning the inorganic components ~~(Table S6)~~, the model reproduced~~predicted well~~ the sulfate measurements within ~~a variance of ±~~ 0.5 μg m^{-3} ~~except for the case of Ispra in Italy~~(Table S6). On the other hand, it has a tendency to overestimate the ammonium nitrate levels and to underestimate the organic aerosol concentration. ~~The model tends to overestimate the mass concentrations of PM$_{2.5}$ ammonium in almost all stations (except for Ispra, Italy) ranging from 0.4 to 1 μg m^{-3}. For nitrate, the model seems to be unable predicting low concentrations in other sites.~~ For the calculation of organic mass concentration, we assumed~~used~~ OA~~M /~~/~~–~~OC = 1.4 (Russell, 2003). ~~Comparing the model to the measured PM$_{2.5}$ OA mass concentration, the model slightly underestimated the OA in most of the stations (Table S7).~~

4.4~~3~~ Comparison to Zeppelin measurements

The Zeppelin measurements were taken every 3 minutes in different heights, while the model predictions are every 15 minutes. To compare the results, the model output was interpolated to the times of the Zeppelin measurement periods. Figure S8 shows the comparison between model predictions and Zeppelin measurements of N_{10} and N_{100} (averages of 2000 points). PMCAMx-UF reproduced more than 80% of the 3-minute N_{10} data of Zeppelin with~~-~~in a factor of 2.

Figure 9 shows the predicted and observed vertical concentration profiles of particle number concentrations for N_{10} and N_{100}, calculated for 80 m altitude bins, averaged over the entire PEGASOS campaign. The average profile is the result of averaging of the 3-min measurements ~~(3-minute)~~ and interpolated predictions from different flights and heights. The model showed a small tendency to underpredict N_{10}, especially at heights between 200 and 400 m. PMCAMx-UF reproduced very well the N_{100} concentration at all heights (except for heights between 200 and 500 m). The average measured N_{10} at all heights was 6050 cm^{-3}, while the predicted concentration was equal to 5250 cm^{-3}. The model also reproduced 75% of the 3-min N_{100} Zeppelin measurements ~~(3-minute)~~ within a factor of 2. The measured average N_{100} at all heights was 1520 cm^{-3} and while the extended PMCAMx-UF predicted 1380 cm^{-3} ~~for the extended PMCAMx-UF~~. The ability of the revised model to reproduce reasonably well the high-time resolution ~~(3-minute)~~ Zeppelin measurements at different ~~multiple~~ altitudes and locations is encouraging.

~~The vertical profiles shown are averages of different flights that collected data in different days and different altitudes each time. There are only a few measurements at the higher altitudes and these took place in periods of relatively high concentrations. This resulted in the peak at 750 m in Figure 9. The model predictions are for the same periods and the same altitudes. This is the reason why the model can reproduce the apparent high concentration layer.~~ The vertical profiles shown are averages of different flights ~~that collected data in~~on different days and different altitudes for each flight~~each time~~. The number of samples at different altitudes changed for each flight creating additional variability in the measured profiles.~~, and also there are only a~~There are relatively few measurements at ~~the~~ higher ~~igher~~ altitudes (above 600 m) which ~~. Also, the measurements at altitudes above 600 m~~ took place in periods with~~of~~ relatively high concentrations, creating the apparent bump in the measurements. The model captured these high concentration periods so it predicted the same bump for the average N_{100} concentration profile. This resulted in the peak at 750 m in Figure 9b. The model predictions are for the same periods and the same altitudes, and it is the reason why the model can reproduce the apparent N_{100} high concentration layer.

4.5~~4~~ Effect of SOA formation on PMCAMx-UF performance

The results of the simulation without SOA condensation were also compared to the measurements. Including the SOA condensation reduced the NMB of N_{10} by 10%. The maximum decrease of N_{10} due to organics condensation appeared at noon when nucleation events took place. The maximum decrease of N_{10} due to organics condensation appeared at noon when nucleation events took place. Simulation of the secondary organics reduced the NMB of N_{100} from -40% to -20%, and the NME from -45% to -40%. The organic condensation increased the average condensation sink from 3.5x10^{-3} s^{-1} to 4.2x10^{-3} s^{-1}. The addition of organics species decreased the average of N_{10} from 6550 cm^{-3} to 6060 cm^{-3} (average observed N_{10} was 3910 cm^{-3}) while increasing the average of N_{100} from 750 cm^{-3} to 930 cm^{-3} (average observed N_{10} was 1080 cm^{-3}) (Tables 1-3).

Simulation of organics condensation improved the average predicted N_{100} at all heights in the Po Valley compared to Zeppelin measurements, by reducing the underprediction of N_{100} from 22% to 10% (Fig S10~~9~~). The model with organics reproduced the measured N_{10} well at most heights, with the exception of the heights between 200 and 400 m (Fig S11~~0~~a). At all heights, the predicted N_{100} with organics was closer to the measurements than the prediction of N_{100} without organics (Fig S11~~0~~b).

4.6 Sensitivity to boundary conditions and emissions

The boundary conditions and emissions (gas and particles) represent potential sources of~~important sources of~~ uncertainty in the particle number concentration predictions by PMCAMx-UF. ~~of particle number concentration are the boundary conditions and emissions (gas and particles).~~ Eight sensitivity simulations~~runs~~ were conducted in which: (i) PM boundary concentrations were reduced by 50%~~ reduction of PM boundary conditions~~, (ii) the boundary concentrations for all gases were reduced by 50%~~ reduction of the boundary conditions for all gases~~, (iii) ~~50% reduction of just~~ the SO_2 boundary conditions were reduced by 50%, (iv) ~~set~~ the SO_2 ~~at the~~ boundary conditions were set~~ries~~ equal to zero, (v)- the PM emissions at all sizes were reduced by 50% ~~reduction of PM emissions at all sizes~~, (vi) ~~50% reduction of~~ the emissions of all gases were reduced by 50%, (vii) the SO_2 emissions ~~50% reduction of just~~were reduced by 50% ~~the SO_2 emissions~~, and (viii) ~~set~~ the SO_2 emissions were set equal to zero.

Table S7~~8~~ shows the predicted domain-average change (%) of particle number concentrations ~~change (%) that the model predicts~~ due to these reductions in emissions and boundary conditions ~~reductions~~. T~~Summarizing, t~~he effect of the changes in ~~the~~ boundary conditions by 50% was less than 5% for all cases, showing that the boundary conditions were not a major driver of the simulation. On the other hand, the emissions of sulfur dioxide, other vapors and particles had a major effect with changes of 10-35% for ~~a~~ corresponding 50% emission changes. Setting the sulfur dioxide emissions to zero resulted in changes of 40-70% in the concentrations in the different particle size ranges showing its importance for new particle formation and growth during this photochemically active period.

5. Conclusions

A new version of PMCAMx-UF was developed including the condensation of organic vapors on ultrafine particles, using the volatility basis set framework. We evaluated the model predictions against field observations collected in Europe, for 34 days during June 5 to July 8, 2012. The measurements included both ground stations across Europe and airborne measurements from a Zeppelin. The goal of this work was to better understand the effect of condensation of semi-volatile organic vapors on regional aerosol number concentration in Europe during a photochemically active period.

Including organic condensation in PMCAMx-UF improved its ability to reproduce the concentration of particles larger than 10 nm (N_{10}) at ground level. The inclusion of organics decreased the NMB of N_{10} from 85% to 75% and the corresponding NME from 100% to 90%. However, the revised model still tends to overpredict N_{10} for the majority of the locations. This overprediction of N_{10} is due to the overprediction of nucleation in some sites and the low number concentration of predicted pre-existing particles (low condensational sink) and consistently low coagulation rate.

The N_{100} predictions by PMCAMx-UF were encouraging in most sites. The NMB of N_{100} was reduced from -40% to -20% after the addition of SOA condensation while the corresponding NME was reduced from 45% to 40%. This underprediction of N_{100} at all sites implies the need of improvement of either the size distribution of the emissions, and/or number of pre-existing particles (condensation sink), and/or the addition of chemical aging of semi-volatile, and/or the effect of extremely low volatility organic vapors in the model (Patoulias et al., 2015).

The condensation of organics decreased the predicted N_{10} concentration across Europe. The condensation of organics both grew ultrafine particles and increased the probability of collision of fresh particles with large particles (coagulation sink). This change dominated over the faster growth of the fresh particles to larger sizes in many, but not all, locations. The larger reduction of N_{10} due to organic condensation (25%) was predicted over Russia, Turkey, Eastern Europe and the Balkans. The SOA condensation increased the number of particles larger than 100 nm (N_{100}) in all locations. This predicted increase was more than 80% in northern Scandinavia and northern Russia.

Compared to the PEGASOS Zeppelin measurements in Po Valley, PMCAMx-UF reproduced the average N_{10} with an error less than 10% and N_{100} with less than 10% at all heights up to 1000 m. The model with the condensation of organics performed better than the one without organics, in reproducing the observed vertical profile of both N_{10} and N_{100}. The model with organics reproduced more than 85% and 75% of 3 min data of Zeppelin within a factor of 2 for N_{10} and N_{100}, respectively.

The increase of N_{100} concentrations and the decrease of N_{10} concentrations in most areas due to the formation of semivolatile organic aerosol during this photochemically active period represent two of the major ~~are significant~~ insights offered by these simulations. As expected,~~,~~ ~~and~~ better simulation of the formation and partitioning of ~~se~~ organic compounds closes the gap between observations and predictions of particle number distributions. The role of chemical aging reactions but also LVOC and ELVOC formation (Ehn et al., 2014; Tröstl et al., 2016), that have been neglected in this study, will be the topic of a forthcoming publication.

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Table 1: Prediction skill metrics of PMCAMx-UF against daily ground measurements of particle number concentration with diameter above 10 nm from 16 stations during 5 June – 8 July 2012.

Station	Mean Observed	Mean Predicted (cm^{-3})		Normalized Mean Bias (NMB) (%)		Normalized Mean Error (NME) (%)	
		With Organics	Without Organics	With Organics	Without Organics	With Organics	Without Organics
N_{10}							
ASP	2090	5533	5496	165	163	165	163
BIR	1937	4950	4608	156	138	160	143
COR	2994	6768	7455	126	149	126	149
FIN	3932	6091	6191	55	57	57	60
HOH	3809	3801	4155	0	9	36	40
HYY	2616	2239	2408	-14	-8	33	35
ISP	6307	10481	11420	66	81	78	91
KPU	5245	6686	8581	27	64	56	82
MAC	822	1965	1758	139	114	149	135
MEL	6045	7325	8680	21	44	60	75
PAT	4858	5333	5449	10	12	50	53
SCH	1286	2913	3279	127	155	127	155
SPC	8319	7398	8547	-11	3	34	33
THE	4022	9755	10334	143	157	143	160
VAV	3230	7561	7601	134	135	136	137
WAL	5036	8194	8852	63	76	74	85
ALL	**3909**	**6062**	**6551**	**75**	**85**	**90**	**100**

Table 2: Prediction skill metrics of PMCAMx-UF against daily ground measurements of particle number concentration with diameter above 50 nm from 16 stations during 5 June – 8 July 2012.

Station	Mean Observed	Mean Predicted (cm^{-3})		Normalize Mean Bias (NMB) (%)		Normalized Mean Error (NME) (%)	
		With Organics	Without Organics	With Organics	Without Organics	With Organics	Without Organics
			N_{50}				
ASP	1353	2419	1835	79	36	81	47
BIR	1046	1364	1111	30	6	61	53
COR	2460	3155	2883	28	17	41	37
FIN	3085	4163	3905	35	27	39	32
HOH	1988	1550	1340	-22	-33	31	35
HYY	1546	1092	829	-29	-46	40	49
ISP	3500	5399	4728	54	35	70	56
KPU	2955	3674	3424	24	16	30	25
MAC	489	315	278	-36	-43	70	67
MEL	2243	2197	1824	-2	-19	23	24
PAT	3249	3211	2983	-1	-8	29	28
SCH	839	1202	1053	43	26	65	54
SPC	3235	3686	3300	14	2	29	23
THE	2334	5147	4545	120	95	120	95
VAV	1628	2192	1812	35	11	45	33
WAL	2050	2295	1882	12	-8	22	16
ALL	**2125**	**2691**	**2358**	**25**	**10**	**50**	**40**

Table 3: Prediction skill metrics of PMCAMx-UF against daily ground measurements of particle number concentration with diameter above 100 nm from 16 stations during 5 June – 8 July 2012.

Station	Mean Observed	Mean Predicted (cm^{-3})		Normalize Mean Bias (NMB) (%)		Normalized Mean Error (NME) (%)	
		With Organics	Without Organics	With Organics	Without Organics	With Organics	Without Organics
			***N*100**				
ASP	540	372	343	-31	-37	45	46
BIR	431	318	229	-26	-47	59	55
COR	1304	1180	914	-9	-30	37	36
FIN	1769	2002	1652	13	-7	29	22
HOH	911	558	448	-40	-50	43	51
HYY	736	309	207	-60	-70	60	70
ISP	1766	1461	1245	-17	-30	32	37
KPU	1526	1486	1228	-3	-20	28	25
MAC	242	116	86	-50	-64	60	65
MEL	998	671	484	-33	-51	38	51
PAT	1758	1471	1154	-16	-34	25	35
SCH	496	442	360	-11	-27	43	36
SPC	1667	1387	1132	-17	-32	31	37
THE	1398	2020	1649	45	18	53	40
VAV	749	438	358	-41	-52	46	54
WAL	924	577	464	-38	-50	39	50
ALL	**1076**	**926**	**747**	**-20**	**-40**	**40**	**45**

$$\text{NMB}=\sum_{i=1}^{n}(P_i-O_i)\Big/\sum_{i=1}^{n}O_i\ ;\qquad \text{NME}=\sum_{i=1}^{n}\left|P_i-O_i\right|\Big/\sum_{i=1}^{n}O_i$$

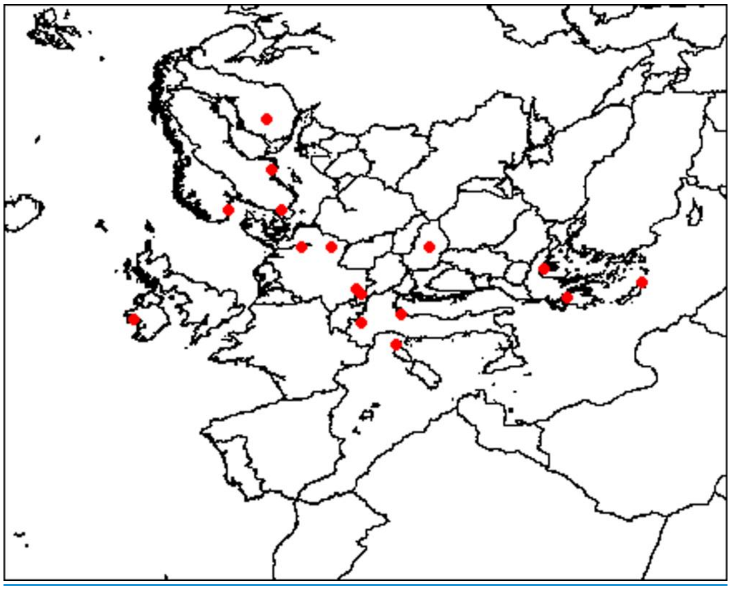


Figure 1: Modeling domain of PMCAMx-UF for Europe. Red dots show the measurement stations of Birkenes (Norway), Hyytiala (Finland), K-Puszta (Hungary), Aspvreten (Sweden), Vavihill (Sweden), Ispra (Italy), San Pietro Capofiume (Italy), Corsica (France), Patras (Greece), Finokalia (Greece), Thessaloniki (Greece), Mace Head (Ireland), Schneefernerhaus (Germany), Hohenpeissenberg (Germany), Melpitz (Germany) and Waldhof (Germany).

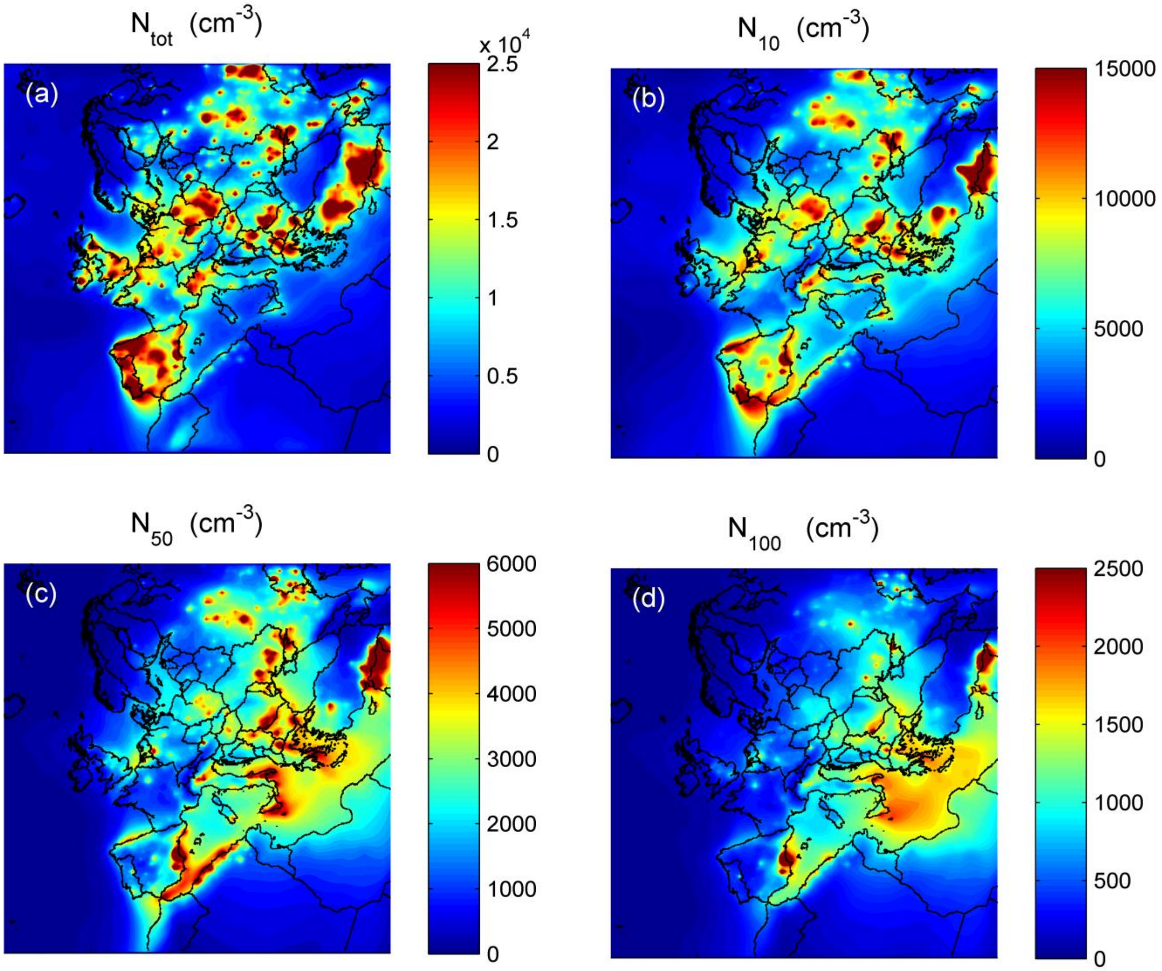


Figure 2: Ground level average number concentrations (cm^{-3}) predicted by the base case simulation during 5 June – 8 July 2012 for: (a) all particles (N_{tot}); and particles above (b) 10 nm (N_{10}); (c) 50 nm (N_{50}); and (d) 100 nm (N_{100}). Different color scales are used.

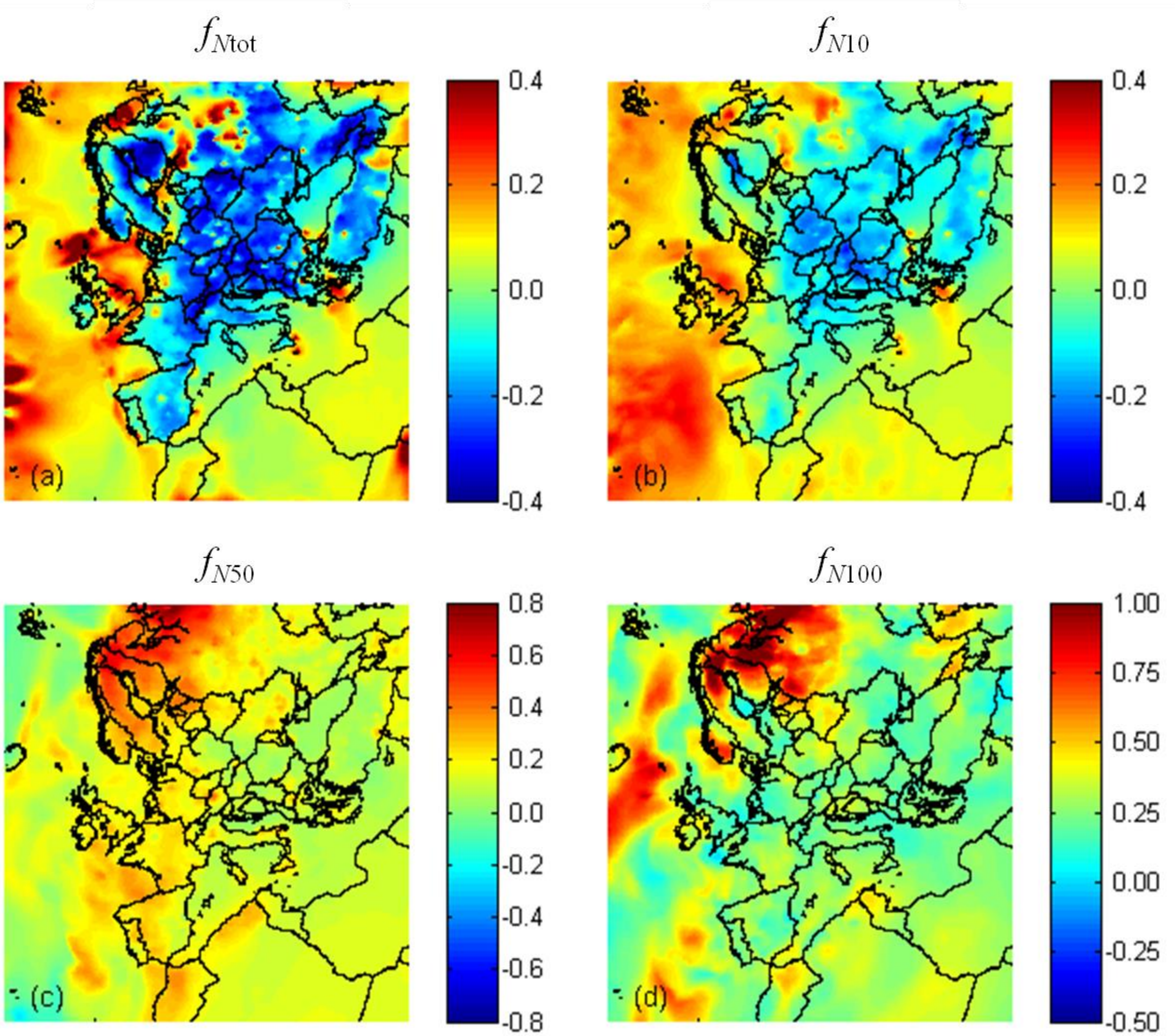


Figure 3: Ground level average fractional increase (f_{Nx}) of number concentration due to the condensation of organic species predicted during 5 June – 8 July for: (a) all particles ($f_{N\mathrm{tot}}$); particles above (b) 10 nm (f_{N10}); (c) 50 nm (f_{N50}); and (d) 100 nm (f_{N100}). Different scales are used.

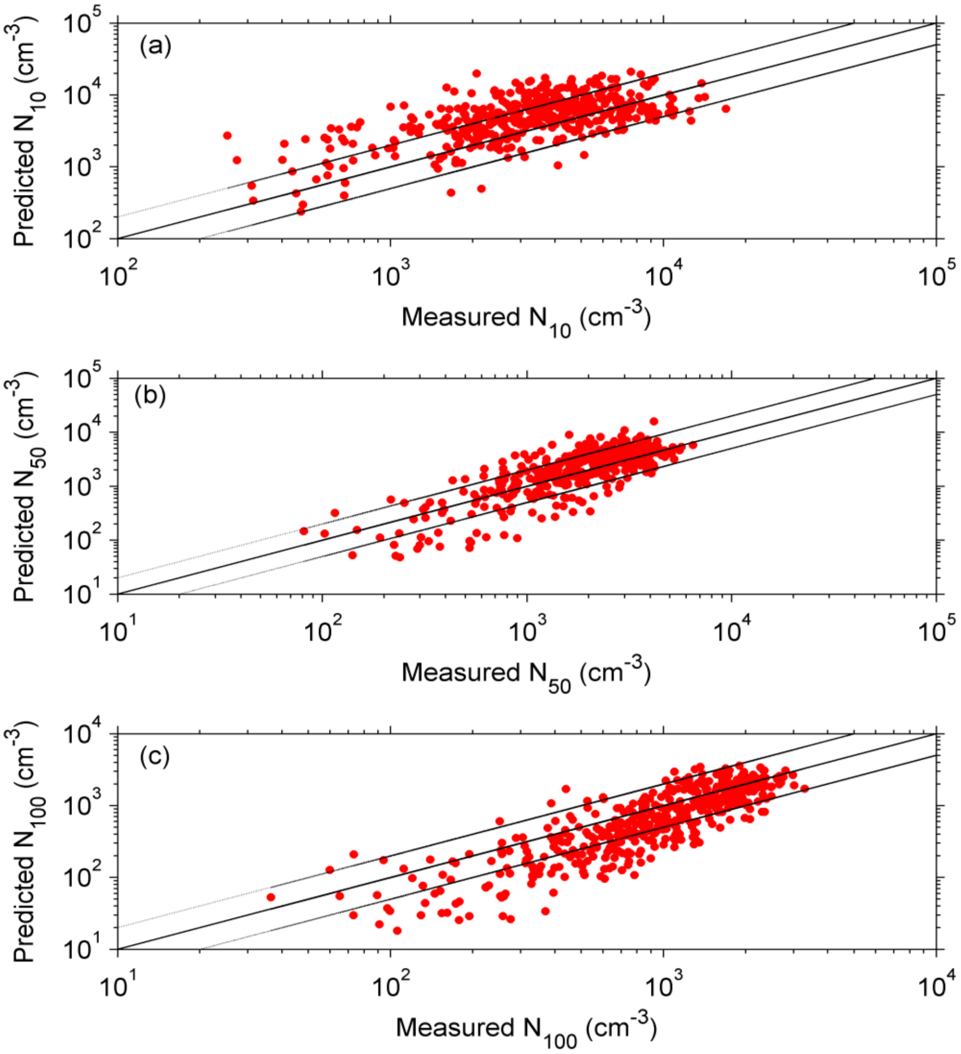


Figure 4: Comparison of predicted versus observed particle number concentrations (cm^{-3}) above 10, 50 and 100 nm from the 16 measurement stations across Europe during 5 June – 8 July 2012. Each point corresponds to a daily average value. Also shown the 1:1, 2:1 and 1:2 lines.

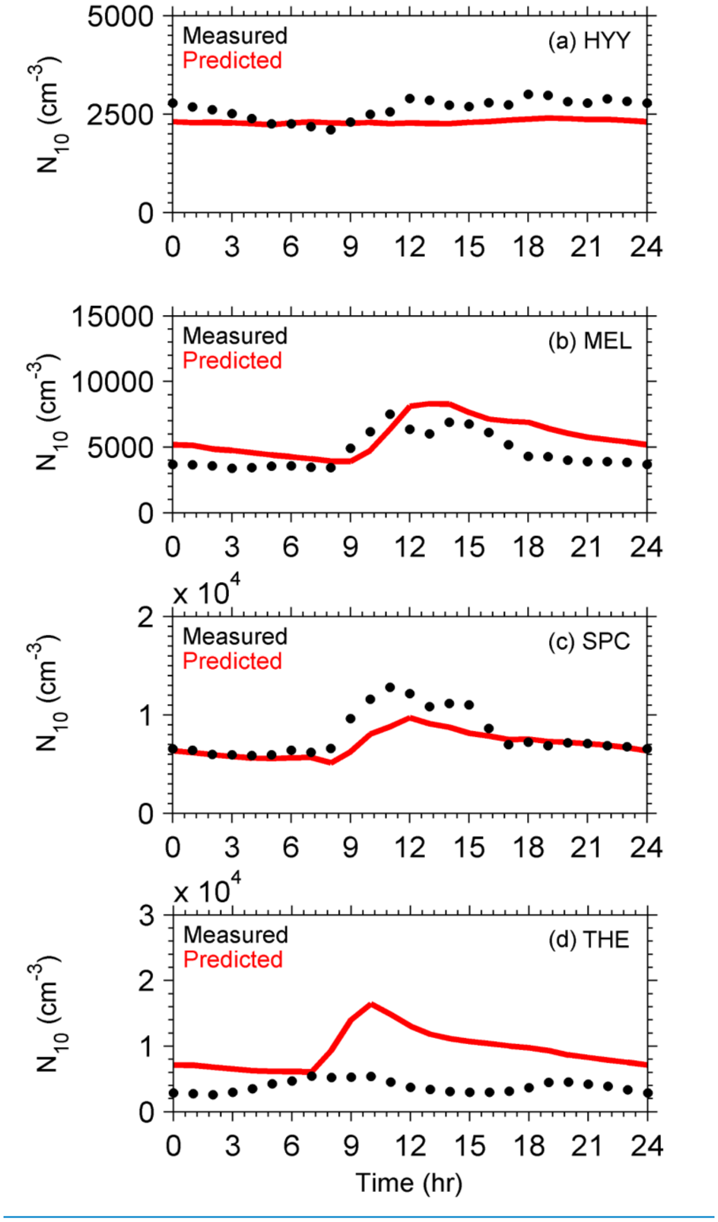


Figure 5: Average diurnal profiles of particle number concentrations (cm^{-3}) above 10 nm in: (a) Hyytiala (Finland); (b) Melpitz (Germany); (c) San Pietro Capofiume (Italy) and (d) Thessaloniki (Greece) during 5 June – 8 July 2012. Red lines correspond to predictions and black symbols to observations.

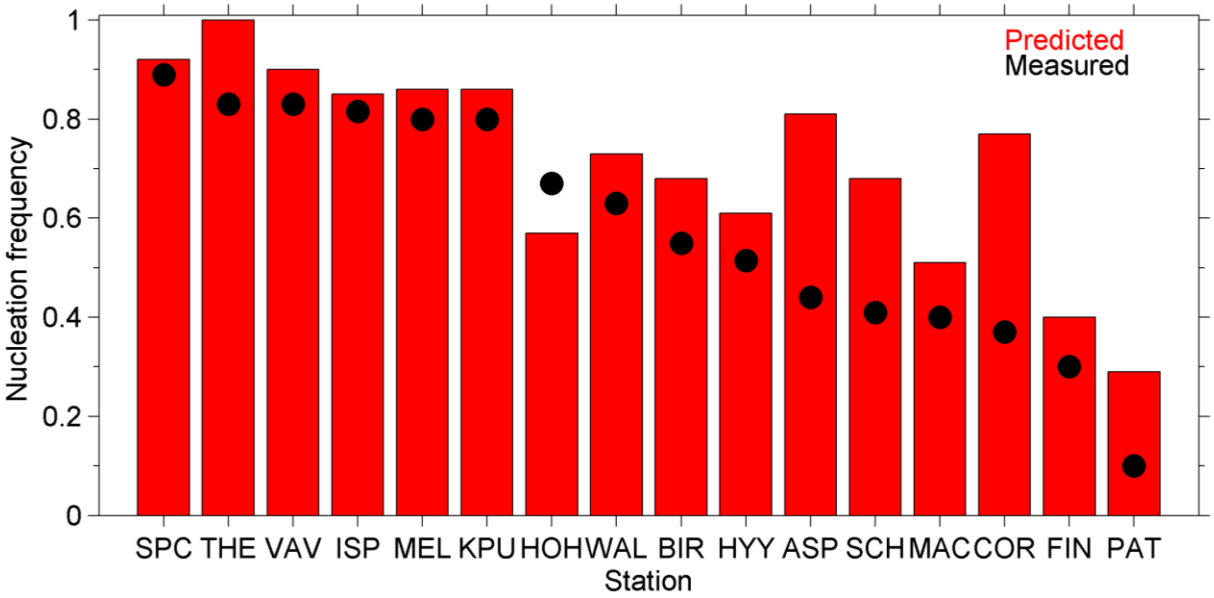


Figure 6: Predicted (red bars) vs. observed (black symbols) nucleation frequencies in the 16 measurement stations during 5 June – 8 July 2012.

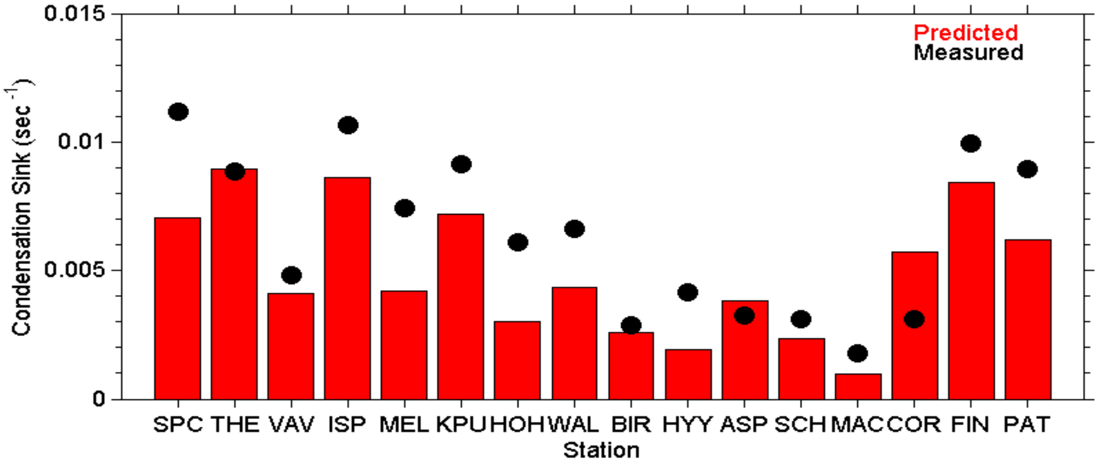


Figure 7: Predicted (red bars) vs. observed (black symbols) condensation sink in the 16 measurement stations during 5 June – 8 July 2012.

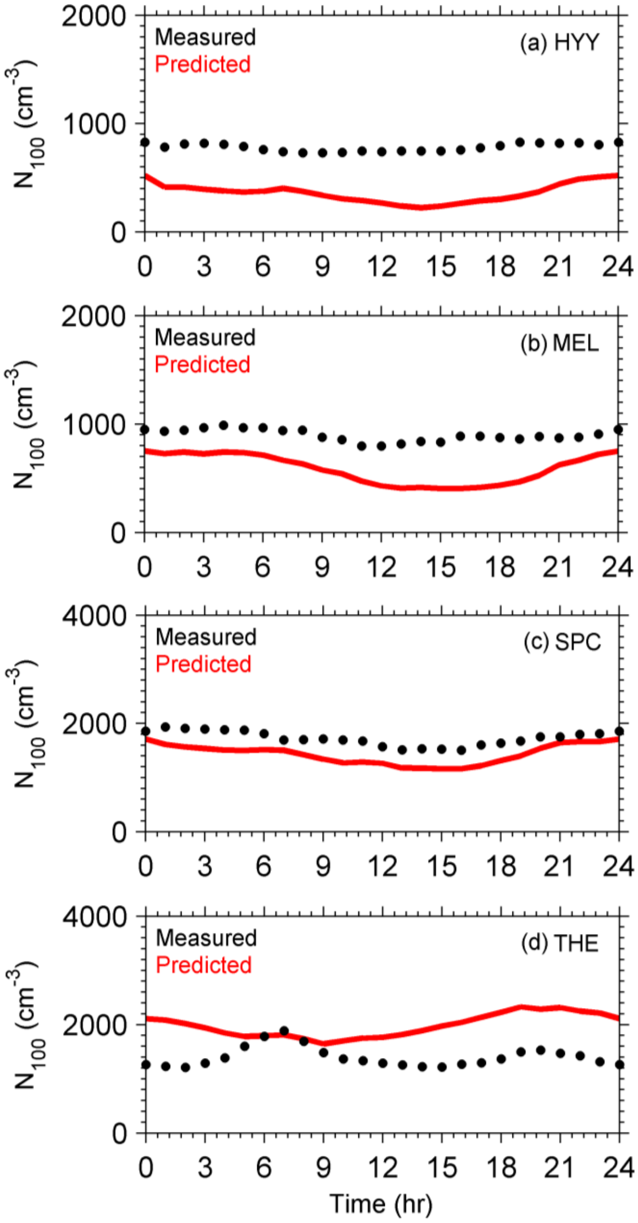
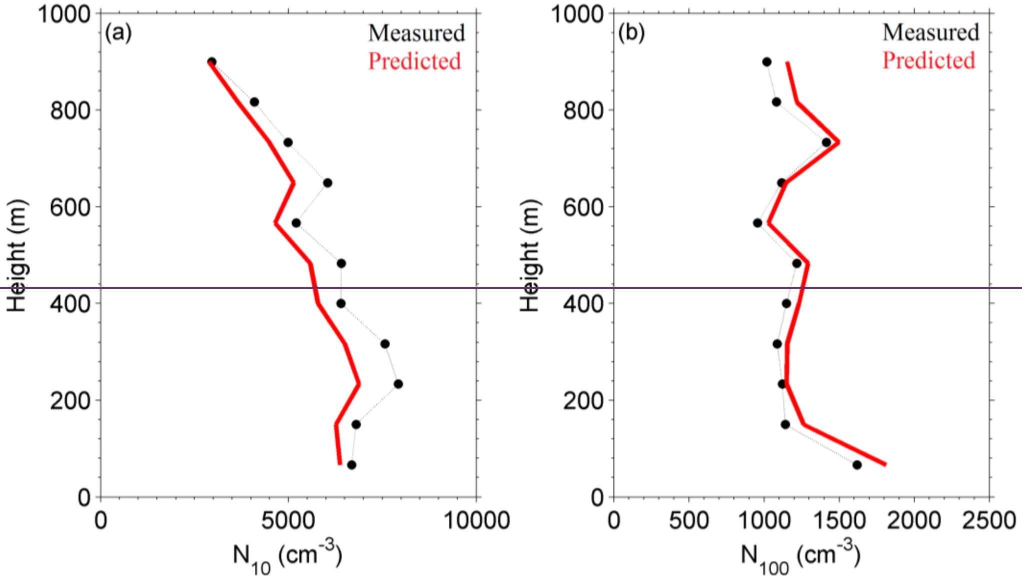


Figure 8: Average diurnal profiles of particle number concentrations (cm^{-3}) above 100 nm: in (a) Hyytiala (Finland); (b) Melpitz (Germany); (c) San Pietro Capofiume (Italy) and (d) Thessaloniki (Greece) ~~(a) Hyytiala (Finland); (b) Corsica (France); (c) and (d) Ispra (Italy)~~ during 5 June – 8 July 2012. Red lines correspond to predictions and black symbols to observations.



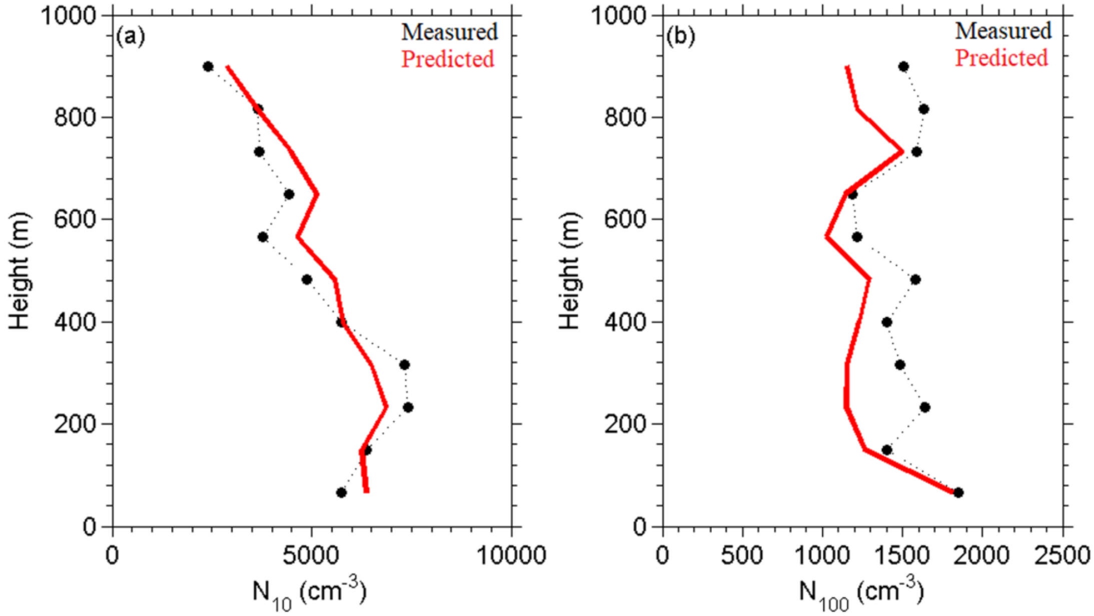


Figure 9: Comparison of predicted PMCAMx-UF (red line) vs. observed (black dots) vertical profiles of averaged particle number concentrations for (a) N_{10} and (b) N_{100} of 25 flights over the Po Valley during the PEGASOS campaign.