



BACCHUS

Impact of Biogenic versus Anthropogenic emissions on Clouds and Climate: towards a Holistic UnderStanding

Collaborative Project

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Summary of results (UMAN, ETHZ, PSI, ULEEDS, MPI-C, UOC, NUIG, CNR-ISAC, KIT)

This task is related to question 1c: What are the critical missing processes in current process models and global ESMs for the simulation of realistic aerosol and cloud properties? How can these missing processes be accounted for, either directly by improving the models or a posteriori as part of the assessment of the model results?

In particular, this deliverable makes the synthesis of the major findings of the WP with regard to the role of both organic and inorganic aerosol for cloud condensation nuclei (CCN)/ ice nucleating particles (INP).

In the atmosphere new aerosol particles are emitted from surface or altitude sources, or formed by nucleation and growth. These aerosol particles can further grow by coagulation and condensation of vapors. A certain fraction of these aerosol particles reaches critical sizes to act as CCN or can act as INP..

Based on combined field measurements, remote sensing and biological/plankton/chemistry laboratory studies as well as detailed process models, BACCHUS has developed parameterizations for CCN and INP as a function of aerosol components accounting for inorganic and organic aerosol impact. These have been tested in various scale models and appropriate parameterizations have been incorporated in ESMs. For INP, parameterizations have been based on laboratory studies of mineral dust and biological particles and have been validated against field measurements of INP.

CCN

Nucleation and growth - Impact of ions and organics

Nucleation of mixtures of sulphuric acid, ammonia and highly oxidized organic molecules (HOMs) in the present-day and pre-industrial atmospheres has been considered in the global models. Overall, two distinct nucleation mechanisms have been observed in the CERN cloud chamber, the one that strongly depends on sulfuric acid concentrations and the second one that depends only on oxidized organics and ions.

Thus, in addition to the earlier studied *binary nucleation of sulphuric acid* and *ternary nucleation of sulphuric acid and ammonia* (Dunne et al., 2016), parameterizations have been developed in BACCHUS to account for *nucleation of organics with sulphuric acid* (Riccobono et al. 2014) as well as for *nucleation of organics alone* (neutral or ion induced) (Kirkby et al., 2016).

Indeed, from recent advances in our understanding on nucleation in the atmosphere, extremely low volatility organics (ELVOC), highly oxidized organics (HOM) and ions have been shown to be important drivers of new particle formation (NPF) in the atmosphere in addition to sulfuric acid and ammonia. Riccobono et al. (2014) parameterized the NPF rate using results from investigations of the initial steps of NPF during CERN cloud chamber experiments. For a system having both gaseous sulfuric acid (H₂SO₄) and biogenic oxidized organic vapors (BioOxOrg), sulfuric acid plays an important role in driving atmospheric NPF (as it was earlier found in numerous field measurements), and organic compounds participate in NPF at the very early stages. Overall, the formation rate of new particles, *J*, could be approximated by equation (1):

$$J = k [H_2SO_4]^p \times [BioOxOrg]^q$$

where k is a multicomponent prefactor, and p (2.17±0.14) and q (0.80±0.23) are fits to the measured chamber data. In the GLOMAP model equation 1 has been modified to equation 2:

$$JR = 0.5 kR [H_2SO_4]^2 [BioOxOrg]$$

where [BioOxOrg] refers to the oxidation products of monoterpenes with OH, $kR = 3.27 \times 10^{21}$, and the factor 0.5 corrects for the large yield of HOMs from α -pinene compared to other terpenes found in Jokinen et al. (2015).

Kirkby et al. (2016) showed that at <u>very low gaseous sulfuric acid</u> concentrations, as those at remote continental sites, or in the pre-industrial atmosphere that are exposed mainly to natural sulfur emissions, NPF rate is affected by both <u>ions and oxidized organic compounds (HOM)</u>: when the HOM concentration is low, ions significantly influence NPF, whereas at high HOM concentrations the formation of new particles is dominated by neutral pathways.

<u>Nucleation of organics alone</u>, have been parameterized as a sum of neutral (Jn) and ion-induced (Jiin) components (Gordon et al., 2016):

Jorg = Jn +Jgcr	(3)
$Jn = a1[HOM]^{(a2+a5)/[HOM]}$	(4)
$J_{iin} = 2n \pm a_{3}[HOM]^{(a4+a_{5})/[HOM]}$	(5)

where the HOM concentration is given in units of 10^7 molecules per cm³, $n\pm$ is the ion concentration, and a1-a5 are parameters fitted to the experimental data.

New measurements from the CLOUD chamber (Tröstl et al., 2016) have also suggested an updated parameterization of the <u>nanoparticle growth rates</u> (GR) due to collision limited sulfuric acid condensation below 3 nm (first term of equation 6) and to the organic compounds fitted by Gordon et al. (2017) as follows (see also D2.3):

 $GR = 7.3 \times 10^{-8} [H_2 SO_4] + 1.41 \times 10^{-7} [HOM]$

(6)

(1)

(2)

Based on these findings global model simulations within BACCHUS suggest that

- The treatment of early growth of nucleated particles by condensation of oxidized organic molecules substantially alters global CCN concentrations by up to ±50% in comparison with previously assumed growth rate parameterizations (Tröstl et al., 2016).
- Accounting for the aerosol formation and growth mechanisms by Extremely Low Volatility Compounds (ELVOC) (Jokinen et al., 2015), projected future increase of biogenic volatile organic compound (BVOC) emission in the Siberian domain provide

a mean for increased nucleation and aerosol growth rates leading to increased CCN concentrations (Arneth et al., 2016, see also Deliverable 2.3).

- New particle formation produces half of the CCN and more precisely between 38 and 66% (around 54%) of CCN at 0.2% supersaturation (CCN0.2%) in the present day atmosphere (Figure 1; Gordon et al., 2017).
- The contribution of NPF to CCN was higher in the pre-industrial atmosphere forming between 45% and 84% (around 67%) of CCN at 0.2% supersaturation (Figure 1; Gordon et al., 2017)



Figure 1: CCN concentrations at 0.2% supersaturation (CCN0.2%) at low cloud level (approximately 460–1100 m altitude), and fractions from NPF. The (a) pre-industrial (PI) and (b) present day (PD) annual mean concentrations; and (c, d) the fractions of these particles that originate from NPF (from Gordon et al., 2017).

- The importance of BVOCs in NPF and CCN formation is greater than previously thought since all secondary organic aerosol from BVOC is calculated to reduce low-cloud-level CCN at 0.2% supersaturation by 26% in the present-day atmosphere and 41% in the preindustrial (Figure 2; Gordon et al., 2017).
- About 75% of the impact of SOA on CCN0.2% is due to the tiny fraction of the oxidation products of BVOCs that have very low volatility and are thus involved in NPF and early growth. Gordon et al (2017) estimated that ion-induced NPF was more important for CCN0.2% production in the preindustrial atmosphere (contributing by

40% for NPFs growing to CCN0.2%) than nowadays (27%). This estimate however has to be seen with caution due to the currently poorly measured ion-induced fraction of NPF involving BVOCs.

- Gordon et al (2017) simulations also suggest that the effect of changes in cosmic ray intensity on CCN is small and unlikely to be comparable to the effect of large variations in natural primary aerosol emissions.
- Because of the simulated production of significant amounts of natural atmospheric aerosol contributing to the baseline preindustrial aerosol concentrations, these finding could lead to a reduction of 27% in estimates of anthropogenic aerosol radiative forcing (Gordon et al., 2016).



Figure 2: Fractions of NPF from organic ("org-ion," "H₂SO₄-org," and "H₂SO₄-org-ion" (green)) and inorganic ("H₂SO₄-ion" (dark red), "H₂SO₄-NH₃" (orange), and "H₂SO₄-NH₃-ion" (orange)) pathways in pre-industrial and present-day atmospheres, annually averaged within 5.8 km of the surface. Biogenic vapors are abbreviated to "org." Neutral and ion-induced NPF fractions are separated. The ion-induced fraction of ternary organic (H₂SO₄-org-ion) NPF is included, but it is not as well constrained by available CLOUD measurements as the overall fraction of ternary organic NPF. Neutral NPF of pure sulfuric acid and pure biogenic vapors is responsible for less than 0.5% of particle formation at these altitudes, so these pathways are not shown (figure from Gordon et al., 2017).

Relative Importance of Organic and Inorganic New Particle Formation Pathways

Gordon et al. (2017) have found that organics played a more important role in NPF and growth to CCN in the preindustrial atmosphere than nowadays compared to inorganic aerosols. By comparing the annual average formation rates of 3 nm particles in the model below 5.8 km altitude, where it is assumed that most of the activation of CCN takes place, they have found that all NPF involves sulfuric acid and 51% of present-day NPF involves organic molecules (Figure 2). In the preindustrial atmosphere, this contribution of organics has been estimated at 86% of NPF. Of the total NPF, NPF involving only organics has been estimated to be between 4.1% (nowadays) and 20% (preindustrial atmosphere). Figure 2 also shows that binary ion-induced NPF of sulfuric acid and water was more important in the preindustrial atmosphere

than it is today because of the lower levels of ammonia in the preindustrial atmosphere. Between 5.8 km altitude and the top of the troposphere, over 85% of NPF is entirely inorganic in both preindustrial and present day. In the present-day atmosphere, 77% of NPF at these altitudes involves only sulfuric acid and water, 16% involves ammonia and 7.2% organics; while these numbers are 88%, 0.1% and 12% for the pre-industrial atmosphere (Gordon et al., 2017)

Note that the uncertainties in the pure inorganic NPF pathways are smaller than those in the organic NPF pathways which are driven by the unknown temperature dependence, the lack of complete chemical mechanisms, and limited knowledge of the atmospheric lifetime of the organic species that nucleate (Yu et al., 2016; Dunne et al., 2016; Gordon et al., 2016; 2017). Additional uncertainties stem from the omission of anthropogenic organic compounds and amines from the system (Gordon et al., 2017).

Hygroscopic growth of particles to CCN

Based on a large perturbed parameter ensemble (PPE) of the HadGEM-UKCA model, it was found that the ability of the organic compounds to take up water is much more important for the direct radiative effect (ERFari), and is one of the major sources of uncertainty in ERFari (explains locally up to 25% of model variance) in regions with strong natural organic sources, such as forest regions (more details can be found in D2.4).

Over remote Southern Ocean regions the organic composition of particles plays an important role in CCN activation, but sub-dominant to the importance of the particle size distribution and number concentration (Deliverable D2.4).

Long-term time series of particle number size distributions, chemical composition and CCN number concentrations from 12 stations were analyzed (Schmale et al., 2016; 2017). The observatories were grouped into categories according to their official classification: coastal background (BRW: Barrow, Alaska; MHD: Mace Head, Ireland; FIK: Finokalia, Crete; NOT: Noto Peninsula, Japan), rural background (MEL: Melpitz, Germany; CES: Cabauw, the Netherlands; VAV: Vavihill, Sweden), alpine sites (PUY: Puy de Dôme, France; JFJ: Jungfraujoch, Switzerland), remote forest sites (ATTO, Brazil; SMR, Hyytiäla, Finland) and the urban environment (SEO: Seoul, South Korea).

Figure 3 shows the ratio of activated particles at several supersaturations and activated particles at SS = 0.5 %. While there is considerable spread in the ratio among coastal stations (panel b), non-coastal observatories exhibit similar behavior, except for the tropical rainforest site ATTO. In the rainforest, most particles activate already at lower supersaturations because of their relatively large size. The spread among the coastal stations can most likely be explained by the various source contributions that range from anthropogenic emissions (NOT, MHD) to biomass burning (FIK) or Arctic Haze (BRW) that influence the chemical composition of the aerosols.



Figure 3: Ratio of activation ratios (AR) for all measured SS % over the activation ratio at 0.5 % SS for each station. At SS = 0.5 % (x-axis) the ratio is 1. Activation ratios are based on particle size distributions starting at 20 nm. (a) shows non-coastal sites, while (b) groups all coastal sites. The black dotted line is the average fit through all curves from panels (a) and (b), whereby y = A*ln(SS%)+b with $A = 0.46 \pm 0.02$ and $b = 1.31 \pm 0.02$ (Schmale et al., 2017).

Figure 4 displays the bulk chemical composition of the submicron aerosol at a subset of the 12 stations where aerosol mass spectrometers were operated (panel a). Figure 4b indicates the monthly values of the hygroscopicity parameter kappa, which tends to be lowest at locations with significant organic aerosol contributions such as SMR or ATTO in the second half of the year. The dependence of kappa on the ratio of organic to inorganic aerosol constituents (ratio OA/IA) is shown in Figure 5. Two aspects can be highlighted: a) at most stations there is at least a 10 % contribution of organic aerosol except for the coastal station MHD in high sea spray periods; b) the variation of kappa at different OA/IA ratios is limited for all stations except those in the forest environments (ATTO, SMR). There the variability of the inorganic aerosol compounds determines the kappa value.

To predict the amount of CCN with \pm 30 % at each of these stations based on the kappa-Köhler theory, simple assumptions of internally mixed particles and kappa = 0.1 for organic aerosol are sufficient (not shown here; Schmale et al., 2017).



Figure 4: (a) Monthly median chemical composition as measured by each station's mass spectrometer (see Table 1 in Schmale et al., 2017, for details on the type of spectrometer). The horizontal dashed line is placed at $1 \mu g m^{-3}$ for easy comparison of mass concentrations between stations. (b) Median (black line) and interquartile range of composition-derived κ values per month. The dashed black line is located at $\kappa = 0.3$ (Schmale et al., 2017).



Figure 5: Relationship of the composition-derived hygroscopicity parameter, κ , to the binned and averaged ratio of organic (OA) to inorganic (IA) aerosol components. The vertical bars denote the standard deviation. Note that asymptotic-like approach of the curves towards a κ value of 0.1 are due to the fact that κ of all organics aerosols was assumed to be 0.1. (Schmale et al., 2017).

<u>Robustness of global CCN simulations and implication for droplet formation: A BACCHUS and AEROCOM intercomparison</u>

This multi-years dataset has been used as benchmark for the ongoing BACCHUS/AEROCOM model intercomparison exercise for CCN simulations (Fanourgakis et al., 2017; manuscript in preparation). This exercise aims i) to assess the accuracy of the global models in the prediction of the chemical composition of aerosol particles and CCN concentrations at various supersaturations, ii) to document the diversity of the global models in the estimation of the particles composition and in aerosol particles, CCN and cloud droplets concentrations at the surface as well as their vertical profile, iii) to present the global distribution of the same quantities on the earth surface and the corresponding model diversity.

In Table 1 the 14 global models participating in the model intercomparison are shown. In Figure 6 the model results for the CCN at supersaturation ratio 0.2% are compared to the observations from nine different observational sites from the Schmale et al. (2016) compilation. It can be seen that with the exception of the Finokalia station, the models on average underestimate the number of CCN. Despite the quantitative differences in the estimation of the CCN concentrations at 0.2% supersaturation, models are able to capture reasonably well the relative differences of CCN at 0.2% supersaturation between the stations, as well as their seasonal variations. Further comparisons between observations and modeling results regarding number of particles of various sizes, showed that on average models slightly underestimate the concentration of particles with sizes relevant to the formation of CCN (N50, N80, N120, i.e. number of particles with dry diameter equal or larger than 50 μ m, 80 μ m and 120 μ m, respectively).

In Figure 7 the model results are compared to the observations for particle sizes >50 nm (N50). The predicted seasonal variations of N50 are in agreement with observations, as for CCN at 0.2%, although the number of particles seems to be slightly underpredicted by the ensemble of the model results (with the exception of Finokalia station). Similar conclusions are drawn for the N80 and N120 particles (not shown). For the high altitude, continental background sites (Puy de Dôme, Jungfraujoch) low number concentrations are observed with high variability between winter and summer that has been attributed to the boundary layer seasonal behavior. This seasonal trend is captured by the models. On the opposite, high number concentrations with low seasonal variability are observed at the rural background stations, Cabauw and Melpitz. More CCN at 0.2% supersaturation are observed during spring, while models simulate higher concentrations during summer and fall. For the other rural background station (Vavihill), both models and observations show lower concentrations and weaker variability, than the previous stations. Different trends are observed between the three coastal sites examined in this study: Due to the clean marine conditions over the Atlantic Ocean (Ovadnevaite et al., 2014), low CCN concentrations at 0.2% supersaturation are observed at the Mace Head site remaining almost constant during all seasons. At the Finokalia station high concentrations are observed mainly due to the long-range transport of pollutants and biomass burning plumes from North-East Europe (Bougiatioti et al., 2016) and East Asia (Iwamoto et al., 2016). High concentrations of CCN at 0.2% supersaturation are also observed over the Noto Peninsula with a maximum during spring. For these two stations, model simulations are in qualitative agreement with observations reproducing the high seasonal variation in the number concentrations of CCN at 0.2% supersaturation during the year.

Table 1: Models participating in the intercomparison exercise. The model names are given in the first column categorized either into chemical transport models (CTM) or general circulation models (GCM). The GCM models are either nudged (nud) to a specified meteorology or are free running (free). The third column gives the model resolution used for this study. The aerosol microphysics module describing particle processes parameterized in each model is given in the fourth column, while in the fifth column the aerosol chemical components considered in the model for CCN calculations are specified. SO4: sulfate, NO3: nitrate, NH4: ammonium, SS: seasalt, DU: dust, BC: black carbon, POA: primary organic aerosol, SOA: secondary organic aerosol, ORG: organic aerosol. Contributors names are given in the last column. (*) one model provided only monthly mean data.

Model	Host Model	Model resolution	Microphysics model	Particles	Contributors
CAM5-Chem- APM	GCM	1.875° × 2.5°, 32 layers	APM (Sectional)	SO4, NO3, NH4, , SS, DU, BC, ORG (POA + SOA)	Gan Luo, Fangqun Yu
CAM5-Chem- ATRAS2	СТМ	1.875° × 2.5°, 32 layers	ATRAS2 (Sectional)	SO4, NO3, NH4, SS, DU, BC, ORG (POA+SOA)	Hitoshi Matsui
CAM5_MAM3	GCM (nudg)	1.875° × 2.5°, 30 layers	MAM3 (modal)	SO4. BC, DU, SS, ORG (POA+SOA)	Hailong Wang, Yang Yang
CAM5_MAM4	GCM (nudg)	1.875° × 2.5°, 56 layers	MAM4 (modal)	SO4, BC, DU, SS, ORG (POA+SOA)	Hamilton, Douglas. S., Mahowald, Natalie. M., Liu, Xiaohong, Wu, Mingxuan.
CAM5.3-Oslo	GCM (nudg)	0.938° × 1.25°, 30 layers	OsloAero (sectional)	SO4. BC, DU, SS, ORG (POA+SOA),	Alf Kirkevåg, Alf Grini
ECHAM5.5- HAM2- ELVOC_UH	GCM (nudg)	1.875° × 1.875°, 31 layers	HAM2 (modal)	SO4, BC, DU, SS, ORG (POA+SOA)	Risto Makkonen
ECHAM6- HAM2	GCM (nudg)	1.875° × 1.875°, 31 layers	HAM2 (modal)	SO4, BC, DU, SS, ORG (POM+SOA)	Duncan Watson-Parris, Philip Stier
ECHAM6- HAM2-AP	GCM (nudg)	1.875° × 1.875°, 31 layers	HAM2-AP (modal)	SO4, BC, DU, SS, ORG (POA+SOA)	David Neubauer, Ulrike Lohmann
GEOS-Chem- APM	СТМ	2° × 2.5°, 38 layers	APM (sectional)	SO4, NO3, NH4, , SS, DU, BC, ORG (POA+SOA)	Gan Luo, Fangqun Yu
GEOS-Chem- TOMAS	СТМ	3.9° × 5.0°, 25 layers	TOMAS (sectional)	SO4, BC, SS, SU, ORG (POA+SOA)	John K. Kodros, Jeffrey R. Pierce
GISS-E2.1- MATRIX	GCM (nudg)	2° x 2.5°,40 layers	MATRIX (modal)	SO4, BC, ORG (POA+SOA), SS, DU	Susanne E. Bauer, Kostas Tsigaridis
GISS-E2- Tomas*	GCM (free)	2° x 2.5°,40 layers	TOMAS (Sectional)	SO4, BC, ORG, DU, SS, NH4	Daniel M. Westervelt

TM4-ECPL	СТМ	2° x 3°,34 layers	M7 (modal)	SO4, BC, DU, SS, ORG (POA+SOA)	Giorgos Fanourgakis, Maria Sfakianaki, Stelios Myriokefalitakis, Nikos Daskalakis, Maria Kanakidou
ТМ5	СТМ	2° × 3°, 34 layers	M7 (modal)	SO4, BC, DU, SS, ORG (POA+SOA), NO3	Tommi Bergman, Roland Schrödner, Risto Makkonen, Twan van Noije



Figure 6: Comparison of the CCN concentration at 0.2% supersaturation ratio (CCN0.2%) between observations (black dots) and models (blue thick lines), at nine different observatories in Europe and in Japan (Noto Peninsula). The monthly values shown have been obtained from hourly values. For the model-averaged results the central 2/3 of the models have been used as in Mann et al. (2014) and the average was obtained as the geometric mean of them. Since the models were thirteen the nine central values were used. The thin blue lines that define the shaded area show the minimum and maximum values of the nine central models, while the green dashed lines the minimum and maximum values of all models.

Regarding the chemical composition of the aerosol particles, the model simulated chemical composition of PM₁ particles (particles with dry diameters < 1 μ m) has been compared (not shown) to the available observations at the Schmale et al. (2016) sites. Sulfate and organics PM₁ chemical components show a seasonal variability similar to that of the CCN and N50. The simulated amount and the seasonal variability of the sulfate mass compares well with observations, while sea-salt mass concentrations are overestimated compared to the available observations. The organic mass simulations on the other hand show similar spatial variability with the CCN and particle numbers, but the total amount is significantly underestimated. An underestimate of the organic aerosol mass by most models was also reported during the recent AEROCOM model intercomparison (Tsigaridis et al., 2014).



Figure 7: Comparison of the N50 concentration (in cm⁻³) between observations (black dots) and models (blue thick lines), at height different observatories with data availability in Europe and in Japan (Noto Peninsula). See Figure 6 for explanations.

In Figure 8 the averages for the year 2011 global surface distribution of the CCN at 0.2% supersaturation, N3 and N50 particles number geometric mean concentrations obtained using the central 2/3 models are shown in the first column, while in the second column the corresponding model diversity is illustrated. This is calculated as the ratio of the highest to the

lowest model results (Mann et al., 2014). The surface distributions of CCN and particle number concentrations, N3 and N50, show similar geographical patterns. The CCN at 0.2% supersaturation reach concentrations close to \sim 2700 cm⁻³, in the most polluted areas (e.g. Seoul). In these regions the diversity of the model results also reaches the highest values, partially driven by differences in the model resolution (Table 1) which at these regions of intense emissions leads to sharp concentration gradients. The model diversity in the CCN at 0.2% supersaturation is also high in central Africa, Indonesia and Latin America. Model diversities of the N3 and N50 particles show also high values. Particles with sizes close to 3 nm and 50 nm are not relevant to the formation of the CCN at a supersaturation ratio of 0.2%, until they undergo a significant growth and reach sizes between 80-120 nm. However, N3 is a measure of the number of the small-size aerosol particles that originate from nucleation and growth or from primary, mainly anthropogenic emissions. The large model diversities found for N3 over continental anthropogenically influenced regions of the northern hemisphere and tropical America, Africa and Indonesia, indicate significant differences between models in the description of the nucleation process and the number of the small-size particles that are directly emitted in the atmosphere by anthropogenic and other combustion sources. Note that in purpose the emissions used in the models have not been forced to the same database for all models but simulations were done as 'best case' simulations for each model similar to Tsigaridis et al (2014) intercomparison for organic aerosols.

In Figure 9, the global distributions of key chemical components of PM₁ particles at the surface are shown. Focusing on the model diversities for each component only at the regions where significant amounts of the respective aerosol component are present, it can be seen that for the sulfate mass mixing ratio model diversities are usually smaller than 3 with larger values over the northern hemisphere where most of the sulfate chemical production takes place. On the other hand, the large model diversity over the southern oceans for the sea-salt can be attributed to the different marine source size-resolved parameterizations used in the models. This uncertainty in the marine source of sea-salt could be linked to the overestimation of the sea-salt found at several observational stations. It is also reflected in the high diversity in the estimation of the organic mass over the open ocean, which can be also attributed to differences in the parameterization of the respective marine source. For the dust mass mixing ratio the model diversity is significantly high close to the source areas and downwind. As in the case of the other natural aerosol components these differences between models may be attributed to differences in the dust source parameterization in the models.



Figure 8: Ensemble annual mean global distributions of CCN and aerosol number concentrations for aerosols of diameters above 3 nm (N3) and above 50 nm (N50) and model diversity: geometric mean of the 10 models (GISS-E2-Tomas has provided only global monthly-mean output) calculated from the annual means of each model after excluding the 2 higher and 2 lower model results per grid box, and model diversity is defined as the ratio of max/min values of these 10 models.



Figure 9: Ensemble global near-surface distributions of aerosol chemical components for PM_1 ($\mu g m^{-3}$) and diversity (ratio). Calculations done as for figure 8.

2- Importance of organics and of the size distribution of their primary emissions

It is found that the primary emitted organic aerosol particles (POA) and secondary organic aerosol (SOA) have a major contribution to the CCN number. This is demonstrated in Figure 10 in which the annual global surface distribution of the CCN at a supersaturation ratio of 0.2% is shown (a) in the presence of both primary and secondary organics (POM) and (b) in the absence of organics. It can be seen that in the absence of organics (noPOM) the number of CCN is reduced by a factor of ~4. Overall the fraction of CCN at 0.2% SS calculated by TM4-EPCL model (details in Deliverables 2.2 and 2.4) associated with organics in the atmosphere maximizes over the tropical and high latitude continental regions (Figure 10c).



Figure 10: Annual global surface distribution of the CCN at a supersaturation ratio of 0.2% (a) in the presence of organics both primary and secondary and (b) in the absence of organics (noPOM) (c) fractional contribution of organics to CCN at supersaturation 0.2% (TM4-ECPL global model results).

Global model simulations also indicate that the CCN-effects of SOA formation are somewhat modulated by the representation of primary-emissions, and suggest that higher level of details in both timing and size-distribution of primary emissions would influence the SOA climate effects (Deliverable 2.4).

This has been further investigated here by performing an additional one-model simulation in which the primary carbonaceous emissions size distribution has been shifted to larger sizes. Figures 11a and b show the N50 distribution for the base case (corresponding to the CCN at 0.2%

supersaturation shown in Figure 10a) and for the test simulation (Figure 11b) where the total mass of the primary emitted organics is the same but less and larger carbonaceous aerosols are emitted from combustion sources and smaller and thus more particles are emitted from vegetation fires; overall less carbonaceous particles are emitted to the atmosphere. Figure 11c depicts the CCN at 0.2% supersaturation for this test simulation, while Figures 11d and 11e show the absolute changes in the CCN at 0.2% supersaturation and in the N50 number concentration respectively (base simulation – test simulation). The size of the direct emitted particles in the atmosphere has therefore a significant contribution to the number of CCN. It can be seen that the number of CCN has been reduced by a factor of ~10% in the most polluted areas (Figure 11c) compared to Figure 10a (base case).



Figure 11: Annual global surface distribution of the N50 a) the N50 at the base case b) the N50 at the test simulations c) the CCN concentrations at super-saturation ratio 0.2% (in cm⁻³) d) Difference in the CCN 0.2% Ssupersaturation concentrations between the base case (Fig 10a) simulation and the test simulation (Fig 11a) e) as b) but for N50 (TM4-ECPL model).

Ice nucleating particles

Ice nucleating particles (INP) were found to be biological particles and naturally emitted dust particles from K-feldspar. Parameterizations to account for INP from dust aerosol for immersion freezing have been developed in BACCHUS (Boose et al., 2016):

The average ice active surface density as a function of temperature, ns(T), of all measured dust samples was fitted by using

ns = exp(-a(T - 273.15 K) + b)

(7)

with the fit parameters $a = 0.33 \text{ K}^{-1}$ and b = 15.64.

The ice nucleation temperature of natural desert dusts varies by up to 10 K. To more adequately describe immersion freezing by desert dust in the atmosphere, mineralogy sensitive emission and transport schemes would be desirable. Boose et al. (2016) suggested that K-feldspar seems to be the most important INP for temperatures above 250 K. At lower temperatures Naplagioclase feldspars and quartz emissions and transport need to be quantified in order to understand INP activity (see also D2.4).

BACCHUS measurements of INP in a coastal environment (Mace Head Observatory (53.33°N, 9.9°W) show that highest concentrations at -15°C were often associated with elevated organics and two specific events indicate important contributions of marine and terrestrial organic aerosol to the total INP population. Nearly all INPs measured during the marine organic aerosol plume were biological in nature. In BACCHUS (Vergara-Temprado et al., 2016) INP from marine organic aerosol has been parameterized based on the sea-spray submicron aerosol emissions and their content in water insoluble organics (WIOM) using chlorophyll concentrations as a proxy (O'Dowd et al., 2015; Rinaldi et al., 2013) and the parameterization developed in Wilson et al (2015) to derive INP from WIOM.

Primary marine organic material is a globally important INP component. BACCHUS model simulations (GLOMAP) show that although on a monthly mean basis INPs from deserts far outnumber INP from sea spray throughout much of the low and mid-latitudes, marine organics become more important in the world's remote oceans (Vergara-Temprado et al., 2016). Furthermore, even over the northern hemisphere, marine organic INP concentrations exceed K-feldspar INP concentrations on 10-30% of the days when the temperature is within the mixed-phase range and the total concentration of INP is larger than 10⁻⁴ L⁻¹. In the Southern Hemisphere, both on a monthly mean basis and on the large majority of days, marine organic aerosols are the dominant INP type from March-November. Figure 12 shows the computed importance of marine organic aerosols for INP as the percentage of days when [INP]_{ambient} from marine organic aerosols is greater than from K-feldspar (figure from Vergara-Temprado et al., 2016).



Figure 12: Percentage of days when [INP]_{ambient} from marine organic aerosols is greater than from K-feldspar. The number of days have been calculated only for times and locations where the total [INP]_{ambient} concentration is larger than 0.1m⁻³. The black contour lines represent seasonal mean isotherms in degrees centigrade (Vergara-Temprado et al., 2017).

A more recent study by Huang et al. (2017) has also investigated the relative importance of marine organic aerosol (MOA) as an INP compared to dust and found strong dependence on the type of ice nucleation parametrization scheme used in the model. Regardless, MOA was not found to affect the microphysical properties of clouds or the radiative balance significantly, due to its relatively weak ice activity and a low sensitivity of cloud ice properties to heterogeneous ice nucleation in the ECHAM6-HAM2 model (Figure 13).

This result can be compared to the values found by Vergara-Temprado et al. (2017), who examined the percentage of days when the INP concentration at ambient temperatures from MOA is greater than that from K-feldspar. As the study by Vergara-Temprado et al. (2017) also used an ice active surface density ns-based freezing parametrization for dust, the most straightforward comparison of the two studies (Vergara-Temprado et al (2016, 2017) and Huang et al (2017)) would be with the "MOA100ns" simulation (Figure 13), in which case slightly lower freezing contributions from MOA are found by Huang et al. (2017), in particular in the Northern Hemisphere and in the higher altitudes of the Southern Hemisphere. As discussed by Huang et al (2017) possible reasons for this include the Vergara-Temprado et al (2017) consideration of freezing by only a fraction of the dust (K-feldspar) instead of all dust types in Huang et al. (2017), which decreases the availability of dust particles in the Vergara-Temprado et al. (2017) study and leads to a more ready scavenging of the dust INP from the atmosphere due to the larger size of feldspar.



Figure 13: The annually and zonally averaged frequency of occurrence when the freezing contribution from MOA is greater than that from dust, diagnosed only for cloudy grid boxes containing supercooled droplets. Contour lines denote the frequency of occurrence (in %) of the above-mentioned favourable cloudy condition containing liquid droplets in the mixed-phase temperature range. All plots are from the respectively titled 10-year free-running simulations. (taken from Huang et al., 2017)

Changes with respect to the DoW

None

Dissemination and uptake

The tested parameterizations are available for the modeling groups to be implemented in regional and earth system models

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