Dear editor,

We thank both reviewers for their insightful comments on our work. The point-by-point responses to all issues raised can be found below. We have also revised the manuscript accordingly. The manuscript revised according to the reviewer suggestions can be found at the end of this letter. In the revision process, we have also added one more co-author, Dr. Lars Ahlm, to the revised manuscript. Furthermore, we have corrected a few typos and the map projections in Fig. 5.

On behalf of the co-authors,

Ilona Riipinen

Prof. Jeffrey Pierce (Reviewer #1)

We thank Prof. Pierce for his time as well as the comments and suggestions for our manuscript. Our point-by-point responses for the issues raised can be found below. The direct quotations from the comments are shown in italics, and our responses with normal font type.

This paper documents the implementation of a new nucleation scheme, based on the ACDC model, into a chemical transport model, PMCAMx-UF over Europe. Also, sensitivities to the radiation scheme and natural emissions were performed. The paper is in review for GMD and has a focus on model development rather than science findings. I feel like the scope of the paper is appropriate for the journal, and the overall research approach is good. However, the paper makes claims that I feel are unsubstantiated, lacks quantitative evaluation in many places, and is unclear in some places. Thus, I feel that the paper needs some substantial revisions before publication.

Thank you for these constructive comments. We hope that you find that our point-by-point responses below address the concerns raised. We will naturally revise the manuscript accordingly.

1) *Lack of quantification against measurements: Figure 2 shows comparison of a single simulation (ACDC-RADM-DE. . . not ACDC-TUV-DE, which seemed to be the default for the other figures). While a few numbers are given for the percentage of points that fall within a factor of 2 of measurements, there aren't other statistics for slope and bias (N10 seems to be biased 5-10x too high on average). Further, why aren't statistics given for the other simulations? It would be straightforward to quantitatively compare the simulations against the measurements in this way, and this would show us which assumptions moved the model closer to measurements. Similarly, this can be done for the vertical profiles. N4 are more than 10x too high with the ACDC scheme throughout most (~70%) of the boundary layer, and N10 is more than a factor of 2 too high for half of the the boundary layer. Please give some summary statistics.*

   We originally decided to leave these statistics out since the changes in the model outputs were (as expected) small as compared with previous versions with less sophisticated NPF descriptions. To illustrate this point, the prediction skill metrics of the simulation ACDC-TUV-DE in the original manuscript are now summarized in Table R1 below, which can be compared to the similar results shown in Table 2 of Fountoukis et al., 2012. Table R2 shows the same metrics for the vertical profiles. It is clear that while the model skill in predicting the number concentrations of particles above 50 and 100 nm is similar as in Fountoukis et al. (2012), the concentrations of the smallest particles are clearly over-predicted as compared with the semi-empirical schemes. We will summarize this information for all the simulations in two supplementary tables to the revised manuscript. The reason the simulation ACDC-RADM-DE was shown in Fig. 2 of the original manuscript was to facilitate comparison with Fountoukis et al., 2012 with only the NPF mechanism changing. To avoid confusion, we will show ACDC-TUV-DE in Fig. 2 of the revised manuscript (see Fig. R1 below).

   It should be noted, however, that the main point of the manuscript is not to prove that the ACDC-based nucleation scheme is more successful than the past semi-empirical schemes in producing the present-day number concentrations (to which the semi-empirical schemes have been fitted) but to rather complement and extend the development of the theoretical understanding of atmospheric particle formation. We probably do not need to resort to semi-empirical schemes for much longer. Having a description that has been evaluated against laboratory data and has e.g. temperature- and RH-dependencies in line with the current theoretical understanding gives a new capacity for e.g. extrapolating back to the pre-industrial atmosphere for which we have very little observational data.

	Mean Observed (cm^{-3})	Mean Predicted (cm^{-3})	NMB (%)	NME (%)	Percent within a factor of 2
			Aspvreten		
N_{10}	2200	7420	237	243	33
N_{50}	1400	1270	-9	47	65
N_{100}	580	330	-44	51	57
			Cabauw		
N_{10}	7700	12245	59	73	69
N_{50}	4760	3300	-31	37	81
N_{100}	1925	1040	-46	50	50
			Hyytiala		
N_{10}	2660	5570	110	127	48
N_{50}	1120	1080	-4	61	57
N_{100}	460	240	-48	57	43
			Ispra		
N_{10}	7800	13240	70	93	62
N_{50}	4040	3035	-25	41	71
N_{100}	1725	1035	-40	49	56
			Mace Head		
N_{10}	3200	11620	263	268	30
N_{50}	1825	1890	4	41	74
N_{100}	950	500	-49	54	35
			Melpitz		
N_{10}	9620	20700	115	143	46
N_{50}	4360	3135	-28	37	81
N_{100}	1740	780	-55	56	40
			Vavihill		
N_{10}	3580	11310	216	224	24
N_{50}	1900	2010	6	36	84
N_{100}	785	550	-30	41	60
			Overall		
N_{10}	5100	11540	127	145	44
N_{50}	2600	2170	-18	41	72
N_{100}	1100	610	-45	51	49

Table R1. The statistics of the agreement between the ACDC-RADM-DE and the in-situ observations.

			N_4			N_{10}			$N_{160\text{-}1040}$		
			R	NMB (%)	NME (%)	R	NMB (%)	NME (%)	R	NMB (%)	NME (%)
Falcon	ACDC-TUV-DE	<2km	0.18	1005	1006	0.20	215	224	0.40	-80	80
		2-11 km	0.49	901	930	0.58	249	283	0.77	-74	81
BAe	ACDC-TUV-DE	<2km	0.08	935	939	-	-	-	0.25	-68	70
		2-6.4 km	-0.11	420	529	-	-	-	0.56	-54	78

Table R2. The statistics of the agreement between the ACDC-TUV-DE and the aircraft observations.

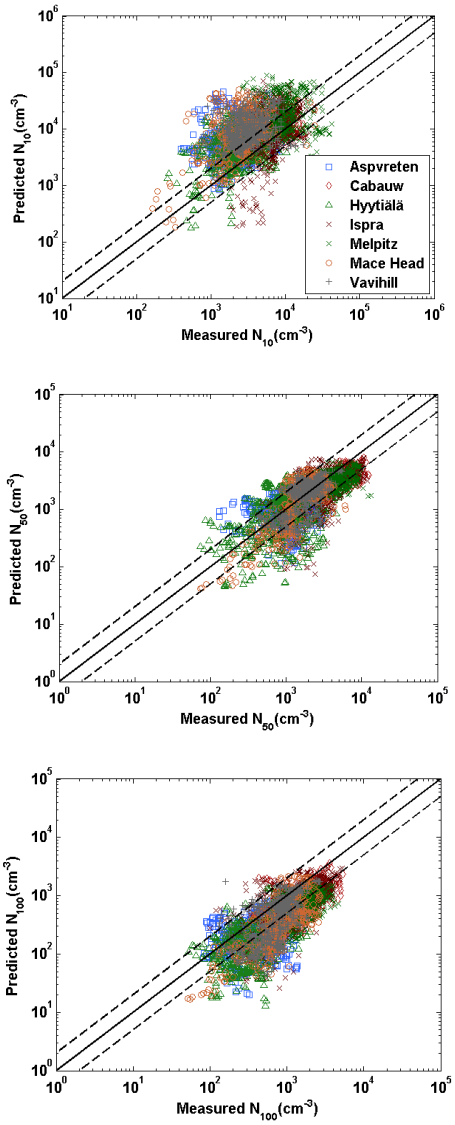

Figure R1. Scatter plots of predicted vs. measured number concentrations of particles larger than 10 (top), 50 (middle) and 100 (bottom) nm in diameter for ACDC-TUV-DE.

2) *Unsubstantiated claims: The paper concludes with, "Overall, we consider our results very promising: a NPF scheme based on first-principles theory and no artificial scaling is shown to be a promising alternative to semi-empirical approaches in the description of particle formation in large scale atmospheric models." There is similar discussion earlier in the conclusions, "reasonable particle concentrations". Obviously, "very promising" and "reasonable" are subjective statements, and different people would view the 10x boundary-layer overprediction for N4 as not "very promising" or "reasonable". We can use Westervelt et al. (2014) for comparison, where they compare simulations using scaled Napari (1E-5 in this case) versus unscaled Napari (also "first principles", and in the unscaled case, without a tuning factor). Table 3 and Figure 2 in Westervelt shows that N10 is only 2x higher in the boundary layer for the unscaled Napari simulation relative to the scaled Napari simulation. . . similar to what was found in the current manuscript in review between ACDC and scaled Napari (1E-6 in the current manuscript). Thus, the overpredictions by the ACDC scheme relative to the scaled Napari in this current manuscript is not unlike comparing scaled and unscaled Napari. I would guess that the nucleation rates predicted by ACDC must be many orders of magnitude faster than scaled Napari in order to get N4 to be 10x too high given all of the microphysical dampening between nucleation rates and N4. While I know that Napari cannot be right for the right reasons, it is very surprising that ACDC does so poorly here considering that it does ok relative to CLOUD measurements (is there a mistake in the lookup tables? are these formation rates per mˆ3 rather than per cmˆ3?). What are the mean nucleation rates predicted at some sites where nucleation rates have been well-characterized (e.g. Hyytiala)?I agree that missing condensible material may be part of the issue here (adding more would likely lower N4 and increase N100). D'Andrea et al. (2013) lowered N10 by about 20-50% over Europe by adding 100 Tg yr-1 globally of non-volatile SOA correlated with anthropogenic CO (see Figure 3). Thus, the N10 bias in the current manuscript may be somewhat fixed by missing condensible material. But regardless, please don't make unsubstantiated claims about the current setup since the ACDC rates seem to be similar to the unscaled Napari scheme that we love to hate.*

   We agree that the wording in the conclusions was too subjective, and we will modify it to the revised manuscript.

   It is important to keep in mind, however, that the implementation of the ACDC-based new particle formation scheme, which included no semi-empirical scaling or fitting, is a significant improvement to earlier new particle formation descriptions and not fundamentally comparable to the "unscaled Napari" scheme. With or without a scaling factor, the Napari scheme is by definition not a first principles NPF scheme: it is a parameterization of data calculated with a classical nucleation theory (CNT) –based approach, which contains several assumptions that are known to be particularly poor for describing the sulfuric acid – ammonia – water system. Some of these shortcomings have been recognized already soon after the publication of the Napari parameterization, and attempts to improve the description by Napari et al. have been ongoing for over a decade (see e.g. Anttila et al. 2005, *Boreal Env. Res.*, 10, 511). Among the most important of additional uncertainties is representing the energetics of the system with bulk thermodynamics e.g. assuming complete proton-transfer which is known not to hold for small clusters and results in drastic errors in the formation free energies and internally inconsistent handling of small stable ammonia-sulfuric acid clusters. These shortcomings cause the parameterization to produce unrealistically high formation rates, which has resulted in the need to scale the rates by five or six orders of magnitude.

   It cannot be concluded from the reported N_{10} or N_4 that the formation rates from the unscaled Napari parameterization would be similar to those of the ACDC-based scheme. Figure R2 below shows formation rates as a function of sulfuric acid concentration, interpolated from the lookup table for conditions

corresponding to those of particle formation experiments in the CLOUD chamber (Almeida et al., *Nature* 2013). The green line corresponds to the experimental conditions of Almeida et al. (2013): T = 278 K, [NH3] = 10 pptv, and RH = 38%. The condensation sink is here set to a representative value of 10^{-3} s^{-1}, corresponding approximately to the sink caused by the chamber walls. However, due to the lack of available quantum chemical data for hydrated clusters at the time of the Almeida et al. (2013) work, the ACDC results presented there correspond to RH = 0%, which have also been added to Fig. R1 for comparison (blue line). Comparison to Fig. 1 in Almeida et al. (2013) shows good agreement with the present lookup table. Increasing the RH to 38% increases the ACDC formation rates. However, there is still around six orders of magnitude difference between the ACDC and unscaled Napari formation rates. It can be seen from Fig. R1 that for sulfuric acid concentrations around 10^6 - 10^7 cm^{-3} the ACDC predictions at 38% range from about 10^{-3} to 1 cm^{-3} s^{-1}, which are comparable to atmospheric observations, although in their lower end. The real atmosphere is of course a much more complex system with many more chemical compounds and processes involved in the particle formation, and sinks of clusters that are not yet well understood. Thus, it is quite understandable that the predictive power of any particle formation scheme for a fixed set of compounds is poorer in the atmosphere than in the CLOUD chamber.

Finally, it should be noted that it is not the purpose of this paper to prove that the parameterizations by Napari et al. are wrong (their disagreement with laboratory data has been well known for a long time), but rather make the positive point that we are finally converging towards a molecular-level understanding of the atmospheric particle formation process involving sulfuric acid, water and ammonia, and that this detailed theoretical knowledge can even be incorporated in regional and global atmospheric models with results that are comparable to the present semi-empirical approaches.

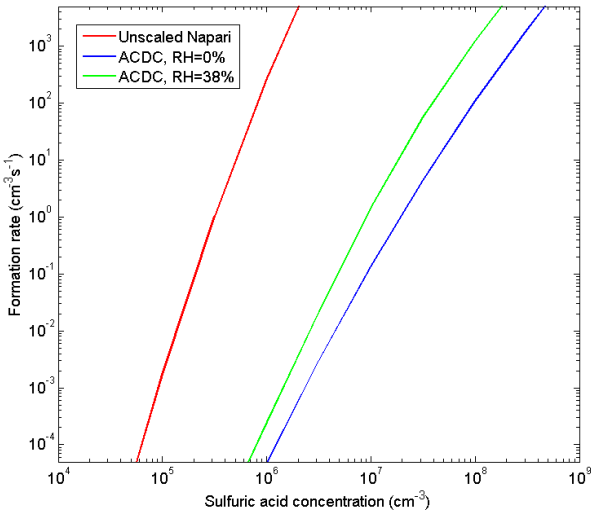

Figure R2. Formation rates of particles with a mobility diameter of ca. 1.3 nm as a function of gas phase sulfuric acid concentration, as predicted by the ACDC model at 0% or 38% relative humidity (RH) (blue and green curves), as well as the original "unscaled" parameterization by Napari et al. (red curve).

Specific comments:

L62: Adams and Seinfeld (2002) did not use the Napari nucleation scheme.

The reviewer is correct. The reference to Adams and Seinfeld will be deleted from the corresponding place in the revised manuscript.

L145: Why not use ACDC with no ammonia for binary nucleation?

This is a good suggestion; using the same framework also for the binary NPF would of course be consistent. However, the small sulfuric acid–water clusters of the binary system are so unstable (Henschel et al., *J. Phys. Chem.* 2016) that we would need to include in the ACDC modeling clusters that are way beyond the size of the current simulation system (of the order of at least tens of molecules) to produce binary formation rates over all the conditions of the look-up table, e.g. at higher temperatures relevant to the boundary layer. As there is no quantum chemical data available for hydrated clusters of more than four sulfuric acid molecules, we decided to instead use the Vehkamäki parameterization for the binary pathway. It has been shown to compare reasonably well with experiments and is also applied in many large-scale models. Given that we do not expect the binary formation pathway to be critical during the summer time at the relatively low altitudes sampled by PMCAMx-UF and the available measurements, we have opted to leave this parameterization as is. Further, in so doing, we isolate the effects of the ternary pathway, which are critical for boundary and mixing layer conditions.

L160-165 (as well as throughout): These lines come out of nowhere but seem important. Were natural sources not included in PMCAMx-UF before? I didn't figure this out until later in the paper. While there is a test simulation turning natural emissions on, there is never much discussion about this in the paper. Why isn't having natural emissions on the default setting in this paper (with a sensitivity simulation with them off). I realize you chose this because you didn't have natural emissions before, but shouldn't the simulations with natural emissions be expected to better simulate the size distribution? Please give attention to the text and discussion of natural emissions throughout to ensure that it is clear.

This is the first time that the natural particle emissions (these consist of biogenic, marine and wildfire sources) have been included in PMCAMx-UF in Europe for the period of May 2008. However, our main focus in this study is assessment of the implementation of the ACDC-based NPF-scheme. To do this, we decided to keep the emission the same as in the previous study by Fountoukis et al (2012) which we refer to as "Default Emissions", which did not include natural emissions. Including the natural emissions resulted in better agreement with the observations as compared with the default case, especially for the small sizes. The NMB for the surface level values for ACDC-TUV-NE are 113 % for N_4, -9% for N_{10}, -45% for N_{100}. For ACDC-TUV-DE the corresponding numbers are 126%, -18% and -45%. The trend is similar for NME, being 131% (N_4), 41% (N_{10}), 52% (N_{100}) for ACDC-TUV-NE and 145% (N_4), 41% (N_{10}), 51% (N_{100}) for ACDC-TUV-DE. The corresponding comparison for the vertical profiles is given in table R3. We summarize this information (with quantification of the improvements given in two new supplementary tables) to the revised manuscript and do our best to ensure the clarity in the revised text.

			N_4			N_{10}			$N_{160\text{-}1040}$		
			R	NMB (%)	NME (%)	R	NMB (%)	NME (%)	R	NMB (%)	NME (%)
Falcon	ACDC-TUV-DE	<2km	0.18	1005	1006	0.20	215	224	0.40	-80	80
		2-11 km	0.49	901	930	0.58	249	283	0.77	-74	81
	ACDC-TUV-NE	<2km	0.17	905	906	0.21	173	184	0.41	-77	77
		2-11 km	0.48	748	779	0.56	207	243	0.84	-66	74
BAe	ACDC-TUV-DE	<2km	0.08	935	939	-	-	-	0.25	-68	70
		2-6.4 km	-0.11	420	529	-	-	-	0.56	-54	78
	ACDC-TUV-NE	<2km	0.16	808	812	-	-	-	0.27	-62	65
		2-6.4 km	-0.07	306	418	-	-	-	0.52	-44	78

Table R3. The statistics of the agreement between the ACDC-TUV-DE and ACDC-TUV-NE, and the aircraft observations.

*L246-247 (and this entire paragraph): Why is TUV *not* called for cells with clouds thinner than optical depth 5? Don't you want to consider radiative transfer here? Earlier you discuss wanting to have the effects of simulated aerosols on photolysis rates. . . so wouldn't you want this for clear-sky or thin-cloud conditions? Confusing.*

This has been a typo. The TUV module is called for optical depth greater than zero. Optical depths smaller than 5 is considered as clear-sky condition with the default cloud-adjustment scheme (i.e. RADM). The text will be modified in the revised manuscript.

L319: "spatial concentration". Do you mean the relative spatial distribution of concentrations? Since you don't show figures for these other simulations, would it make sense to quantify this in some way, e.g. a correlation coefficient between simulations?

Yes, this referred to the spatial distribution of concentrations simulated by ACDC-TUV-DE as compared with that simulated by Napari-RADM-DE. This will be modified for clarity in the revised manuscript. The correlation coefficients for monthly average concentrations throughout the domain between the different simulation cases and the ACDC-TUV-DE as the base case are generally high, ranging from 0.827 (for N_{tot} for Napari-TUV-DE vs. the base case) to 0.999 (for N_{tot} and N_{100} for ACDC-RADM-DE vs. the base case). It is clear that the simulated

concentrations are very similar, with largest differences observed for the smallest particles if the Napari scheme is used. We will summarize these results in the revised manuscript.

Figures: Why is the default simulation shown in figures sometimes ACDC-TUV-DE (most figures) and sometimes ACDC-RADM-DE (Figure 2)?

This presentation was chosen to directly compare the Fig. 2 with Fig. 3 in Fountoukis et al. (2012) to isolate the effect of the NPF scheme. To avoid confusion, we will show results from ACDC-TUV-DE in Fig. 2 of the revised manuscript.

Figures 3 and 4: Why is the height axis log scale? Do we want to focus mostly on the boundary layer?

The vertical resolution of model is finer in lower levels (see Fig. S1 for the model layer resolution). We have used log-scale to see the variation better.

L377-379: "somewhat closer"? Within 1.5x for scaled Napari vs. outside of 10x for ACDC for most of the boundary layer?! Please be quantitative and avoid subjective judgement.

This is a very good point, the statement was unsubstantiated. We will clarify this in the revised manuscript, basing our statements on the statistics given in the supporting information for the revised manuscript (see Table R1 for an example).

General grammar comment: Adverbs modifying an adjective do not need a hyphen (and should not have a hyphen), e.g. "vertically resolved", "chemically resolved", "newly formed", "hourly averaged". There is no ambiguity in the meaning with or without a hyphen. These should be removed. On the other hand, it is extremely useful to hyphenate joint adjectives. For example, "Aitken-mode particles" should have a hyphen as they are particles in the "Aitken mode". There are not "mode particles" that are "Aitken". Same with "chemical-transport models". They are not "transport models" that are "chemical". How about "large scale atmospheric models"? What is a "scale atmospheric model", and what is so large about it? It is commonplace, unfortunately in my opinion, to omit hyphens when the writer thinks the meaning is unambiguous. However, if a writer never hyphenates joint adjectives, we get into trouble when the writer writes, "slow moving van". Is it a "moving van" that is going slow? Or is it a regular van that is "slow moving"? If a writer establishes that they will hyphenate whenever it is appropriate, we would know that "slow moving van" means a "moving van" that is going slow (else they would have written "slow-moving van").

Thank you for this advice on grammar. We will remove hyphens from adverbs modifying an adjective, and make the usage of e.g. large-scale or Aitken-mode uniform throughout the manuscript. We have also consulted two native English speakers (one with American one with British English as the mother tongue) on the use of hyphenation for joint adjectives.

Reviewer #2:

This manuscript presents the implementation of a new ternary H2SO4-H2O-NH3 parameterization, into the PMCAMx-UF model. The authors explore the ability of the model to reproduce observed number concentration during May 2008, when the intensive observation period of EUCAARI project took place. Apart from the testing of the new parameterization, sensitivity tests using the scaled Napari parameterization and sensitivity to the radiation scheme and natural emissions were performed. The topic and overall approach fits with GMD; therefore, I am in favor of accepting this work for publication in GMD after the authors have addressed the issues summarized below.

We thank the reviewer for his /her encouraging comments. Below you can find our point-by-point responses to all the issues raised.

While several sensitivity tests are done, the paper lacks a proper statistics for each test. Figure 2 shows the results coming from ACDC-RADM-DE sensitivity study, however no information is given for the other studies presented in Table 1. It would be nice to see some numbers (r, over/under estimation factor, bias), to endorse the statement "Overall, we consider our results very promising: a NPF scheme based on first-principles theory and no artificial scaling is shown to be a promising alternative to semi-empirical approaches in the description of particle formation in large scale atmospheric models."

This issue was also raised by Prof. Pierce in his review. Table R1 below shows an example statistics for the results presented in Fig. 2 of the original manuscript. We have calculated similar statistics for all simulations and will add them as supplementary information and summarize them in the revised manuscript.

	Mean Observed (cm^{-3})	Mean Predicted (cm^{-3})	NMB (%)	NME (%)	Percent within a factor of 2
		Aspvreten			
N_{10}	2200	7420	237	243	33
N_{50}	1400	1270	-9	47	65
N_{100}	580	330	-44	51	57
		Cabauw			
N_{10}	7700	12245	59	73	69
N_{50}	4760	3300	-31	37	81
N_{100}	1925	1040	-46	50	50
		Hyytiala			
N_{10}	2660	5570	110	127	48
N_{50}	1120	1080	-4	61	57
N_{100}	460	240	-48	57	43
		Ispra			
N_{10}	7800	13240	70	93	62
N_{50}	4040	3035	-25	41	71
N_{100}	1725	1035	-40	49	56
		Mace Head			
N_{10}	3200	11620	263	268	30
N_{50}	1825	1890	4	41	74
N_{100}	950	500	-49	54	35
		Melpitz			
N_{10}	9620	20700	115	143	46
N_{50}	4360	3135	-28	37	81
N_{100}	1740	780	-55	56	40
		Vavihill			
N_{10}	3580	11310	216	224	24
N_{50}	1900	2010	6	36	84
N_{100}	785	550	-30	41	60
		Overall			
N_{10}	5100	11540	127	145	44
N_{50}	2600	2170	-18	41	72
N_{100}	1100	610	-45	51	49

Table R1. The statistics of the agreement between the ACDC-RADM-DE and the in-situ observations.

L82: Should be "Matsui et al., 2011, 2013", not "Matsui et al., 2011a, 2013c".

Thank you for pointing this out, we will modify this in a revised version of the manuscript.

L88-90: Matsui et al., 2013 study, already mentioned by the authors, have also assessed the ability of WRF-Chem to reproduce the vertical profile of observed Aitken particles for South Asia.

Thank you for pointing this out, we will modify the manuscript accordingly.

L133-134: Should be "Yu et al., 2006", not "Yu et al., 2006a".

Thank you for pointing this out, we will correct this in the revised manuscript.

L210-213: I assume that if the H2SO4, NH3, RH, temperature and condensation sink are not falling into the mentioned range, the Vehkamaki et al., 2002, parameterization is applied. Is that right?

The Vehkamaki et al. (2002) parameterization is called as long as the H_2SO_4 concentration is greater than 10^4 cm^{-3}. As mentioned in section 2.1, the ternary and binary pathways are operating simultaneously. The ternary pathway is called only if the vapor concentrations of both H_2SO_4 and NH_3 are above the lower limit of the lookup table. At lower concentrations the formation rate is practically zero, as the boundaries of the lookup table are chosen so that they should cover the atmospherically relevant range. When the ternary pathway is called, the H_2SO_4, NH_3, RH, temperature and condensation sink are limited to the bounds of the ACDC lookup table if any of the parameters fall outside of the boundaries. Although we did not count the frequency of any exceedances above or below the lookup table bounds, we are confident that these exceedances are few since the bounds are so large compared to atmospherically relevant conditions. Furthermore, even if e.g. the vapor concentrations exceed the upper limits, the rate is likely already converged to a plateau, making it safe to use the values at the limits. We will clarify this in the revised manuscript.

L330-336: The authors show the scatter plots of predicted PNC using ACDC-RADMDE simulation vs observed PNC in several size ranges. Yet, at line 303 they state that ACDC-TUV-DE is the baseline simulation. Do they have any particular reason not to present the results coming from the default simulation? As can be seen in Table 1 the differences between the ACDC-RADM-DE and ACDC-TUV-DE simulations are minors. Furthermore, they use the ACDC-TUV-DE simulation results for the following plots. A little bit confusing.

The reason for presenting ACDC-RADM-DE in Fig. 2 of the original manuscript was to show a direct comparison with Fig. 3 of Foutoukis et al. (2012) with the only difference being the different NPF scheme. To avoid confusion, we will show results from ACDC-TUV-DE in Fig. 2 of the revised manuscript.

L373-379: Could you give an explanation why N4 concentration increases in the upper boundary layer for ACDC-TUV-DE simulation? May you could present the particle formation rates for the ACDC-TUV-DE and Napari-TUV-DE simulation. Also, could you give an overestimation factor?

This is most likely due to the simultaneous drop in temperature and concentrations of larger particles (i.e. the coagulation sink for the newly-formed particles), which enhance both the particle formation rate and their survival. In fact, the temperature dependence is one of the key differences between the new ACDC-based NPF representation and the previous semi-empirical approaches: while the latter do not usually have an explicit temperature dependence of the formation rates, the former does. The ACDC-TUV-DE simulations over-predict N_4 with a factor of 8-10 below 2 km and 4-9 above 2 km (see also responses to Prof. Pierce). We will revise the manuscript accordingly to clarify these issues.

L384-389: An index of agreement will sustain "the scaled Napari NPF scheme agrees reasonably well with the observations throughout the atmospheric column" and "reasonably well" statements.

We agree that these are subjective statements that need to be backed up by quantitative data. As discussed above, we will add two supplementary tables (showing the NMB, NME and correlation coefficients for all the simulations vs. in-situ and aircraft data, respectively) and summarize these statistics in the text. We have also calculated indexes of agreement for all our data (surface level and aircraft). For the Napari-TUV-DE simulations these values range from about 0.2 to 0.7 for all the size ranges throughout the atmospheric column, while for the ACDC-TUV-DE shows a large difference between the in-situ (0.3-0.6 for all sizes) and aircraft (0.02-0.7 for all sizes, with the poorest agreement for the smallest particles) data sets. We hope the inclusion of more statistical metrics will now do the job and will also go through the revised manuscript to remove all unnecessary subjective statements.

L433_435: The following sentence for a more scientifically sound expression should be rephrased: "We believe this is the first time that reasonable particle concentrations have been produced in a large-scale atmospheric a

Good point. We will modify the revised manuscript accordingly.

The authors should be more restrictive in using "reasonably well", "are somewhat overpredicted by the ACDC-based NPF scheme", "very promising" statements due to the fact that the lack of statistics throughout the paper does not sustain their claims.

Besides adding the aforementioned more quantitative analysis to support these statements, we will limit the usage of the phrases in question in the revised manuscript.

Implementation of state-of-the-art ternary new particle formation scheme to the regional chemical transport model PMCAMx-UF in Europe

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Abstract

The particle formation scheme within PMCAMx-UF, a three dimensional chemical transport model, was updated with particle formation rates for the ternary H_2SO_4-NH_3-H_2O pathway simulated by the Atmospheric Cluster Dynamics Code (ACDC) using quantum chemical input data. The model was applied over Europe for May 2008, during which the EUCAARI-LONGREX campaign was carried out providing aircraft vertical profiles of aerosol number concentrations. The updated model reproduces the observed number concentrations of particles larger than

4 nm within one order of magnitude throughout the atmospheric column. This agreement is encouraging considering the fact that no semi-empirical fitting was needed to obtain realistic particle formation rates. The cloud adjustment scheme for modifying the photolysis rate profiles within PMCAMx-UF was also updated with the TUV (Tropospheric Ultraviolet and Visible) radiative transfer model. Results show that although the effect of the new cloud adjustment scheme on total number concentrations is small, enhanced new particle formation is predicted near cloudy regions. This is due to the enhanced radiation above and in the vicinity of the clouds, which in turn leads to higher production of sulfuric acid. The sensitivity of the results to including emissions from natural sources is also discussed.

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1 Introduction

Formation of new particles from atmospheric vapors (new particle formation, NPF) is potentially an important source of particulate matter in the atmosphere, especially in the ultrafine (<100 nm in diameter) size range (Kulmala et al., 2004; Merikanto et al., 2009; Jung et al., 2010; Fountoukis et al., 2012; Kerminen et al., 2012; Fuzzi et al, 2015). In the past, in modeling studies on the role of in-situ NPF as a particle source, particle formation has been represented with various parameterizations including binary (Vehkamäki et al., 2002) or ternary (Napari et al., 2002) nucleation based on the classical nucleation theory (CNT), semi-empirical activation (Kulmala et al., 2006), kinetic (McMurry, 1980) or organic-enhanced (Paasonen et al., 2010) NPF and/or ion-mediated nucleation (Yu and Luo, 2009). These parameterizations have generally assumed sulfuric acid (H_2SO_4), water (H_2O), ammonia (NH_3), or different organic species as the compounds forming the new particles. The activation, kinetic and organic-enhanced mechanisms are semi-empirical, based on the observed dependence of particle formation rates on concentrations of sulfuric acid and/or organic vapors (Sihto et al., 2006; Paasonen et al., 2010). The advantage of such methods is that they are simple and produce nucleation rates of the same order as those observed. However, as they are fit to specific experiments usually at ground level, they are most reliable at locations and conditions similar to those at which the data has been obtained. The ternary H_2SO_4-H_2O-NH_3 parameterization by Napari et al. (2002) has been used with some success (Jung et al., 2008; Jung et al., 2010; Fountoukis et al., 2012; Westervelt et al., 2014), but with quite drastic correction factors necessary to reproduce ambient particle number concentrations. In many previous studies (Spracklen et al., 2006; Makkonen et al., 2009; Yu et al., 2010) the binary H_2SO_4-H_2O nucleation has been assumed to dominate in the upper atmosphere and be negligible at lower altitudes, and it has often been superimposed with one of the other mechanisms.

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Sulfuric acid, water and ammonia have long been established as important molecules forming new particles in the atmosphere (Korhonen et al., 1999; Kulmala et al., 2000; Laaksonen et al., 2008). However, standard theoretical descriptions of the ternary H_2SO_4-H_2O-NH_3 particle formation pathway have not been able to reproduce measured

particle formation rates – hence the need to resort to semi-empirical parameterizations and correction factors to describe this process in atmospheric models. Recent experimental (Kirkby et al., 2011; Almeida et al., 2013; Jen et al., 2014) and computational developments have, however, changed this picture drastically. Flexible computational models (such as the Atmospheric Cluster Dynamics Code, ACDC, Olenius et al., 2013) which simulate the kinetics of a population of molecular clusters combined with cluster free energies calculated from first-principles methods, can now reproduce laboratory observations of particle formation rates in H_2SO_4-NH_3 as well as H_2SO_4-amine systems with reasonable accuracy (Almeida et al., 2013), without the need for empirical scaling of the predicted particle formation rate.

Predictions of particle number concentration from regional-scale chemical transport models have been evaluated typically with data from ground-level observations (Jung et al., 2008; Matsui et al., 2011, 2013; Fountoukis et al., 2012; Cui et al., 2014; Lupascu et al., 2015). Meanwhile, there is much to gain from assessing the model against vertically resolved particle number observations, as many of the uncertainties in the model relate to particle scavenging, by hydrometeors as well as other particles, and mixing of air masses. The possible biases introduced from parameterizing new particle formation rates with ground-level data makes it all the more imperative to evaluate and constrain models with observations taken at altitude. Recent studies (Reddington et al., 2011; Matsui et al., 2013; Lupascu et al., 2015) have begun assessing global- and regional-scale models in this way against data from European, Asian and US field campaigns involving aircraft measurements. Furthermore, it is worthwhile to explore the vertical variability in chemical and environmental precursors to NPF (e.g. H_2SO_4, NH_3, *T*, RH, etc.) and particle number concentrations.

In this work we describe the implementation of a H_2SO_4-H_2O-NH_3 new particle formation scheme based on the output of the ACDC model to the regional chemical transport model PMCAMx-UF (Jung et al., 2010, Fountoukis et al., 2012). We test the new scheme by simulating the evolution of atmospheric gas-phase and aerosol particle concentrations during May 2008 in Europe. We evaluate the model against ground-based and airborne observations of aerosol particle number size distributions during the simulated period. Furthermore, we implement an updated radiative transfer scheme TUV (Tropospheric Ultraviolet and Visible radiative transfer model; Madronich, 2002) for PMCAMx-UF and discuss its implications for predictions of NPF and particle number concentrations in the European domain.

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2 Methods

2.1 PMCAMx-UF model description

PMCAMx-UF is a three-dimensional regional chemical transport model that simulates both the size-dependent particle number and chemically resolved mass concentrations (Jung et al. 2010). PMCAMx-UF utilizes the framework of the air quality model PMCAMx (Gaydos et al., 2007, Karydis et al., 2007), where the description of vertical and horizontal advection and dispersion, wet and dry deposition, and gas-phase chemistry are based on the CAMx air quality model, and the variable size-resolution model of Fahey and Pandis (2001) is used for aqueous-phase chemistry. To treat the aerosol microphysics, including NPF, condensation and coagulation, PMCAMx-UF uses the Dynamic Model for Aerosol Nucleation (DMAN) module by Jung et al. (2006). DMAN uses the Two-Moment Aerosol Sectional (TOMAS) algorithm (Adams and Seinfeld, 2002) to track the aerosol number and mass distributions. DMAN divides the aerosol particles into 41 logarithmically-spaced size bins between 0.8 nm and 10 μm.

The aerosol species modeled in PMCAMx-UF include sulfate, ammonium, water, elemental carbon, crustal material, chloride, sodium, nitrate, primary organic aerosol and four secondary organic aerosol surrogate compounds. The version of TOMAS used in the model applied here tracks explicitly the mass transfer of sulfate and ammonium while that of water is treated assuming equilibrium. Within the DMAN aerosol microphysics module the remaining compounds are represented by inert surrogate species. The pseudo-steady-state approximation method (Pierce and Adams, 2009), which assumes steady-state concentration for sulfuric acid, is used for the calculation of NPF and sulfuric acid condensation rates. The condensation of ammonia is calculated independently following the approach described in Jung et al. (2006).

New particle formation rates in the standard version of PMCAMx-UF have been calculated in previous studies using a scaled version of the ternary H_2SO_4-NH_3-H_2O parametrization by Napari et al. (2002), hereafter referred to as the "scaled" Napari parameterization. The original Napari parameterization is based on predictions of the CNT assuming that the energetics of the molecular clusters follow bulk thermodynamics. While it has been shown to perform better than a range of other nucleation parameterizations in predicting the occurrence of new particle formation events (Jung et al. 2008), it is also known to overpredict ultrafine particle number concentrations (Gaydos et al., 2005; Yu et al., 2006; Jung et al., 2006; Merikanto et al., 2007b; Zhang et al., 2010). Thus a semi-empirical correction factor of 10^{-6} has been applied previously in PMCAMx-UF to scale the formation rates produced by the Napari parameterization and better match the observations (Jung et al., 2010; Fountoukis et al., 2012; Ahlm et al., 2013).

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Encouraged by the good agreement between particle formation rates predicted by the ACDC model and the state-of-the-art experimental data (Almeida et al., 2013), we have updated the particle formation scheme within PMCAMx-UF with ACDC-based particle formation rates for the NH_3-H_2SO_4-H_2O (see Sect. 2.2 for details and the Results section for comparison to the scaled Napari parameterization). In addition to applying the ternary H_2SO_4-NH_3- H_2O NPF scheme, we also include a binary H_2SO_4-H_2O NPF pathway. This pathway is operating simultaneously with the ternary pathway and is based on the Vehkamäki et al. (2002) CNT-parameterization.

PMCAMx-UF was applied for the period of May 2008 for the European domain which consists of a 5400 × 5832 km^2 region with a 36 × 36 km^2 grid resolution and 14 vertical layers reaching an altitude of approximately 20 km. The PMCAMx-UF output data are hourly averaged. The meteorological inputs, described in detail in Fountoukis et al. (2011; 2012), were created using the Weather Research and Forecasting model version 2 (Skamarock et al., 2005) and include horizontal wind components, vertical dispersion coefficients, temperature, pressure, water vapor mixing ratios, cloud optical depths and rainfall rates. Hourly gridded emissions include anthropogenic emission rates of primary particulate matter and gases. For the particle emissions the Pan-European anthropogenic Particle Number Emission Inventory (Denier van der Gon et al., 2009; Kulmala et al., 2011) and the Pan-European Carbonaceous Aerosol Inventory (Kulmala et al., 2011) were used. The anthropogenic gas emissions include both land emissions from the GEMS data set (Visschedijk et al., 2007) and international shipping emissions. These emission inputs are the same as have been used previously for the May 2008 period in PMCAMx-UF (in Fountoukis et al., 2012; Ahlm et al., 2013), and thus in order to enable comparison to the previous works these inputs are used in all of the base model runs of the present paper. To assess how much the particle number concentrations are affected by emissions from natural sources we have performed simulations with and without these emissions. The natural emissions include both particulate matter and gases and combine three different datasets: emissions from ecosystems based on the MEGAN model (Guenther et al., 2006), marine emissions based on the model of O'Dowd et al. (2008), and wildfire emissions (Sofiev et al., 2008a, b).

2.2 Improved treatment of the ternary NPF pathway

The ternary H_2SO_4–NH_3–H_2O particle formation rate at approximately 1.3 nm in mobility diameter was calculated with the Atmospheric Cluster Dynamics Code (ACDC; Olenius et al., 2013; Almeida et al., 2013; Henschel et al., 2015). ACDC simulates the dynamics of a population of molecular clusters by numerically solving the cluster birth–death equations. Instead of considering only collisions and evaporations of single vapor molecules, an often-used assumption applied in the CNT framework, ACDC allows all possible collision and fragmentation processes within the cluster population. As input the ACDC code needs the corresponding rate constants, of which the most challenging to assess are the cluster evaporation rates, generally calculated from the free energies of formation of the clusters. The evaporation rates play a significant role in determining the number concentration and

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consequently the formation rate of small particles. The liquid drop model, commonly used in CNT to calculate the free energies of cluster formation, is based on macroscopic thermodynamics and is thus not expected to give reliable results for small clusters (Merikanto et al., 2007a). Among the most important of additional uncertainties is representing the energetics of the system with bulk thermodynamics e.g. assuming complete proton-transfer which is known not to hold for small clusters and results in drastic errors in the formation free energies and internally inconsistent handling of small stable ammonia-sulfuric acid clusters. The most accurate theoretical method to compute the free energies of clusters consisting of specific molecules is quantum chemistry. This modeling approach is able to reproduce the general trends in cluster formation, and leads to, thus far, the best quantitative agreement between observations and modeling with no fitting parameters (Almeida et al., 2013). Having a description that has been evaluated against laboratory data and has e.g. temperature- and RH-dependencies in line with the current theoretical understanding gives a new capacity for e.g. extrapolating back to the pre-industrial atmosphere for which we have very little observational data (see e.g. Carslaw et al., 2013; Kirkby et al., 2016).

In the ACDC simulations of this work, hard-sphere collision rates were used for the collision rate coefficients, and the evaporation rate coefficients were calculated from the Gibbs free energies of formation of the clusters computed with quantum chemical methods at the B3LYP/CBSB7//RICC2/aug-cc-pV(T+d)Z level (Ortega et al., 2012; Henschel et al., 2014). This level of theory has been tested against higher level methods and was shown to give reliable cluster formation free energies at an affordable computational cost. The simulation included clusters containing up to three H_2SO_4 and three NH_3 molecules, hydrated by up to four or five water molecules. Sulfuric acid and ammonia were explicitly treated in the simulation, and water was implicitly included by assuming that the clusters are in equilibrium with respect to water and by using hydrate averaged collision and evaporation rates. An external sink term corresponding to scavenging by larger particles was used for all the clusters. The steady-state particle formation rate was obtained as the flux of clusters growing out of the simulation system considering boundary conditions based on cluster stability. Details of the simulated ternary H_2SO_4–NH_3–H_2O system can be found in Henschel et al. (2015).

The ACDC results were implemented in the PMCAMx-UF framework as a look-up table consisting of a comprehensive set of particle formation rates computed at different values of H_2SO_4 and NH_3 concentrations, temperature, RH, and coagulational loss rate due to scavenging by the population of larger particles (described by the condensation sink, see e.g. Dal Maso et al., 2002). The formation rate data produced by theoretical models have been traditionally fitted to a multivariable functional form (Napari et al, 2002; Merikanto et al., 2007b), with the resulting parameterization then utilized by large-scale models. However, finding a suitable functional form to cover satisfactorily the whole parameter space becomes increasingly difficult with increasing number of input

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parameters, with increasing number of species participating in NPF, and with the tendency of formation rates to exhibit rapid, step function–like changes with respect to one or more parameters. Thus interpolating from a look-up table provides formation rates that are more closely in line with the original theoretical model, with a relatively minor additional computational cost. The parameter space encompasses sulfuric acid concentration between $1.00 \cdot 10^4$ and $3.16 \cdot 10^9$ molecules cm^{-3}, ammonia concentration between 10^6 and 10^{11} molecules cm^{-3}, relative humidity between 0 and 100 %, temperature between 180 and 320 K and condensation sink between 10^{-5} and 10^{-1} s^{-1}. These conditions bound the environmental and chemical conditions predicted by typical PMCAMx-UF runs for Europe in May. PMCAMx-UF uses multilinear interpolation to extract formation rates from the look-up table. The newly formed particles are added to the second lowest size bin of PMCAMx-UF, corresponding to the size for which the ACDC formation rates were calculated. This approach provides PMCAMx-UF with formation rates that are based on the full kinetic treatment of the cluster population.

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2.3 Radiative transfer and photolysis rates

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Aerosols and clouds can enhance or reduce photolysis of relevant gas-phase chemical species in the atmosphere by reflecting, scattering, or absorbing solar radiation. Modifications of photolysis rates via this interaction lead to changes in the production rate of sulfuric acid, which lead directly to changes in the new particle formation rates. Previous versions of PMCAMx-UF employed a parameterization originally used by the Regional Acid Deposition Model (RADM; Chang et al., 1987) to treat the modification of photolysis rates due to cloud presence. This approach required the cloud optical depth from the meteorological input data and the solar zenith angle in order to calculate the time- and layer-dependent adjustment factors for the photolysis rates. This method, however, did not use aerosol concentrations predicted online by the transport model. Instead, a reference aerosol profile was used for every time step and column of grid cells.

To more realistically treat the effects of clouds on the photolysis rates profile of the atmospheric column, we updated the online approach in PMCAMx-UF to a streamlined form of the two-stream radiative transfer module, TUV (Tropospheric Ultraviolet and Visible radiative transfer model; Madronich, 2002). The implementation of TUV was completed as documented by Emery et al. (2010). This simplified module employs a reduced number of wavelength bands and plane-parallel two-stream approximations. Inputs needed include the cloud optical depth, solar zenith angle, three-dimensional aerosol concentration profile, and optical properties of the aerosol components provided by Takemura et al., 2002.

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The total cloud optical depth τ above a current grid cell to the top of troposphere is approximated offline by

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$$\tau = \frac{3L\Delta z_c}{2\rho_w r}, \quad (1)$$

here L is the mean cloud liquid water (g m^{-3}), Δz_c is the mean depth of cloudy layer (m) in the cell, ρ is the density of water (10^6 g m^{-3}), and r is the mean cloud drop radius (10^{-5} m). The module also uses the time- and space-dependent vertical profile of dry and wet (with an RH-dependent lensing effect) aerosols predicted by PMCAMx-UF.

The module outputs a modified actinic flux that can then be applied, using the clear-sky actinic flux for reference, to adjust the clear-sky photolysis rates. Adjustments due to clouds and aerosols tend to reduce photolysis below clouds but often enhance rates above clouds because of the reflection from the top of the cloud. Emery et al. (2010) implemented the module in the Comprehensive Air Quality Model with Extensions (CAMx) and evaluated it for ozone prediction in the Houston area. That study found decreased ozone surface concentrations with maximum decreases of approximately 10 ppb. However, they did not report the impacts that the radiation feedback would have on particulate mass or number. We compare particle number and sulfuric acid vapor profiles with and without the radiation update in place to better understand the importance of correctly representing this phenomenon.

2.4 Model evaluation with particle number and size distribution data

During the European Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) project (Kulmala et al., 2009; 2011) particle number size distributions within the atmospheric boundary layer were measured at various European Supersites for Atmospheric Aerosol Research (EUSAAR). May 2008 was one of the intensive observation periods of the project. In this study the predicted ground-level hourly averaged particle number concentrations are evaluated against the data from Aspvreten (Sweden), Cabauw (Netherlands), Hyytiälä (Finland), Ispra (Italy), Mace Head (Ireland), Melpitz (Germany) and Vavihill (Sweden) similarly to Fountoukis et al. (2012). These locations represent seven different types of European environments (Ahlm et al., 2013). More information about the characteristics and topography of these sites is available elsewhere (Asmi et al., 2011 and Fountoukis et al., 2012). The particle size distribution measurements were carried out using either a Differential Mobility Particle Sizer (DMPS) or Scanning Mobility Particle Sizer (SMPS) systems in the mobility diameter size range above 10 nm.

To evaluate the vertical profile of the particle size distribution, we used the observational data measured by the German DLR Falcon 20 and the British FAAM BAe-146 research aircrafts, operating between 6 and 24 May 2008. The aircraft data was collected during the LONGREX campaign (Hamburger et al., 2011), which was also a part of the EUCAARI project. The FAAM BAe-146 flights mainly flew in the boundary layer and lower free

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troposphere while the DLR Falcon 20 aircraft mostly probed the free troposphere up to the tropopause level (Hamburger et al., 2011). The Condensation Particle Size Analyser (CPSA) (Fiebig et al., 2005; Feldpausch et al., 2006), installed aboard the DLR Falcon 20, and the Passive Cavity Aerosol Spectrometer Probe (PCASP-100X) (Liu et al., 1992), operated aboard both aircraft, measured the particle number concentrations. Consistent with Reddington et al. (2011), we used the measurements from two channels of the CPSA onboard the DLR Falcon 20 with lower cut-off diameters of 4 and 10 nm, yielding the number concentrations of particles above these sizes, denoted as N_4 and N_{10}. The temporal resolution of the CPSA dataset is 1 s. The nominal size range of PCASP-100X is 0.12-3.5 µm with 15 channels. The PCASP-100X raw data was sampled with 1 Hz frequency, but the data used here is based on averaging over a constant interval of 5 s. We used the measured particle number concentrations obtained from channels 3 to 10 of the PCASP-100X covering the diameter range of 160-1040 nm, representative of the accumulation mode, also to facilitate comparisons with the results reported by Reddington et al. (2011). We also used a TSI 3786 Condensational Particle Counter (CPC) aboard the FAAM BAe-146 aircraft to measure the number concentrations of particles larger than 4 nm.

A map of flight tracks by the Falcon 20 and BAe-146 and more details about EUCAARI-LONGREX dataset are available elsewhere (Reddington et al., 2011; Hamburger et al., 2012). Measurements from the LONGREX campaign span altitudes corresponding to 13 of the 14 vertical layers of PMCAMx-UF (Fig. S1 in the supplement). The model data were paired with the aircraft data by converting the time-dependent latitude, longitude, and altitude of the plane to a model grid-cell index.

3 Results

3.1 Surface-level particle number concentrations

In this study we explore the sensitivity of PMCAMx-UF to cases (1) with an updated NPF scheme with ACDC-based formation rates, (2) with an updated cloud adjustment scheme with TUV implementation, and (3) including natural particle number emissions. The baseline simulation (hereafter ACDC-TUV-DE; see Table 1) represents a prediction of the particle number concentrations with implementation of ACDC-based NPF scheme and TUV cloud adjustment scheme while using the default (i.e. only anthropogenic) particle emissions similarly to Fountoukis et al. (2012). Table 1 summarizes the simulations reported in this study. Figure 1 shows the arithmetic mean number concentration over May 2008 at ground-level for each PMCAMx-UF grid cell for particles larger than 10 (N_{10}), 50 (N_{50}) and 100 (N_{100}) nm and all particles (N_{tot}) as predicted using the baseline simulation ACDC-TUV-DE. The first two days of the simulation were excluded from the analysis to minimize the impact of the initial conditions on the results. The domain mean during May 2008 for N_{tot} is 59200 cm^{-3}, for N_{10} the corresponding number is 7100 cm^{-3}, for N_{50} 1300 cm^{-3}, and for N_{100} 360 cm^{-3}. The spatial pattern of the predicted number

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concentrations is similar to the results reported by Fountoukis et al. (2012), which were obtained using the simulation Napari-RADM-DE. The highest number concentrations are predicted over Eastern Europe during this photochemically active period while the lowest particle number concentrations are predicted over Nordic countries. The simulation Napari-TUV-DE predicts the domain mean of N_{tot}, N_{10}, N_{50} and N_{100} of 8100, 4000, 1500 and 410, respectively. Although updating the NPF scheme of PMCAMx-UF with ACDC-based formation rates significantly affects the number of small particles with diameter below 10 nm, the spatial concentration remains unchanged. Updating the model cloudiness scheme by implementing the TUV radiative transfer module did not greatly affect the spatial distribution of number concentrations but caused a minor change in the number concentration values. This is confirmed by the arithmetic domain mean values during May 2008 of N_{tot}, N_{10}, N_{50} and N_{100} predicted by the ACDC-RADM-DE simulation, which are 62000, 6800, 1200 and 340 cm^{-3}, respectively, and thus very similar to the baseline simulation. Including the natural particle emissions (in simulation ACDC-TUV-NE) resulted in 48300, 6200, 1300 and 380 cm^{-3} for N_{tot}, N_{10}, N_{50} and N_{100}, respectively, therefore predicting lower number concentrations of small particles (i.e. diameter < 10 nm) compared to that predicted by the baseline simulation. This is probably due to the higher sink of newly formed particles caused by the added natural particle emissions.

igure 2 shows scatter plots of the predicted (ACDC-TUV-DE) versus measured hourly averaged N_{10}, N_{50} and N_{100} at the seven EUSAAR measurement sites during May 2008. The prediction skill metrics of the simulations presented in Table 1 as compared with surface observations are summarized in Supplementary Table S1. The model generally tends to overpredict the N_{10} (NMB = 126 % for the base simulation) and the predicted N_{10} are subject to scatter (NME = 145 % for the base simulation) (see Table S1 for all the simulations). The reason for this overprediction is most likely linked to the missing condensable vapors and particle growth mechanisms in the simulations reported here (see Fountoukis et al., 2012; Ahlm et al., 2013; Patoulias et al., 2015). At most of the measurement sites, the predicted N_{50} is in fairly-good agreement with the observations with about 70% of the data points falling within a factor of two of the measurements except for two sites Mace Head (56%) and Hyytiälä (59%) (see Fig. 2 for the base simulation). The N_{50} predictions are overall slightly biased (NMB = -18 % for the base simulation) but subject to scatter (NME = 41 % for the base simulation). The predicted N_{100} are more biased (NMB = -45%) and scattered (NME = 51 %) compared with N_{50}. Overall, the model performance is comparable to that reported by Fountoukis et al., (2012) and between the five simulations conducted here, with largest differences observed for the smallest particles if the scaled Napari scheme is used (see Table S1): linear correlation coefficients for monthly average concentrations throughout the domain between the different simulation cases and the ACDC-TUV-DE range from 0.827 (for N_{tot} for Napari-TUV-DE vs. the base case) to 0.999 (for N_{tot} and N_{100} for ACDC-RADM-DE vs. the base case). As expected, including the natural emissions resulted in better agreement

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with the observations as compared with the default case, especially for the small sizes (see Table S1 for comparison between ACDC-TUV-NE and ACDC-TUV-DE).

The biases presented here and in the following figures can thus be considered conservative estimates. Furthermore, in this study we have only considered the ternary sulfuric acid - water - ammonia particle formation scheme. There may be other significant mechanisms present, e.g. sulfuric acid - amine particle formation (Bergman et al., 2015), with a geographical pattern resembling that of our results. Both mechanisms depend on sulfuric acid concentration predictions, which may be inaccurate as well. We compared the modeled and measured acid concentrations at one of the measurement sites (Melpitz), and found that the modeled concentrations were slightly overpredicted (Fig. S2 in the supplement). This may also contribute to the overprediction of the small particle sizes.

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3.2 Vertical profiles of particle number concentrations

In this section we investigate the vertical distribution of the means of N_{tot}, N_{10}, N_{50} and N_{100} along with parameters relevant for predicting NPF for the base case simulations (Fig. 3). These parameters include gas-phase concentrations of H_2SO_4, NH_3, RH and T. In the results shown in Fig. 3 the TUV radiation scheme has been used, thus representing the baseline simulation ACDC-TUV-DE. As can be seen from Fig. 3, particles smaller than 10 nm contribute significantly to the total number concentration throughout the tropospheric column, N_{tot} is about one order of magnitude greater than N_{10} and two and three orders of magnitudes greater than N_{50} and N_{100}, respectively. Values of N_{10}, N_{50} and N_{100} decrease monotonically with altitude, dropping significantly at approximately 1 km (layers 6-8 of the model). The vertical distribution of N_{tot} shows a different trend at higher altitudes where a bump in N_{tot} occurs at around 6-11 km, although no significant increase in the gas-phase concentration of H_2SO_4 and NH_3 are predicted at these altitudes (Fig. 3). The increase in N_{tot} is mostly due to a significantly decreased coagulation sink for the newly formed particles, as the number of larger particles dramatically decreases with altitude, and partly due to the rapidly decreasing temperature. PMCAMx-UF predicts the particle formation rates to decrease rapidly from around 2 km upward. The temperature, RH and sulfuric acid profile have similar relative trends as the N_{10}, N_{50} and N_{100} profiles. There is a plateau in temperature and RH (at the temperature range 285-288 K and RH range 80-83 %) profile up to altitude 1.2 km. Above this altitude, however, the RH and temperature values decrease rapidly. The sharp decreases in the relative humidity, temperature and particle number concentrations are consistent with the location of the boundary layer height. This is in agreement with Ferrero et al., (2010) who showed that mixing height estimations (over the city of Milan) derived from particle number concentration, temperature and relative humidity are correlated with one another.

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Figure 4 shows the comparison of the two simulations ACDC-TUV-DE and Napari-TUV-DE (see Table 1) with the observational data collected during the EUCAARI-LONGREX campaign measured by German DLR Falcon

20 and the British FAAM BAe-146 aircraft. The overall statistics of the comparisons between the modeled concentrations in all the simulations using the TUV radiation scheme and the aircraft data are presented in Supplementary Table S2. The model using the ACDC-based formation rates predicts the number concentration profile of particles larger than 4 nm (N_4) within about one order of magnitude of the observed N_4 profile throughout the atmospheric column. The scaled Napari NPF scheme leads to N_4 concentrations closer to the observations than those using the ACDC scheme with biases less than 50 %. As mentioned above, the vertical profiles presented in Figure 4 are produced by the model using the TUV radiation scheme. A similar analysis of the vertical profiles using the RADM radiation scheme (simulation ACDC-RADM-DE), which is not shown here, results in exactly the same shape of the number concentration profiles. The vertical profiles using the RADM radiation scheme show minimal, yet worse, difference in the absolute number concentrations from the observations compared to the TUV radiation scheme. The number concentrations of particles larger than 10 nm (N_{10}) predicted by the model using the scaled Napari NPF scheme agree well with the observations throughout the atmospheric column (NMB less than 20 %, see Table S2). The model using the ACDC formation rates tends to overpredict the N_{10} profile (NMB between 173-249 %). The shape of the observed N_{10} vertical profile is captured throughout the atmospheric column regardless of the NPF scheme used. Both model versions have almost the same performance for the $N_{160\text{-}1040}$ profile within the boundary layer; both simulations (i.e. ACDC-TUV-DE and Napari-TUV-DE) underpredicting the $N_{160\text{-}1040}$ profile by about a factor of five. This behavior is seen in the $N_{160\text{-}1040}$ profile corresponding to both observational data sets (i.e. Falcon 20, Fig. 4-d, and BAe 146, Fig 4-e, aircraft data). This is at least partly due to the lack of sources of organic condensable vapors to grow the particles to larger sizes in the model (Patoulias et al., 2015), which will be investigated in a future study. The underprediction decreases for all model versions at altitudes above the boundary layer improving the agreement with observational data.

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The results for the model using the ACDC-based formation rates are comparable to previous studies. For example, Reddington et al. (2011) tested different NPF parameterizations in the BL including activation, kinetic and combined organic-H_2SO_4 parameterizations, which are implemented in the Global Model of Aerosol Processes (GLOMAP). The evaluation of the modeled vertical profiles of particle number concentrations against the aircraft measurements showed that all of the mentioned NPF schemes dramatically underpredicted particles in nucleation (normalized mean bias (NMB) varies from -33 to -96) and Aitken mode sizes (-44 < NMB < -59). The larger particles (N_{100}) however were generally well-captured by the model. Furthermore, Lupascu et al. (2015) compared simulated number concentrations with aircraft measurements collected during the Carbonaceous Aerosol and Radiative Effects Study (CARES) campaign. They also tested different NPF parameterizations including activation, kinetic and combined organic-H_2SO_4 parameterizations, which are implemented in the regional scale model WRF-Chem one-at-a-time using a sectional framework to simulate the NPF. They found that their simulations overpredicted the particle number concentrations, especially in the smallest sizes (normalized mean bias of 126-608 % for N_3 and N_{10}). The nucleation scheme had very little impact on the magnitude of the CCN-sized particle number concentrations.

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3.3 Effect of the radiative transfer scheme on predictions of particle number concentrations

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Updating the radiative transfer scheme to the TUV scheme has a small effect on the predicted number concentrations; the vertical profile of the relative difference (N_{TUV} - N_{RADM}) × 100 / N_{RADM} in the May-2008 domain mean particle number concentrations shows a maximum reduction of about -5.5 % in N_{tot} (at altitude 2.2 km) and a maximum increase of about 9 % in N_{100} (at altitude range 0.7-2.2 km). Figure 5 shows the spatial distribution of the absolute difference of the H_2SO_4 gas phase concentration and total particle number concentrations between the simulations ACDC-TUV-DE and ACDC-RADM-DE (see Table 1) at 12:00 UTC on May 5, 2008. Figure 5 also presents the cloud optical depth fields to illustrate the link between the cloud fields and changes in the particle number concentrations due to the new cloud adjustment scheme. The TUV scheme results in higher particle formation rates above and in the vicinity of the cloudy regions due to enhanced radiation and sulfuric acid production. This is in agreement with observations reported by Wehner et al. (2015). They concluded that the cloudy regions provide a favorable environment for NPF above and at the edges of clouds due to enhanced upward spectral irradiance and cloud-reflected spectral radiance around them. Sulfuric acid concentration is reduced below cloud in the TUV scheme, due to the enhanced UV attenuation scaling down the photolysis rates. However, as pointed out above, the effect on the total particle number concentrations is generally small.

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4 Conclusions

We have updated the new particle formation (NPF) scheme within PMCAMx-UF with particle formation rates for the ternary H_2SO_4-NH_3-H_2O pathway simulated by the Atmospheric Cluster Dynamics Code using quantum chemical input data. The ACDC results were implemented in PMCAMx-UF as a lookup table from which the formation rates were interpolated. We believe this is the first time that reasonable particle concentrations have been produced in a large-scale atmospheric model with a NPF scheme without any scaling factors or location/condition dependent semi-empiricism. In addition to the updated NPF description, we have also updated PMCAMx-UF treatment of the cloudiness effect on the photolysis rates (i.e. cloud adjustment scheme) profile by implementing a streamlined version of the Tropospheric Ultraviolet and Visible radiative transfer model (Madronich, 2002).

We used the updated PMCAMx-UF to simulate particle number concentration during May 2008 over Europe. During this period, the EUCAARI campaign was performed to measure the particle number size distributions within the atmospheric boundary layer at various European Supersites for Atmospheric Aerosol Research (EUSAAR) in addition to higher altitude data collected by two research aircraft during the LONGREX campaign. Comparing the measured particle number concentrations at the EUSAAR sites to the predictions of the updated PMCAMx-UF shows that the model slightly overpredicts concentrations for particles with diameters between 10-100 nm. Particles larger than 100 nm are slightly underpredicted. For details of the model performance statistics, the reader is referred to Supporting Tables S1 and S2.

Vertical profiles of particle number concentrations show that predicted concentrations of small particles are within one order of magnitude of the aircraft measurements. The predicted Aitken- and accumulation mode number concentrations are in quite good agreement with the observational data throughout the atmospheric column, while the concentrations of smaller particles are somewhat overpredicted by the ACDC-based NPF scheme. Including organic condensation onto the ultrafine particles could improve these predictions.

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References

Ahlm, L., Julin, J., Fountoukis, C., Pandis, S. N., and Riipinen, I.: Particle number concentrations over Europe in 2030: the role of emissions and new particle formation, Atmos. Chem. Phys., 13, 10271-10283, doi:10.5194/acp-13-10271-2013, 2013.

Adams, P. J., and Seinfeld, J. H, Predicting global aerosol size distributions in general circulation models, J. Geophys. Res., 107, 4370, doi:10.1029/2001JD001010, 2002.

Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere. Nature, 502: 359-363, doi:10.1038/nature12663, 2013.

Asmi, A., Wiedensohler, A., Laj, P., Fjaeraa, A.-M., Sellegri, K., Birmili, W., Weingartner, E., Baltensperger, U., Zdimal, V., Zikova, N., Putaud, J.-P., Marinoni, A., Tunved, P., Hansson, H.-C., Fiebig, M., Kivekäs, N., Lihavainen, H., Asmi, E., Ulevicius, V., Aalto, P. P., Swietlicki, E., Kristensson, A., Mihalopoulos, N., Kalivitis, N., Kalapov, I., Kiss, G., de Leeuw, G., Henzing, B., Harrison, R. M., Beddows, D., O'Dowd, C., Jennings, S. G., Flentje, H., Weinhold, K., Meinhardt, F., Ries, L., and Kulmala, M.: Number size distributions and seasonality of submicron particles in Europe 2008–2009, Atmos. Chem. Phys., 11, 5505-5538, doi:10.5194/acp-11-5505-2011, 2011.

Bergman, T., Laaksonen, A., Korhonen, H., Malila, J., Dunne, E. M., Mielonen, T., Lehtinen, K. E. J., Kühn, T., Arola, A., and Kokkola, H.: Geographical and Diurnal Features of Amine-Enhanced Boundary Layer Nucleation J. Geophys. Res. Atmos., 120, 9606–9624, 2015.

Carslaw, K. S., Lee, L. A., Reddington, C. L., Pringle, K. J., Rap, A., Forster, P. M., Mann, G. W., Spracklen, D. V., Woodhouse, M. T., Regayre, L. A., Pierce, J. R.: Large contribution of natural aerosols to uncertainty in indirect forcing, Nature 503, 67–71, doi:10.1038/nature12674, 2013.

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Chang, J. S., Brost, R. A., Isaksen, I. S. A., Madronich, S., Middleton, P., Stockwell, W. R., and Walcek, C. J.: A three-dimensional Eulerian acid deposition model: Physical concepts and formulation, J. Geophys. Res., 92(D12), 14681–14700, doi:10.1029/JD092iD12p14681, 1987.

Cui, Z., Gadian, A., Blyth, A., Crosier, J., and Crawford, I.: Observations of the Variation in Aerosol and Cloud Microphysics along the 20°S Transect on 13 November 2008 during VOCALS-Rex, J. Atmos. Sci., 71, 2927–2943, doi: http://dx.doi.org/10.1175/JAS-D-13-0245.1, 2014.

Dal Maso, M., Kulmala, M., Lehtinen, K. E. J., Mäkelä, J. M., Aalto, P., and O'Dowd, C. D.: Condensation and coagulation sinks and formation of nucleation mode particles in coastal and boreal forest boundary layers, J. Geophys. Res., 107(D19), doi:10.1029/2001JD001053, 2002.

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), 2009.

Emery, C., J. Jung, J. Johnson, G. Yarwood, and D. Boyer: Improving cloud impacts on photolysis using an on-line radiation model in CAMx, presented at the 9th Annual CMAS Conference, pp. 9–14, 2010.

Ferrero, L., Perrone, M. G., Petraccone, S., Sangiorgi, G., Ferrini, B. S., Lo Porto, C., Lazzati, Z., Cocchi, D., Bruno, F., Greco, F., Riccio, A., and Bolzacchini, E.: Vertically-resolved particle size distribution within and above the mixing layer over the Milan metropolitan area, Atmos. Chem. Phys., 10, 3915-3932, doi:10.5194/acp-10-3915-2010, 2010.

Fahey K. M., and Pandis, S. N.: Optimizing model performance: Variable size resolution in cloud chemistry modeling, Atmos. Environ., 35, 4471-4478, doi:10.1016/S1352-2310(01)00224-2, 2001.

Feldpausch, P., Fiebig, M., Fritzsche, L., and Petzold, A.: Measurement of ultrafine aerosol size distributions by a combination of diffusion screen separators and condensation particle counters, J.Aerosol Sci., 37, 577–597, doi:10.1016/j.jaerosci.2005.04.009, 2006.

Fiebig, M., Stein, C., Schroder, F., Feldpausch, P., and Petzold, A.: Inversion of data containing information on the aerosol particle size distribution using multiple instruments, J. Aerosol Sci., 36, 1353–1372, doi:10.1016/j.jaerosci.2005.01.004, 2005.

Fountoukis, C., Racherla, P. N., Denier van der Gon, H. A. C., Polymeneas, P., Charalampidis, P. E., Pilinis, C., Wiedensohler, A., Dall'Osto, M., O'Dowd, C., and Pandis, S. N.: Evaluation of a three-dimensional chemical transport model (PMCAMx) in the European domain during the EUCAARI May 2008 campaign, Atmos. Chem. Phys., 11, 10331-10347, doi:10.5194/acp-11-10331-2011, 2011.

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, doi:10.5194/acp-12-8663-2012, 2012.

Fuzzi, S., Baltensperger, U., Carslaw, K., Decesari, S., Denier van der Gon, H., Facchini, M. C., Fowler, D., Koren, I., Langford, B., Lohmann, U., Nemitz, E., Pandis, S., Riipinen, I., Rudich, Y., Schaap, M., Slowik, J. G., Spracklen, D. V., Vignati, E., Wild, M., Williams, M., and Gilardoni, S.: Particulate matter, air quality and climate: lessons learned and future needs, Atmos. Chem. Phys., 15, 8217-8299, doi:10.5194/acp-15-8217-2015, 2015.

Gaydos, T. M., Stanier, C. O., and Pandis, S. N.: Modelling of in situ ultrafine atmospheric particle formation in the eastern United States, J. Geophys. Res., 110, D07S12, doi:10.1029/2004JD004683, 2005.

Gaydos, T., Pinder, R., Koo, B., Fahey, K., Yarwood, G., and Pandis, S. N.: Development and application of a three-dimensional aerosol chemical transport model, PMCAMx, Atmos. Environ., 41, 2594–2611, doi:10.1016/j.atmosenv.2006.11.034, 2007.

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, doi:10.5194/acp-6-3181-2006, 2006.

Hamburger, T., McMeeking, G., Minikin, A., Birmili, W., Dall'Osto, M., O'Dowd, C., Flentje, H., Henzing, B., Junninen, H., Kristensson, A., de Leeuw, G., Stohl, A., Burkhart, J. F., Coe, H., Krejci, R., and Petzold, A.: Overview of the synoptic and pollution situation over Europe during the EUCAARI-LONGREX field campaign, Atmos. Chem. Phys., 11, 1065-1082, doi:10.5194/acp-11-1065-2011, 2011.

Hamburger, T., McMeeking, G., Minikin, A., Petzold, A., Coe, H., and Krejci, R.: Airborne observations of aerosol microphysical properties and particle ageing processes in the troposphere above Europe, Atmos. Chem. Phys., 12, 11533-11554, doi:10.5194/acp-12-11533-2012, 2012.

Henschel, H., Navarro, J. C. A., Yli-Juuti, T., Kupiainen-Määttä, O., Olenius, T., Ortega, I. K., Clegg, S. L., Kurtén, T., Riipinen, I., and Vehkamäki, H.: Hydration of atmospherically relevant molecular clusters: Computational chemistry and classical thermodynamics. J. Phys. Chem. A., 118: 2599-2611, doi:10.1021/jp500712y, 2014.

Henschel, H., Kurtén, T., and Vehkamäki, H.: A computational study on the effect of hydration on new particle formation in the sulfuric acid/ammonia and sulfuric acid/dimethylamine systems, submitted to Journal of Physical Chemistry, 2015

Jen, C. N., P. H. McMurry, and D. R. Hanson: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, J. Geophys. Res., 119, 7502–7514, doi:10.1002/2014JD021592, 2014.

Jung, J., Adams, P. J., and Pandis, S. N.: Simulating the size distribution and chemical composition of ultrafine particles during nucleation events, Atmospheric Environment, 40(13), 2248-2259,doi:2248-2259,doi:10.1016/j.atmosenv.2005.09.082, 2006.

Jung, J. G., Pandis, S. N., and Adams, P. J.: Evaluation of nucleation theories in a sulfur-rich environment. Aerosol Sci. Technol., 42(7), 495-504, doi:10.1080/02786820802187085, 2008.

Jung, J., Fountoukis, C., Adams, P. J., and Pandis, S. N.: Simulation of in situ ultrafine particle formation in the eastern United States using PMCAMx-UF, J. Geophys. Res., 115, D03203, doi:10.1029/2009JD012313, 2010.

Karydis, V. A., Tsimpidi, A. P., and Pandis, S. N.: Evaluation of a three-dimensional chemical transport model (PMCAMx) in the eastern United States for all four seasons, J. Geophys. Res., 112, D14211, doi:10.1029/2006JD007890, 2007.

Kerminen, V.-M., Paramonov, M., Anttila, T., Riipinen, I., Fountoukis, C., Korhonen, H., Asmi, E., Laakso, L., Lihavainen, H., Swietlicki, E., Svenningsson, B., Asmi, A., Pandis, S. N., Kulmala, M., and Petäjä, T.: Cloud condensation nuclei production associated with atmospheric nucleation: a synthesis based on existing literature and new results, Atmos. Chem. Phys., 12, 12037-12059, doi:10.5194/acp-12-12037-2012, 2012.

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Kirkby, J., Duplissy, J., Sengupta, K., Frege, C., Gordon, H., Williamson, C., Heinritzi, M., Simon, M., Yan, C., Almeida, J., Tröstl, J., Nieminen, T., Ortega, I. K., Wagner, R., Adamov, A., Amorim, A., Bernhammer, A., Bianchi, F., Breitenlechner, M., Brilke, S., Chen, X., Craven, J., Dias, A., Ehrhart, S., Flagan, R. C., Franchin, A., Fuchs, C., Guida, R., Hakala, J., Hoyle, C. R., Jokinen, T., Junninen, H., Kangasluoma, J., Kim, J., Krapf, M., Kürten, A., Laaksonen, A., Lehtipalo, K., Makhmutov, V., Mathot, S., Molteni, U., Onnela, A., Peräkylä, O., Piel, F., Petäjä, T., Praplan, A. P., Pringle, K., Rap, A., Richards, N. A. D., Riipinen, I., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Scott, C. E., Seinfeld, J. H., Sipilä, M., Steiner, G., Stozhkov, Y., Stratmann, F., Tomé, A., Virtanen, A., Vogel, A. L., Wagner, A. C., Wagner, P. E., Weingartner, E., Wimmer, D., Winkler, P. M., Ye, P., Zhang, X., Hansel, A., Dommen, J., Donahue, N. M., Worsnop, D. R., Baltensperger, U., Kulmala, M., Carslaw, K. S., Curtius, J.: Ion-induced nucleation of pure biogenic particles, Nature 533, 521-526, doi:10.1038/nature17953, 2016.

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné, S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., and Breitenlechner, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature 476, 429-433, doi:10.1038/nature10343, 2011.

Korhonen, P., Kulmala, M., Laaksonen, A., Viisanen, Y., McGraw, R. and Seinfeld, J. H.: Ternary nucleation of H_2SO_4, NH_3, and H_2O in the atmosphere, J. Geophys. Res., 104, 26349–26353, doi:10.1029/1999JD900784, 1999.

Kulmala, M., Liisa, P, and Mäkelä, J. M.: Stable sulphate clusters as a source of new atmospheric particles, *Nature* 404, no. 6773, 66-69, doi: 10.1038/35003550, 2000.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, and W., McMurry, P.H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J Aerosol Sci., 35:143-76, doi:10.1016/j.jaerosci.2003.10.003, 2004.

Kulmala, M., Lehtinen, K. E. J., and Laaksonen, A.: Cluster activation theory as an explanation of the linear dependence between formation rate of 3 nm particles and sulphuric acid concentration, Atmos. Chem. Phys., 6, 787–793, doi:10.5194/acp-6-787-2006, 2006.

Kulmala, M., Asmi, A., Lappalainen, H. K., Carslaw, K. S., Pöschl, U., Baltensperger, U., Hov, Ø., Brenquier, J.-L., Pandis, S. N., Facchini, M. C., Hansson, H.-C., Wiedensohler, A., and O'Dowd, C. D.: Introduction: European Integrated Project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI) – integrating aerosol research from nano to global scales, Atmos. Chem. Phys., 9, 2825-2841, doi:10.5194/acp-9-2825-2009, 2009.

Kulmala, M., Asmi, A., Lappalainen, H. K., Baltensperger, U., Brenguier, J.-L., Facchini, M. C., Hansson, H.-C., Hov, Ø., 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.,

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Reddington, C. L., Roberts, G., Rosenfeld, D., Schwarz, J., Seland, Ø., Sellegri, K., Shen, X. J., Shiraiwa, M., Siebert, H., Sierau, B., Simpson, D., Sun, J. Y., Topping, D., Tunved, P., Vaattovaara, P., Vakkari, V., Veefkind, J. P., Visschedijk, A., Vuollekoski, H., Vuolo, R., Wehner, B., Wildt, J., Woodward, S., Worsnop, D. R., van Zadelhoff, G.-J., Zardini, A. A., Zhang, K., van Zyl, P. G., Kerminen, V.-M., S Carslaw, K., and Pandis, S. N.: 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, 13061-13143, doi:10.5194/acp-11-13061-2011, 2011.

Laaksonen, A., Kulmala, M., Berndt, T., Stratmann, F., Mikkonen, S., Ruuskanen, A., Lehtinen, K. E. J., Dal Maso, M., Aalto, P., Petäjä, T., Riipinen, I., Sihto, S.-L., Janson, R., Arnold, F., Hanke, M., Ücker, J., Umann, B., Sellegri, K., O'Dowd, C. D., and Viisanen, Y.: SO_2oxidation products other than H_2SO_4 as a trigger of new particle formation. Part 2: Comparison of ambient and laboratory measurements, and atmospheric implications, Atmos. Chem. Phys., 8, 7255-7264, doi:10.5194/acp-8-7255-2008, 2008.

Liu , P. S. K., Leaitch , W. R. , Strapp, J. W., and Wasey, M. A.: Response of Particle Measuring Systems Airborne ASASP and PCASP to NaCl and Latex Particles, Aerosol Sci. Technol., 16, 83-95, doi:0.1080/02786829208959539, 1992.

Lupascu, A., Easter, R., Zaveri, R., Shrivastava, M., Pekour, M., Tomlinson, J., Yang, Q., Matsui, H., Hodzic, A., Zhang, Q., and Fast, J. D.: Modeling particle nucleation and growth over northern California during the 2010 CARES campaign, Atmos. Chem. Phys. Discuss., 15, 19729-19801, doi:10.5194/acpd-15-19729-2015, 2015.

Madronich, S., National Center for Atmospheric Research, Boulder, Colorado, (2002). Tropospheric ultraviolet and visible radiation model. [Available online at http://acd.ucar.edu/models/UV/TUV/index.html.]

Makkonen, R., Asmi, A., Korhonen, H., Kokkola, H., Järvenoja, S., Räisänen, P., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., Järvinen, H., Lohmann, U., Bennartz, R., Feichter, J., and Kulmala, M.: Sensitivity of aerosol concentrations and cloud properties to nucleation and secondary organic distribution in ECHAM5-HAM global circulation model, Atmos. Chem. Phys., 9, 1747-1766, doi:10.5194/acp-9-1747-2009, 2009.

Matsui, H., M. Koike, Y. Kondo, N. Takegawa, A. Wiedensohler, J. D. Fast, and R. A. Zaveri: Impact of new particle formation on the concentrations of aerosols and cloud condensation nuclei around Beijing, J. Geophys. Res., 116, D19208, doi:10.1029/2011JD016025, 2011.

Matsui, H., M. Koike, N. Takegawa, Y. Kondo, A. Takami, T. Takamura, S. Yoon, S.-W. Kim, H.-C. Lim, and J. D. Fast: Spatial and temporal variations of new particle formation in East Asia using an NPF-explicit WRF-chem model: North-south contrast in new particle formation frequency, J. Geophys. Res. Atmos., 118, 11,647–11,663, doi:10.1002/jgrd.50821, 2013.

McMurry, P.: Photochemical aerosol formation from SO_2: A theoretical analysis of smog chamber data, J. Colloid Interface Sci., 78(2), 513–527, doi:10.1016/0021-9797(80)90589-5, 1980.

Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., and Carslaw, K. S.: Impact of nucleation on global CCN, Atmos. Chem. Phys., 9, 8601-8616, doi:10.5194/acp-9-8601-2009, 2009.

Merikanto J., Zapadinsky E., Lauri A., Vehkamäki H.: Origin of the Failure of Classical Nucleation Theory: Incorrect Description of the Smallest Clusters, Phys. Rev. Lett., 98, 145702, doi:10.1103/PhysRevLett.98.145702, 2007a.

Merikanto, J., Napari, I., Vehkamäki, H., Anttila, T., and Kulmala, M.: New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric conditions, J. Geophys. Res., 112, D15207, doi:10.1029/2006JD007977, 2007b.

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Napari, I., Kulmala, M., and Vehkamaki, H.: Ternary nucleation of inorganic acids, ammonia, and water, J. Chem. Phys., 117, 8418– 8425, doi:10.1063/1.1511722, 2002.

O'Dowd, C. D., B. Langmann, S. Varghese, C. Scannell, D. Ceburnis, and M. C. Facchini: A combined organic-inorganic sea-spray source function, Geophys. Res. Lett., 35, L01801, doi:10.1029/2007GL030331, 2008.

Olenius, T., Kupiainen-Määttä, O., Ortega, I. K., Kurtén, T., and Vehkamäki, H.: Free energy barrier in the growth of sulfuric acid–ammonia and sulfuric acid–dimethylamine clusters, J. Chem. Phys., 139: 084312, doi:10.1063/1.4819024, 2013.

Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen, V., and Vehkamäki, H.: From quantum chemical formation free energies to evaporation rates, Atmos. Chem. Phys., 12, 225-235, doi:10.5194/acp-12-225-2012, 2012.

Paasonen, P., Nieminen, T., Asmi, E., Manninen, H. E., Petäjä, T., Plass-Dülmer, C., Flentje, H., Birmili, W., Wiedensohler, A., Hõrrak, U., Metzger, A., Hamed, A., Laaksonen, A., Facchini, M. C., Kerminen, V.-M., and Kulmala, M.: On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation, Atmos. Chem. Phys., 10, 11223–11242, doi:10.5194/acp-10-11223-2010, 2010.

Patoulias, D., Fountoukis, C., Riipinen, I., and Pandis, S. N.: The role of organic condensation on ultrafine particle growth during nucleation events, Atmos. Chem. Phys., 15, 6337-6350, doi:10.5194/acp-15-6337-2015, 2015.

Pierce, J. R. and Adams, P. J.: A computationally efficient aerosol nucleation/ condensation method: pseudo-steady-state sulfuric acid, aerosol science and technology, 43:3, 216-226, doi: 10.1080/02786820802587896, 2009.

Reddington, C. L., Carslaw, K. S., Spracklen, D. V., Frontoso, M. G., Collins, L., Merikanto, J., Minikin, A., Hamburger, T., Coe, H., Kulmala, M., Aalto, P., Flentje, H., Plass-Dülmer, C., Birmili, W., Wiedensohler, A., Wehner, B., Tuch, T., Sonntag, A., O'Dowd, C. D., Jennings, S. G., Dupuy, R., Baltensperger, U., Weingartner, E., Hansson, H.-C., Tunved, P., Laj, P., Sellegri, K., Boulon, J., Putaud, J.-P., Gruening, C., Swietlicki, E., Roldin, P., Henzing, J. S., Moerman, M., Mihalopoulos, N., Kouvarakis, G., Ždímal, V., Zíková, N., Marinoni, A., Bonasoni, P., and Duchi, R.: Primary versus secondary contributions to particle number concentrations in the European boundary layer, Atmos. Chem. Phys., 11, 12007-12036, doi:10.5194/acp-11-12007-2011, 2011.

Sihto, S.-L., Kulmala, M., Kerminen, V.-M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J.: Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms, Atmos. Chem. Phys., 6, 4079–4091, doi:10.5194/acp-6-4079-2006, 2006.

Skamarock, W. C., Klemp, J. B., Dudhia, J., Gill, D. O, Barker, D. M., and Wang, W.: A Description of the Advanced Research WRF Version 2, NCAR Technical Note (http://opensky.ucar.edu/islandora/object/technotes%3A479/datastream/PDF/view), doi:10.5065/D6DZ069T, 2005.

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 Transactions on Ecology and the Environment, 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 Transactions on Ecology and the Environment, 119, 353–361, 2008b.

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Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Mann, G. W., and Sihto, S.-L.: The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales, Atmos. Chem. Phys., 6, 5631-5648, doi:10.5194/acp-6-5631-2006, 2006.

Takemura, T., T. Nakajima, O. Dubovik, B.N. Holben, S. Kinne: Single scattering albedo and radiative forcing of various aerosol species with a global threedimensional model. J. Climate, 15, 333352, doi:10.1175/1520-0442(2002)015<0333:SSAARF>2.0.CO;2, 2002.

Vehkamäki, H., Kulmala, M., Napari, I., Lehtinen, K. E. J., Timmreck, C., Noppel, M., and Laaksonen, A.: An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions, J. Geophys. Res., 107, 4622, doi:10.1029/2002JD002184, 2002.

Visschedijk, A. J. H., Zandveld, P., and Denier van der Gon, H. A. C.: TNO Report 2007 A R0233/B: A high resolution gridded European emission database for the EU integrated project GEMS, Netherlands, Organization for Applied Scientific Research, 2007.

Westervelt, D. M., Pierce, J. R., and Adams, P. J.: Analysis of feedbacks between nucleation rate, survival probability and cloud condensation nuclei formation, Atmos. Chem. Phys., 14, 5577-5597, doi:10.5194/acp-14-5577-2014, 2014.

Yu, F.: Effect of ammonia on new particle formation: A kinetic H_2SO_4-H_2O-NH_3 nucleation model constrained by laboratory measurements, J. Geophys. Res., 111, D01204, doi:10.1029/2005JD005968, 2006a.

Yu, F., and Luo, G.: Simulation of particle size distribution with a global aerosol model: contribution of nucleation to aerosol and CCN number concentrations, Atmos. Chem. Phys., 9, 7691– 7710, doi:10.5194/acp-9-7691-2009, 2009.

Yu, F., Luo, G., Bates, T. S., Anderson, B., Clarke, A., Kapustin, V., Yantosca, R. M., Wang, Y., and WU, S.: Spatial distributions of particle number concentrations in the global troposphere: Simulations, observations, and implications for nucleation mechanisms, J. Geophys. Res., 115, D17205, doi:10.1029/2009JD013473, 2010.

Zhang, Y., McMurry, P. H., Yu, F., and Jacobson, M. Z.: A comparative study of nucleation parameterizations: 1. Examination and evaluation of the formulations, J. Geophys. Res., 115, D20212, doi:10.1029/2010JD014150, 2010.

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Figures and figure captions

able 1. Summary of PMCAMx-UF model simulations reported in this study. The arithmetic mean of ground-level number concentration during May 2008 for particles larger than 0.8 nm (N_{tot}), 50 nm (N_{50}) and 100 nm (N_{100}) is given for each simulation.

Simulation name	NPF scheme	Cloud adjustment scheme	Emissions	Domain mean number concentration (cm^{-3})		
				N_{tot}	N_{50}	N_{100}
ACDC-TUV-DE*	ACDC-based	TUV	Default	59200	1300	360
ACDC-RADM-DE	ACDC-based	RADM	Default	62000	1200	340
ACDC-TUV-NE*	ACDC-based	TUV	Updated	48300	1300	380
Napari-TUV-DE	Scaled Napari et al., 2002	TUV	Default	8100	1500	410
Napari-RADM-DE	Scaled Napari et al., 2002	RADM	Default	9000	1500	400

* DE = default emissions. The "default emissions" refer to the emissions used in Fountoukis et al., 2012 (simulation Napari-RADM-DE).

* NE = new emissions, including natural emissions from biogenic, marine and wildfire sources.

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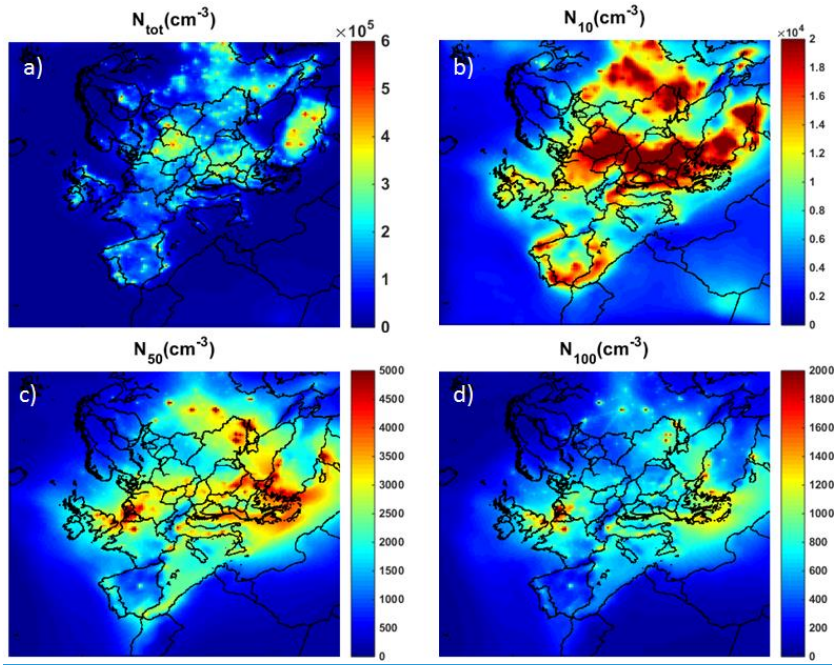

Figure 1. The simulated spatial distribution of the arithmetic mean of ground-level number concentration during May 2008 for particles larger than (a) 0.8 nm (N_{tot}), (b) 10 nm (N_{10}), (c) 50 nm (N_{50}), and (d) 100 nm (N_{100}). The PMCAMx-UF baseline simulation ACDC-TUV-DE is used (see Table 1). Note that different color bar scales are used for the different size ranges for readability.

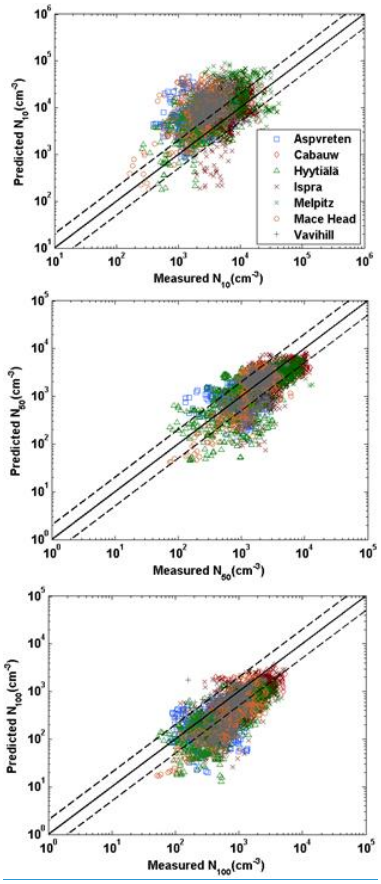

Figure 2. Comparison of predicted vs. measured hourly averaged number concentration of particles larger than 10 nm (N_{10}), 50 nm (N_{50}) and 100 nm (N_{100}) during May 2008 from the 7 EUSAAR measurement stations during the EUCAARI project. Lines corresponding to 1:1 (solid line), and 1:2 and 2:1 (dashed lines) are shown. The PMCAMx-UF model simulation ACDC-TUV-DE is used (see Table 1).

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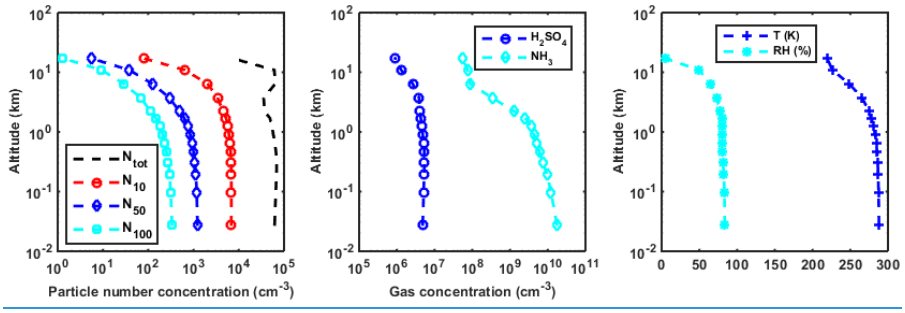

Figure 3. Vertical profiles of simulated variables averaged (arithmetic mean) over May 2008 and the whole simulation domain. Left panel: number concentration (cm^{-3}) of particles larger than 0.8 nm (N_{tot}), 10 nm (N_{10}), 50 nm (N_{50}) and 100 nm (N_{100}). Middle panel: gas phase concentration (cm^{-3}) of sulfuric acid (H_2SO_4) and ammonia (NH_3). Right panel: temperature (K) and relative humidity (%). The PMCAMx-UF baseline simulation ACDC-TUV-DE is used (see Table 1).

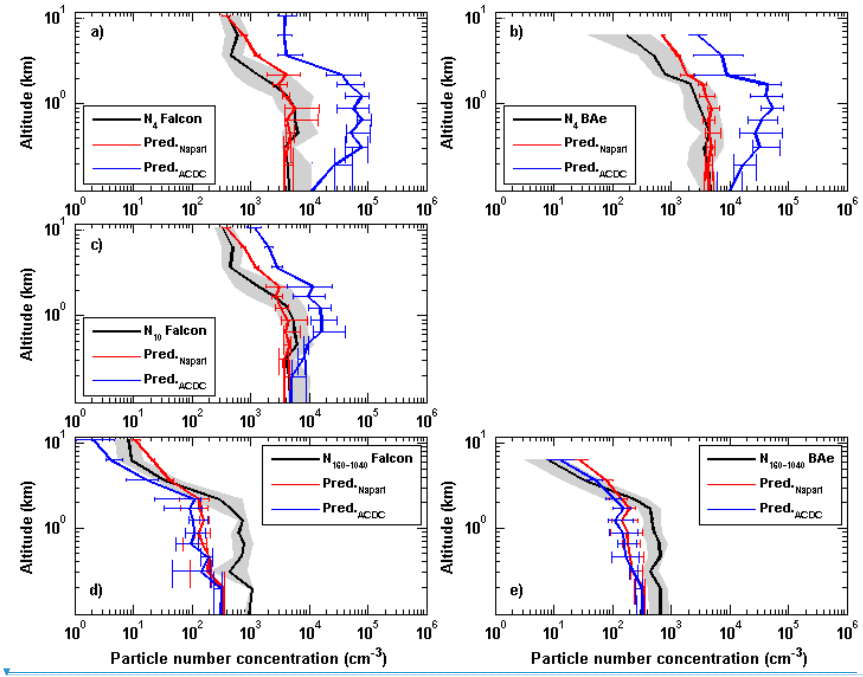

Figure 4. Vertical profiles of measured (black) and predicted (red and blue) particle number concentrations for the size ranges: (a) and (b) Larger than 4 nm (N_4) measurements collected by Falcon and BAe 146, respectively, (c) larger than 10 nm (N_{10}) measurements collected by Falcon 20, (d) and (e) 160-1040 nm ($N_{160\text{-}1040}$) measurements collected by Falcon and BAe 146, respectively, during May 2008. Red and blue lines show the predicted particle number concentrations by the PMCAMx-UF model using ACDC-based formation rates (ACDC-TUV-DE) and scaled Napari new particle formation scheme (Napari-TUV-DE), respectively. The lines show the median values of data points within each model layer, and the error bars and grey shading indicate the values between 25-th and 75-th percentiles of the model results and observations, respectively. Concentrations are given at ambient temperature and pressure.

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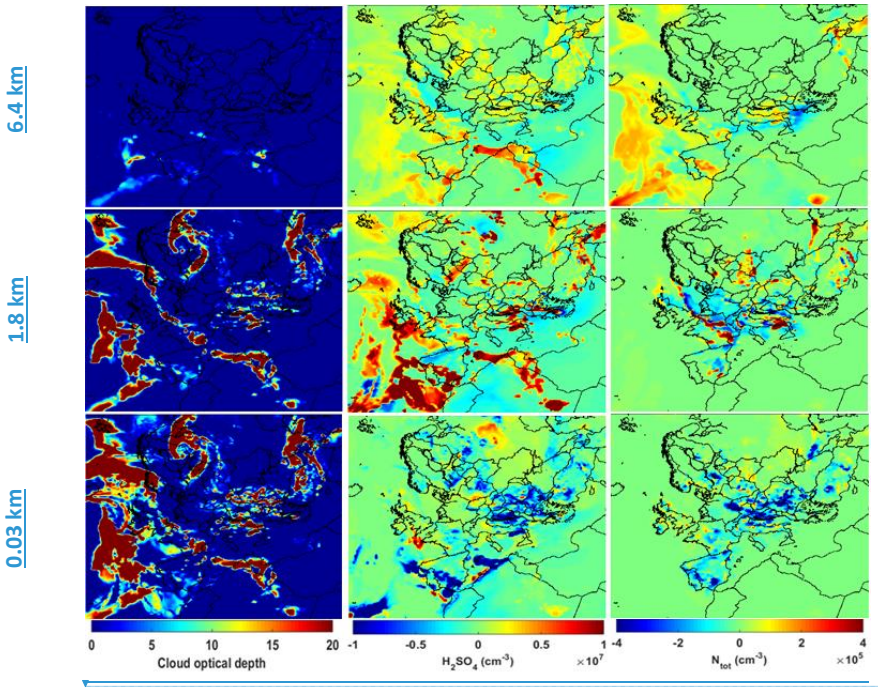

Figure 5. Left column: the total cloud optical depth supplied by WRF meteorology model. Middle column: the absolute difference between the predictions using the TUV (the simulation ACDC-TUV-DE; see table 1) and RADM (the simulation ACDC-RADM-DE) radiative transfer schemes within PMCAMx-UF for H_2SO_4 concentration. Right column: absolute difference between prediction using TUV and RADM schemes for total particle number concentrations N_{tot}. The parameters shown in the figure are snapshots on May 5, 2008 12:00 UTC at model layers 1 (mid-point altitude 0.03 km), 9 (mid-point altitude 1.7 km) and 12 (mid-point altitude 6.4 km).

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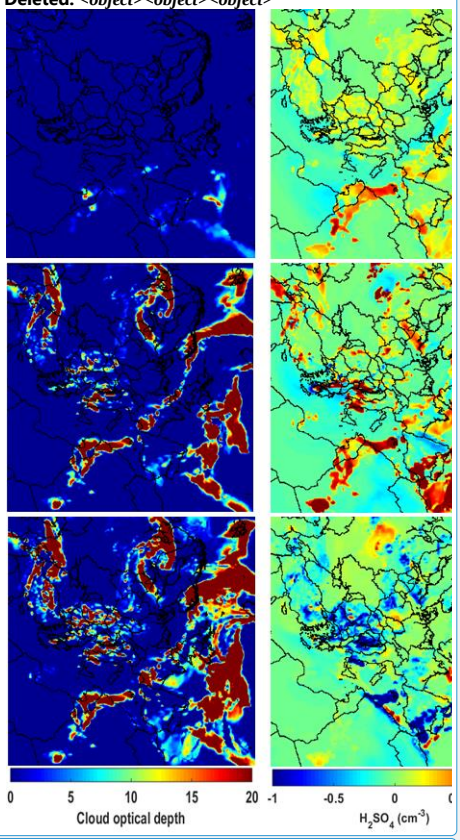

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