UNIVERSITY OF LEEDS

This is a repository copy of *Global atmospheric particle formation from CERN CLOUD measurements*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/107269/

Version: Accepted Version

Article:

Dunne, EM, Gordon, H orcid.org/0000-0002-1822-3224, Kürten, A et al. (56 more authors) (2016) Global atmospheric particle formation from CERN CLOUD measurements. Science, 354 (6316). pp. 1119-1124. ISSN 0036-8075

https://doi.org/10.1126/science.aaf2649

© The Authors 2016. This is the author's version of the work. It is posted here by permission of the AAAS for personal use, not for redistribution. The definitive version was published in Science, Vol. 354, Issue 6316, pp. 1119-1124, DOI: 10.1126/science.aaf2649.

Reuse
Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

White Rose
university consortium
Universities of Leeds, Sheffield & York

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

Title: Global atmospheric particle formation from CERN CLOUD measurements

One sentence summary: Laboratory measurements and model simulations establish the main causes of new particle formation throughout the troposphere.

Authors: Eimear M. Dunne,[1,†,‖] Hamish Gordon,[2,*,‖] Andreas Kürten,[3] João Almeida,[2,3] Jonathan Duplissy,[4] Christina Williamson,[3,‡] Ismael K. Ortega,[5,§] Kirsty J. Pringle,[1] Alexey Adamov,[6] Urs Baltensperger,[7] Peter Barmet,[7] Francois Benduhn,[8] Federico Bianchi,[6,7] Martin Breitenlechner,[9,a] Antony Clarke,[10] Joachim Curtius,[3] Josef Dommen,[7] Neil M. Donahue,[11,6] Sebastian Ehrhart,[2,3] Richard C. Flagan,[12] Alessandro Franchin,[6] Roberto Guida,[1] Jani Hakala,[6] Armin Hansel,[9,13] Martin Heinritzi,[3] Tuija Jokinen,[6,b] Juha Kangasluoma,[6] Jasper Kirkby,[2,3] Markku Kulmala,[6] Agnieszka Kupc,[14,‡] Michael J. Lawler,[15,b] Katrianne Lehtipalo,[6,7] Vladimir Makhmutov,[16] Graham Mann,[1] Serge Mathot,[2] Joonas Merikanto,[6] Pasi Miettinen,[15] Athanasios Nenes,[17,18,19] Antti Onnela,[2] Alexandru Rap,[1] Carly L. S. Reddington,[1] Francesco Riccobono,[7] Nigel A. D. Richards,[1] Matti P. Rissanen,[6] Linda Rondo,[3] Nina Sarnela,[6] Siegfried Schobesberger,[6,c] Kamalika Sengupta,[1] Mario Simon,[3] Mikko Sipilä,[6] James N. Smith,[15,b] Yuri Stozkhov,[16] Antonio Tomé,[20] Jasmin Tröstl,[7] Paul E. Wagner,[14] Daniela Wimmer,[3,6] Paul M. Winkler,[14] Douglas R. Worsnop[6,21] and Kenneth S. Carslaw[1]

Affiliations:

[1]School of Earth and Environment, University of Leeds, LS2 9JT, UK.

[2]European Organization for Nuclear Research (CERN), 1211 Geneva, Switzerland.

[3]Goethe-University Frankfurt am Main, Institute for Atmospheric and Environmental Sciences, Altenhöferallee 1, 60438 Frankfurt am Main, Germany.

[4]Helsinki Institute of Physics, FI-00014 Helsinki, Finland.

[5]Laboratoire de Physique des lasers, Atomes et Molécules (PhLAM) Université Lille 1, UMR 8523 CNRS, 59655 Villeneuve d'Ascq, France.

[6]Department of Physics, P.O. Box 64, FI-00014 University of Helsinki, Finland.

[7]Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen, Switzerland.

[8]Institute for Advanced Sustainability Studies, Berliner Strasse 130, D-14467 Potsdam, Germany.

[9]Institute of Ion Physics and Applied Physics, Leopold-Franzens University, Technikerstraße 25, 6020, Innsbruck, Austria.

[10]Department of Oceanography, University of Hawaii, 1000 Pope Rd., Honolulu, HI 96822, USA.

[11]Center for Atmospheric Particle Studies, Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15213, USA.

[12]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA.

[13]Ionicon GesmbH, 6020 Innsbruck, Austria.

[14]Faculty of Physics, University of Vienna, Boltzmanngasse 5,1090 Vienna, Austria.

[15]University of Eastern Finland, P.O. Box 1627, 70211 Kuopio, Finland.

[16]Lebedev Physical Institute, Solar and Cosmic Ray Research Laboratory, 119991 Moscow,

Russia.
[17]Schools of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA.
[18]ICE-HT, Foundation for Research and Technology, Hellas, 26504 Patras, Greece.
[19]Institute for Environmental Research and Sustainable Development, National Observatory of Athens, I. Metaxa & Vas. Pavlou, 15236 Palea Penteli, Greece.
[20]CENTRA-SIM, University of Lisbon and University of Beira Interior, 1749-016 Lisbon, Portugal.
[21]Aerodyne Research Inc., Billerica, MA 01821, USA.

[||]These authors contributed equally to this work.
[*]To whom correspondence should be addressed; E-mail: hamish.gordon@cern.ch.
[†] Present address: Finnish Meteorological Institute, Atmospheric Research Centre of Eastern Finland, PL 1627, 70211 Kuopio, Finland.
[‡]Present address: Chemical Sciences Division, Earth Systems Research Laboratory, 325 Broadway, NOAA, Boulder, CO 80305, USA and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309, USA.
[§]Present address: ONERA -The French Aerospace Lab, F-91123 Palaiseau, France.
[a]Present address: School of Engineering and Applied Sciences, Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA.
[b]Present address: Chemistry Department, University of California, 1102 Natural Science II, Irvine, CA 92697, USA.
[c]Present address: Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195, USA.

Abstract: Fundamental questions remain about the origin of newly formed atmospheric aerosol particles because data from laboratory measurements have been insufficient to build global models. In contrast, gas-phase chemistry models have been based on laboratory kinetics measurements for decades. Here we build a global model of aerosol formation using extensive laboratory-measured nucleation rates involving sulfuric acid, ammonia, ions and organic compounds. The simulations and a comparison with atmospheric observations show that nearly all nucleation throughout the present-day atmosphere involves ammonia or biogenic organic compounds in addition to sulfuric acid. A significant fraction of nucleation involves ions, but the relatively weak dependence on ion concentrations indicates that for the processes studied variations in cosmic ray intensity do not significantly affect climate via nucleation in the present-day atmosphere.

Main Text: Nucleation of particles occurs throughout Earth's atmosphere by condensation of trace vapors (*1–3*). Around 40-70% of global cloud condensation nuclei (CCN) (*4–6*) are thought to originate as nucleated particles, so the process has a major influence on the microphysical properties of clouds and the radiative balance of the global climate system. However, laboratory measurements are needed to disentangle and quantify the processes that contribute to particle formation, and very few laboratory measurements exist under atmospheric conditions (*7–10*). This leaves open fundamental questions concerning the origin of particles on a global scale. First, it is not known whether nucleation is predominantly a neutral process, as assumed in most models (*11–13*), or whether atmospheric ions are important (*6, 14–16*). This relates to the question of whether solar-modulated galactic cosmic rays (GCRs) affect aerosols, clouds and climate (*17–21*). Second, the lack of measurements of nucleation rates at low temperatures means that the origin of new particles in the vast regions of the cold free troposphere has not yet been experimentally established. Third, whereas it has been shown that nucleation of sulfuric acid-water particles in the boundary layer requires stabilising molecules such as ammonia, amines or oxidized organic compounds (*7, 22–25*), it is not yet known from existing experimental data over how much of the troposphere these molecules are important for nucleation. Robust atmospheric models to answer these questions need to be founded on direct measurements of nucleation rates. At present, to simulate nucleation over a very wide range of atmospheric conditions, global models must use theoretical nucleation models (*26, 27*), which can require adjustments to the nucleation rates of several orders of magnitude to obtain reasonable agreement with ambient observations (*28, 29*).

The lack of an experimentally based model of global particle nucleation is in stark contrast to gas phase chemistry of the global atmosphere, which has been based on laboratory kinetics measurements since the 1970s (*30, 31*). Here we build a model of the global aerosol system based on laboratory nucleation rate measurements that is able to explain global particle concentrations without any adjustment to the rates. We derive some selected implications for CCN, cloud albedo and hence Earth's radiative forcing.

Chamber measurements of inorganic nucleation

In Figure 1, we present approximately 350 measurements of ion-induced and neutral particle formation from sulfuric acid (H_2SO_4) and ammonia (NH_3) vapors conducted in the CLOUD chamber at the CERN Proton Synchrotron. To enable globally applicable nucleation rate expressions to be developed, we have combined around 250 earlier measurements (*7, 24, 32*) with around 100 new measurements covering a much wider range of vapor concentrations than was achieved in the previous experiments. We also studied ternary nucleation at temperatures as low as 208 K, typical of the upper troposphere. We combine these 350 inorganic measurements with data on organic-mediated nucleation (*25*) to quantify nucleation rates throughout the troposphere. The experiments were performed under neutral, natural GCR and charged pion beam conditions (Supplementary Material (SM), and Ref. (*33*)). GCRs create ion pairs in the chamber at a rate of about 2 $cm^{-3}s^{-1}$, characteristic of the lower atmosphere, while the controllable pion beam reproduces equilibrium ion-pair concentrations between ground level and the upper troposphere (*34*). Neutral conditions are achieved by removing ions from the chamber with an electric field.

Figure 1 shows how our full dataset of inorganic nucleation rates depends on H_2SO_4, NH_3, temperature and ionization rates. At 208 K, the nucleation rates are up to 10^4 times higher than at 248 K, the lowest temperature investigated in any previous study (*7*). The enhancement of the neutral nucleation rate caused by natural GCR ionization reaches about a factor 15 at temperatures found in the lower troposphere. However, we measure no significant enhancement due to ions at lower temperatures corresponding to the upper troposphere, indicating that evaporation of the corresponding neutral clusters is strongly suppressed. Ammonia mixing ratios of a few pptv greatly enhance the nucleation rate. For example, at 223 K the neutral rate rises by more than a factor 1000 when NH_3 is increased from an estimated 0.05 pptv contaminant level to 6 pptv (Fig. 2B). The negative ion cluster composition (SM Fig. S1, Ref. (*35*)) confirms that NH_3 molecules are participating in and enhancing ion-induced nucleation, although binary nucleation of sulfuric acid and water without ammonia cannot be neglected.

While most of our measurements were conducted at 38% relative humidity (RH), the dependence of nucleation rates on RH was also measured (SM Sect. 9), and found to be stronger than the dependence on ion concentrations but weaker than that on other factors. At 223 and 208 K, typical of the upper free troposphere, a change in RH between 20 and 100%

induces at most a factor 5, and typically 50-100%, change in the nucleation rate, while ambient atmospheric concentrations of H_2SO_4 and NH_3 vary over many orders of magnitude. At 298 K the nucleation rate increases by around a factor 10 between 40% and 80% RH, but this does not strongly affect CCN concentrations (see model results below).

The inorganic nucleation rates are parameterised in four dimensions (temperature, $[H_2SO_4]$, $[NH_3]$ and ion concentrations) and fitted to our full dataset of 350 inorganic measurements. The RH dependence was not included in the fit due to insufficient data, although we tested its effect in separate model sensitivity studies, described below. Because one of our objectives is to determine the relative importance of binary and ternary nucleation in the global atmosphere, we used the molecular composition of the charged nucleating clusters from APi-TOF mass spectrometry measurements to unambiguously verify the amount of ammonia or organic species in, or their absence from, the charged nucleating clusters (*35, 36*) (SM Sect. 6). Guided by these mass spectra, the four-dimensional global fit enables us to determine the dependence on trace gas concentrations and ions even though the data are quite sparse in any one dimension. Over almost the full range of the measurements (see SM Sect. 8) the nucleation rate varies approximately as $[H_2SO_4]^3$, linearly with $[NH_3]$ and linearly with ion concentration.

Global particle formation pathways

The CLOUD nucleation rate measurements allow us to evaluate the global importance of competing particle sources for the first time based on experimental data. The model is described in SM Sects. 11-16. The total nucleation rate is determined by adding the inorganic rates (previous section) to the neutral and ion-induced ternary organic H_2SO_4-BioOxOrg-H_2O nucleation rates from our earlier CLOUD chamber measurements reported in Ref. (*25*). Here BioOxOrg is a proxy for α-pinene oxidation products and we use the term “ternary” by treating them as a single class of vapors.

Figure 2 shows that the binary nucleation rates peak in the upper troposphere, consistent with earlier models that considered only binary neutral or ion-induced H_2SO_4-H_2O nucleation above the boundary layer (*6, 11–13*). However, we find that the fractional contributions to the production rate of 3 nm particles below 15 km altitude are 15% binary (2.6% neutral, 12% ion-induced), 65% ternary inorganic with ammonia (54% neutral and 11% ion-induced) and 21% ternary organic. We are unable to quantify the fraction of ternary organic nucleation that is ion-induced as accurately as for inorganic nucleation (see SM Sect. 15), but we estimate that 28% of all new particles are formed via ion-induced nucleation. Overall, ion-induced nucleation is the dominant process over large regions of the troposphere where particle formation rates are low. Consequently, it produces more particles than neutral nucleation in 67% of the troposphere below 15 km. Thus almost all new particle formation over the entire troposphere involves NH_3 or organic compounds, and much of this is ion-induced.

While our model of global nucleation rates accounts for the most important tropospheric variables, there remain some missing pieces. The most important are that we are unable to fully account for the variation of nucleation rates with relative humidity, we do not include the contribution of amines to nucleation, and we assume that the organic nucleation rate is independent of temperature. The third of these possible variations is not yet constrained by CLOUD laboratory measurements. If we assume a ternary organic rate that increases with decreasing temperature according to theoretical estimates (SM Sects. 10,20), the ternary organic fraction of nucleation increases to 69%. We note that this temperature dependence is likely an extreme estimate because terpene oxidation products are less oxidised at lower temperatures because isomerization rates are lower (*37, 38*). This will offset the increased ease with which highly oxidised organic molecules condense at lower temperatures. An estimate of a more likely temperature dependence (SM Sect. 20) results in a fraction of organic nucleation of 43%. Further numerical studies of the uncertainties in the fractions of nucleation from different pathways are detailed in SM Table S7. As the neutral and ion-induced organic nucleation pathways have different, but unknown, dependencies on temperature (SM Sect. 20), the overall fraction of ion-induced nucleation is affected by this shortcoming. In the sensitivity tests in Table S6, the highest fraction of ion-induced nucleation is around 63% and the lowest is 9%.

Amines can also nucleate with sulphuric acid (*24,39–41*) but they are unlikely to influence nucleation in the free troposphere due to their short atmospheric lifetimes (*42*) and low fluxes. However, they are important in polluted areas of the boundary layer (*43*). A preliminary calculation (SM Sect. 17 and Fig. S14) with a slightly different global model suggests 6% of new particles below 500 m altitude are formed via an amine-driven mechanism, with a large uncertainty range 3-27%. Amine-driven nucleation is almost certainly negligible above 500 m due to the short lifetime of amines in the atmosphere. The amine-driven nucleation has only a minimal effect on CCN concentrations (Fig. S14C) as the highest amine emissions are in polluted areas with high condensation sinks, which suppress nucleation.

When we included a temperature-dependent factor to model the RH dependence of the binary nucle ation rate with a polynomial function (SM Sect. 9), we found a 4.5% change in the concentration of 3 nm particles and a 0.3% change in the concentration of soluble 70 nm diameter particles (approximately representative of CCN) in the troposphere up to 15 km altitude. If we assume the ternary inorganic and organic nucleation rates depend on RH in the same way as the binary rate, we find the change in tropospheric 3 nm particle concentrations increases by 14% and the 70 nm particle concentration increases by 6.5%. At cloud base level, the concentration of soluble 70 nm particles increases by 6.0%. Ternary nucleation should be affected less by relative humidity than binary nucleation, so this change represents an upper bound. All of these numbers are comparable to typical differences between the model and observations.

Evidence from global aerosol measurements

Comparison of the global model results with atmospheric observations helps to establish how different nucleation pathways contribute to global particle concentrations. The simplest inorganic pathway (binary neutral nucleation) systematically underestimates particle concentrations measured in the lower atmosphere, and fails to explain their seasonal variation (SM Sect. 18). Across 35 global surface sites (*44*), including mountain tops, this binary simulation, together with primary particle emisssions, can account for only 31% of the particles observed in the Northern Hemisphere winter and 25% in summer (Fig. S15 in SM). When we include ternary H_2SO_4-NH_3-H_2O nucleation, 65% of particles are explained in winter but only 36% in summer. By further including ternary H_2SO_4-BioOxOrg-H_2O nucleation the modelled seasonal cycle of particle concentrations represents the observations well, explaining 71% of observed particles in winter and also 71% in summer. These comparisons suggest that ternary inorganic nucleation is a major source of particles in the Northern Hemisphere winter whilst ternary organic nucleation is a major source in summer.

We have compared the predictions of the model with aircraft measurements at higher altitude, which is a region of the atmosphere in which new particle formation is frequently modelled by binary nucleation of sulfuric acid. The aircraft campaigns (SM Sect. 18 and references therein) aimed to determine the most favorable chemical and meteorological conditions for nucleation in the troposphere (*45*). Relatively low model resolution prevents us from fully simulating the effects of meteorology on nucleation, especially humidity variations near clouds (*46, 47*). Nevertheless, the full model shows good agreement with observations (Fig. 3B). In contrast, as is the case at the surface, a model with binary neutral nucleation alone can account for only 25% of the observed particle concentrations (Fig. 3C), with especially large biases of up to a factor 5 in the lower troposphere below about 6 km altitude.

In addition to our imperfect coverage of the full parameter space of tropospheric nucleation rates, uncertainties in the model might also affect the confidence in our conclusions about the causes of global nucleation. Tables S6 and S7 (SM) summarize the principal sources of uncertainty in the CLOUD measurements and parameterization, as well as implementation of the parameterization in the global model. The dominant sources of uncertainty, we estimate, are vapor concentrations in the model itself rather than the parameterized nucleation rates. These, and other important sources of uncertainty such as the aerosol microphysical processes, precursor gas and primary aerosol emissions, and removal processes have been studied comprehensively in this model for CCN (*48*) and 3 nm diameter particle concentrations (*49*) by perturbing 28 model parameters in a way that allows combined uncertainties to be quantified. If we assume that the relative effect of these uncertainties on particle concentrations would be similar in the current model, then we can assess where we can be confident that free-tropospheric nucleation is mainly binary and where it is mainly ternary. For the remote southern-most observations south of Australia in Fig. 3 (ACE-1 measurements, see SM Sect. 18), the standard deviation of 3 nm particle concentrations from the 28 uncertainties is about 60% of the mean at 850 m altitude. So the binary neutral model plus one standard deviation would still lie about a factor 5 below the observations. While the binary model is closer to observations in some areas, such as over the Pacific, overall, its low bias versus observations suggests that ternary nucleation (H_2SO_4 with organics or NH_3) is the primary source of particles below about 6 km altitude in the environments that we have analyzed. We therefore conclude that binary nucleation becomes important only at the highest altitudes in the troposphere, and at lower altitudes nucleation is dominated by ternary nucleation.

Implications for the atmosphere

The quantified effects of NH_3, oxidized organic compounds and ions on global particle formation rates enable us to estimate the effect of changes in environmental conditions on climate via nucleation. We tested the effect of changes in the GCR ionization rate that occur between solar maximum and minimum (SM Sect. 13, Ref. (*17*)). Over the solar cycle, the global mean change in CCN at cloud base altitude (915 hPa, usually around 850 m above the surface) is only 0.1% (Fig. 4B) with local changes of no more than 1%. This is expected from the experimentally derived sub-linear dependence of the inorganic nucleation rate on ionization rate (SM Sect. 8) and consistent with previous assessments (*50, 51*). The results in Ref. (*25*) suggest, with a large uncertainty, that organic nucleation is less sensitive to ionization rate than inorganic nucleation, so would be unlikely to substantially increase the effect.

We have also studied the effect of the estimated 80% increase in NH_3 emissions over the industrial period (*52*). To calculate the baseline aerosol-cloud albedo radiative forcing, we simulated pre-industrial aerosol by removing anthropogenic emissions and keeping other model parameters constant, and compared it to our present-day simulation. We then simulated present-day aerosol keeping ammonia concentrations at pre-industrial levels. In this simulation, the present-day global mean CCN concentration at cloud base level is 1.7% lower than in the usual present-day simulation (and locally up to 10-20%, Fig. 4C). Comparing the present-day simulation with pre-industrial ammonia to the pre-industrial simulation allows us to calculate the aerosol-cloud albedo forcing without the effect of ammonia. We can infer that ammonia has led to a strengthening of the anthropogenic aerosol-cloud radiative forcing from $-0.62\ \mathrm{Wm}^{-2}$ to $-0.66\ \mathrm{Wm}^{-2}$. The $0.04\ \mathrm{Wm}^{-2}$ change in global mean forcing is within the uncertainty of forcing previously calculated for this model (*53*). However, the effect of ammonia on nucleation is a new process in the model, so the entire probability distribution of forcing reported in Ref. (*53*) would be shifted to lower values.

Global aerosol concentrations may be affected by future temperature changes via the temperature dependence of the formation rates. When we increase the temperatures used to calculate the inorganic nucleation rate by 2.2 K (the projected global mean change by 2100 (*54*)), mean CCN concentrations decrease by 1.0% at cloud base (locally 10%) and cause a radiative effect of 0.02 $\mathrm{W m^{-2}}$. Therefore a temperature-driven climate feedback via changes in inorganic nucleation (*55*) is likely to be small compared to the large greenhouse gas forcings that are projected to occur by 2100. It also shows that global inorganic aerosol nucleation provides a pervasive source of CCN that is relatively insensitive to environmental perturbation. The effect of rising global temperatures on organic ternary nucleation and CCN is less straightforward to calculate because there is probably compensation between decreasing nucleation rates (so far not measured in the laboratory) and rising biogenic vapor emissions. Available observations suggest the net effect could be to increase particle concentrations (*56*).

Conclusions

Atmospheric aerosol nucleation has been studied for over 20 years, but the difficulty of performing laboratory nucleation rate measurements close to atmospheric conditions means that global model simulations have not been directly based on experimental data. This contrasts with chemical transport modeling, which is well founded on reaction rate constants measured under controlled laboratory conditions over the past few decades (*57*). The multi-component inorganic and organic chemical system is highly complex and is likely to be impossible to adequately represent in classical nucleation theories, just as *ab initio* prediction of reaction rate constants remains largely out of reach. This highlights the importance of replacing theoretical calculations with laboratory measurements as we have done here. The CERN CLOUD measurements comprise the most comprehensive laboratory measurements of aerosol nucleation rates so far achieved, and the only measurements under conditions equivalent to the free and upper troposphere.

The results lead to a new understanding of global particle formation based almost entirely on ternary rather than binary nucleation, with ions playing a major but sub-dominant role. Our results suggest that about 43% of cloud-forming aerosol particles in the present-day atmosphere originate from nucleation, which is similar to a previous estimate of 45% using the same chemical transport model and non-experimental nucleation rates (*4*) (SM Sect. 16) and broadly consistent with other studies (*5, 6*). An experimentally based model of global nucleation provides a basis for understanding how this complex system of inorganic and organic molecules responds to changes in trace gas emissions and environmental factors, and therefore how these factors affect past and future climate.

Acknowledgments:

We would like to thank CERN for supporting CLOUD with important technical and financial resources, and for providing a particle beam from the CERN Proton Synchrotron. We also thank P. Carrie, L.-P. De Menezes, J. Dumollard, K. Ivanova, F. Josa, I. Krasin, R. Kristic, A. Laassiri, O.S. Maksumov, B. Marichy, H. Martinati, S.V. Mizin, R. Sitals, H.U. Walther, A. Wasem and M. Wilhelmsson for their important contributions to the experiment. The computer modeling simulations were performed on ARC1 and ARC2, part of the High Performance Computing facilities at the University of Leeds, UK. This work also made use of the POLARIS facility of the N8 HPC Centre of Excellence, provided and funded by the N8 consortium and EPSRC (Grant No.EP/K000225/1). The Centre is co-ordinated by the Universities of Leeds and Manchester. This research has received funding from the EC Seventh Framework Programme (Marie Curie Initial Training Networks 'CLOUD- ITN' (no. 215072) and 'CLOUD-TRAIN' (no. 316662)), ERC-Starting MOCAPAF grant no. 5736 and ERC Advanced 'ATMNUCLE' grant no. 227463, the German Federal Ministry of Education and Research (project nos. 01LK0902A and 01LK1222A), the Swiss National Science Foundation (project nos. 200020 135307 and 206620 141278), the Academy of Finland (Center of Excellence project no. 1118615 and other projects 135054, 133872, 251427, 139656, 139995, 137749, 141217, 141451, 138951), the Finnish Funding Agency for Technology and Innovation, the V.is.l. Foundation, the Nessling Foundation, the Austrian Science Fund (FWF; project no. J3198- N21), the Portuguese Foundation for Science and Technology (project no. CERN/FP/116387/2010), the Swedish Research Council, Vetenskapsrådet (grant 2011-5120), the Presidium of the Russian Academy of Sciences and Russian Foundation for Basic Research (grants 08-02-91006-CERN and 12-02-91522-CERN), the U.S. National Science Foundation (grants AGS1136479, AGS1447056, AGC1439551 and CHE1012293), the U.S. Department of Energy (grant DE-SC0014469), the PEGASOS project funded by the European Commission under the Framework Programme 7 (FP7-ENV- 2010-265148), the Davidow Foundation, and the NERC GASSP project under grant NE/J024252/1. We acknowledge financial support from the Royal Society Wolfson Merit Award. The nucleation rates used in our manuscript are available online as a csv file, separately to the SM text.

Figure Captions

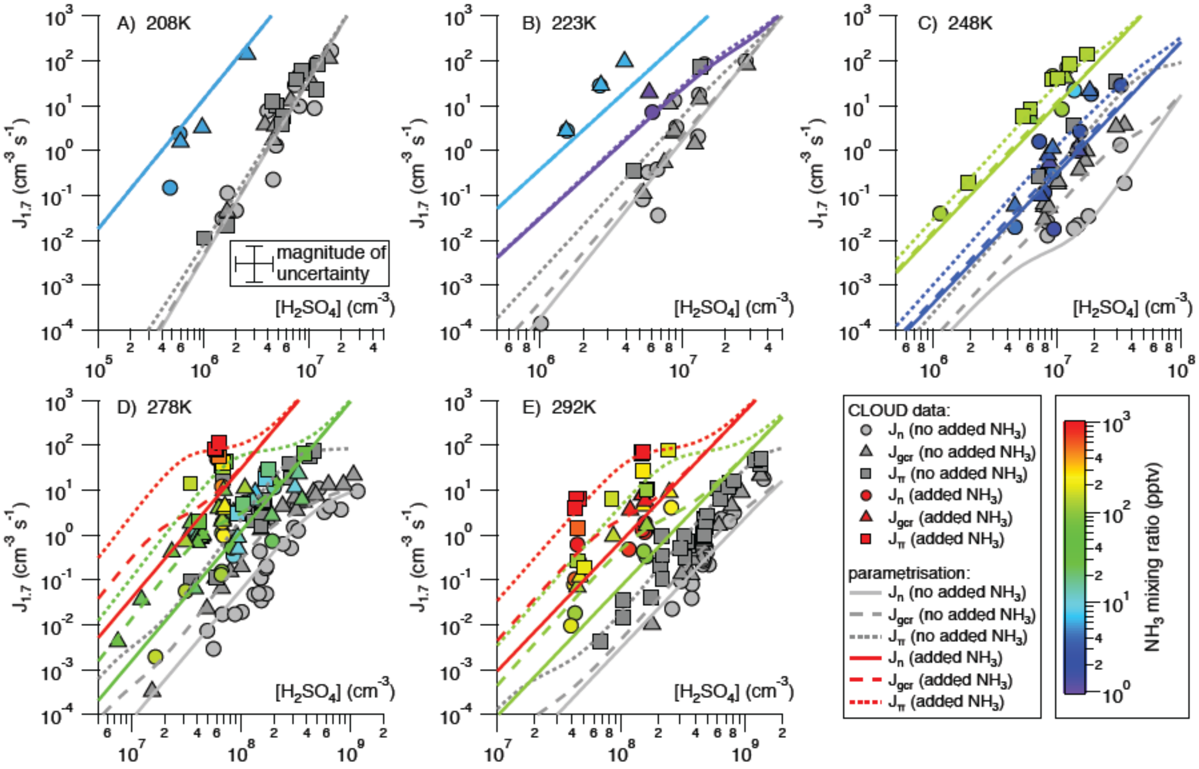

Figure 1. Measured and parameterized nucleation rates. Neutral, GCR and pion-beam nucleation rates are shown at 1.7 nm mobility diameter as a function of sulfuric acid

concentration. Rates at (A) 208 K, (B) 223 K, (C) 248 K, (D) 278 K, and (E) 292 K. The symbols show measured values of nucleation rates: circles for neutral rates (q = 0 cm^{-3}s^{-1}); triangles for GCR rates (q = 2 cm^{-3}s^{-1}); squares for pion beam rates (q around 75 cm^{-3}s^{-1}). The lines show parameterized nucleation rates (SM Sect. 8): solid lines for neutral rates; dashed lines for GCR rates; dotted lines for pion beam rates. Grey symbols and lines indicate contaminant concentrations of NH_3 below the detection limit of the instruments (SM Sect. 6), while colored symbols and lines represent measurements at NH_3 concentrations indicated by the color scale. For clarity, the uncertainties on each data point are not shown, but the overall uncertainty of a factor 2.5 on nucleation rate and a factor 1.5 on [H_2SO_4] is shown separately from the real data in subfigure (A). The contaminant level of ammonia increases as temperature increases. This explains why the ionisation effect without added ammonia at 292 K is smaller than that 278 K and the nucleation rates without added ammonia are similar at these temperatures.

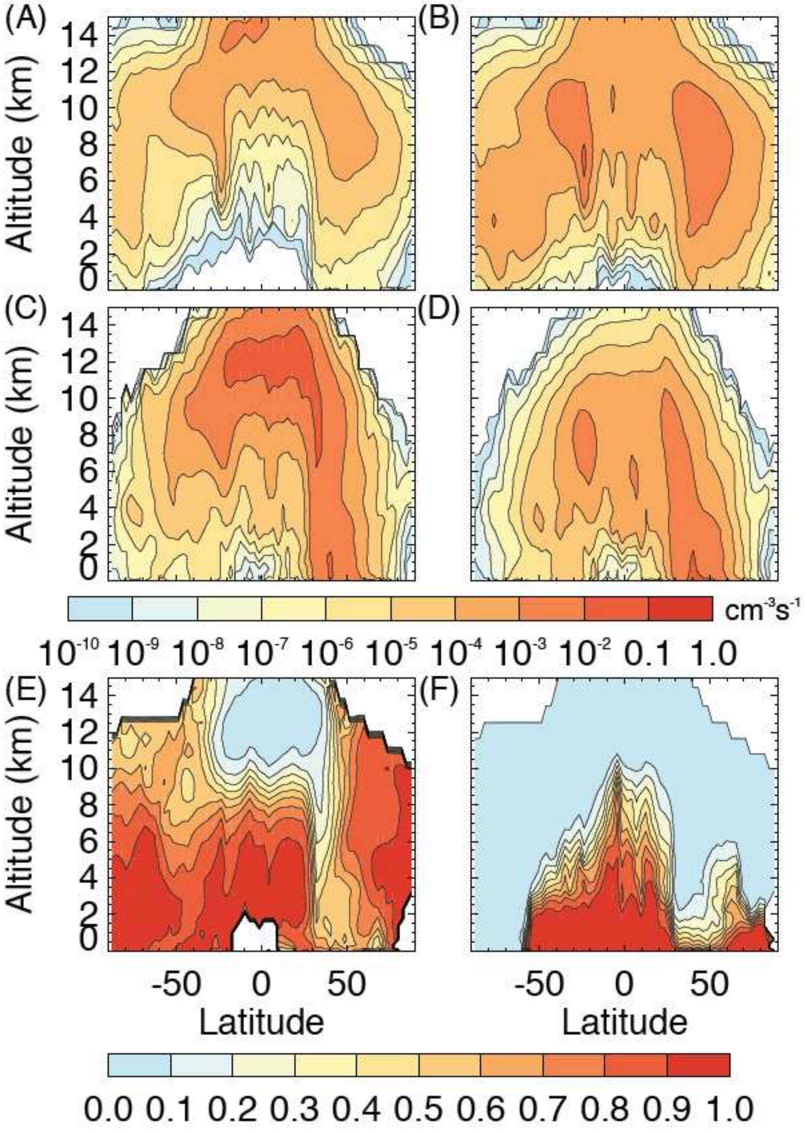

Figure 2. Modeled zonal and annual mean particle formation rates, in $cm^{-3}s^{-1}$, at 3 nm diameter. (A) Binary (H_2SO4-H_2O) neutral nucleation rate; (B) binary ion-induced nucleation rate; (C) ternary (H_2SO_4-NH_3-H_2O) neutral nucleation rate; (D) ternary ion-induced nucleation; (E) ion-induced fraction of inorganic nucleation; (F) fraction of all nucleation from ternary organic nucleation (H_2SO_4- BioOxOrg-H_2O). In panels (E) and (F) the model data are shown only where the overall mean nucleation rate exceeds 10^{-6} $cm^{-3}s^{-1}$.

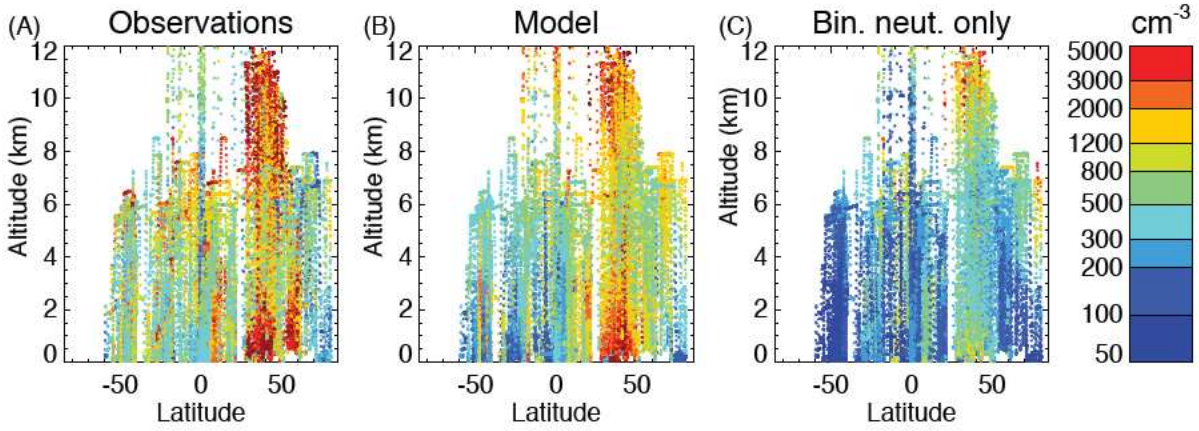

Figure 3. Comparison of measured and modeled particle concentrations: (A) Measured 3 nm diameter particle concentrations versus latitude and altitude (SM Fig. S17, Ref. (*45*)). (B) Modeled particle concentrations (all processes). (C) Modeled particle concentrations including only primary particle emissions and binary neutral nucleation of sulfuric acid and water. Note that modeled particle concentrations in (C) are much higher than the concentrations that result from the binary-only pathway in the full model because the losses due to the condensation sink for these particles in the full model are higher than those in the binary-only model.

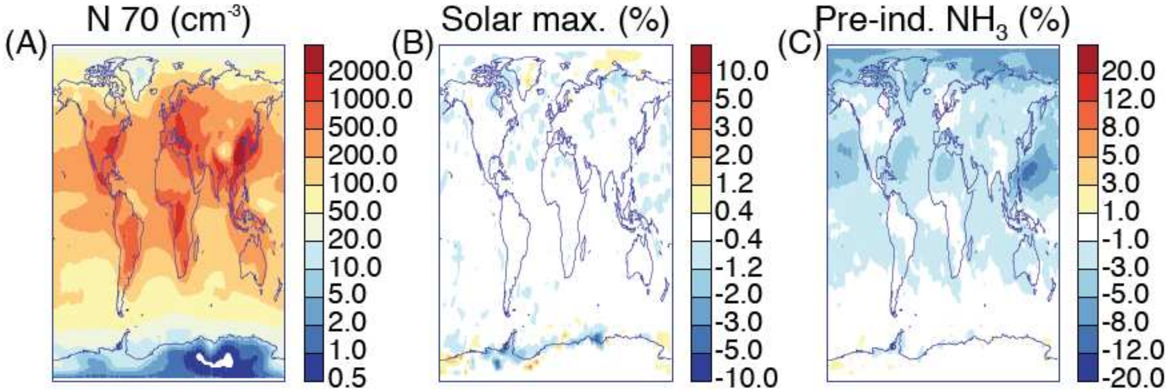

Figure 4. Modeled present-day CCN concentrations and the effect of perturbations. Here hygroscopic particles above 70 nm diameter are used as a proxy for CCN. (A) Annual mean CCN concentrations at approximate cloud base altitude (915 hPa). (B) Effect of changing the heliospheric modulation potential from solar minimum to maximum. (C) Effect of reducing

ammonia concentrations to pre-industrial levels. Perturbations are shown as percentage changes from the baseline shown in panel (A) where concentrations are higher than 5 cm^{-3}.

References and Notes:

1. M. Kulmala, L. Laakso, K. E. J. Lehtinen, I. Riipinen, M. Dal Maso, T. Anttila, V. M. Kerminen, U. Hõrrak, M. Vana, H. Tammet, Initial steps of aerosol growth, *Atmospheric Chemistry and Physics* **4**, 2553–2560 (2004).
2. C. A. Brock, P. Hamill, J. C. Wilson, H. H. Jonsson, K. R. Chan, Particle formation in the upper tropical troposphere: A source of nuclei for the stratospheric aerosol, *Science* **270**, 1650-1653 (1995).
3. A. D. Clarke, Atmospheric nuclei in the remote free-troposphere, *Journal of Atmospheric Chemistry* **14**, 479–488 (1992).
4. J. Merikanto, D. V. Spracklen, G. W. Mann, S. J. Pickering, K. S. Carslaw, Impact of nucleation on global CCN, *Atmospheric Chemistry and Physics* **9**, 8601-8616 (2009).
5. M. Wang, J. E. Penner, Aerosol indirect forcing in a global model with particle nucleation, *Atmospheric Chemistry and Physics* **9**, 239–260 (2009).
6. F. Yu, G. Luo, Simulation of particle size distribution with a global aerosol model: contribution of nucleation to aerosol and CCN number concentrations, *Atmospheric Chemistry and Physics* **9**, 7691-7710 (2009).
7. J. Kirkby, J. Curtius, J. Almeida, E. Dunne, J. Duplissy, S. Ehrhart, A. Franchin, S. Gagne, L. Ickes, A. Kürten, A. Kupc, A. Metzger, F. Riccobono, L. Rondo, S. Schobesberger, G. Tsagkogeorgas, D. Wimmer, A. Amorim, F. Bianchi, M. Breitenlechner, A. David, J.

Dommen, A. Downard, M. Ehn, R.C. Flagan, S. Haider, A. Hansel, D. Hauser, W. Jud, H. Junninen, F. Kreissl, A. Kvashin, A. Laaksonen, K. Lehtipalo, J. Lima, E. R. Lovejoy, V. Makhmutov, S. Mathot, J. Mikkila, P. Minginette, R. Mogo, T. Nieminen, A. Onnela, P. Pereira, T. Petäjä, R. Schnitzhofer, J. H. Seinfeld, M. Sipilä, Y. Stozhkov, F. Stratmann, A. Tomé, J. Vanhanen, Y. Viisanen, A. Vrtala, P. E. Wagner, H. Walther, E. Weingartner, H. Wex, P. M. Winkler, K. S. Carslaw, D. R. Worsnop, U. Baltensperger, M. Kulmala, Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, *Nature* **476**, 429-433 (2011).

8. R. Zhang, I. Suh, J. Zhao, D. Zhang, E. C. Fortner, X. Tie, L. T. Molina, M. J. Molina, Atmospheric new particle formation enhanced by organic acids, *Science* **304**, 1487-1490 (2004).

9. S. M. Ball, D. R. Hanson, F. L. Eisele, P. H. McMurry, Laboratory studies of particle nucleation: Initial results for H_2SO_4, H_2O, and NH_3 vapors, *Journal of Geophysical Research: Atmospheres* **104**, 23709–23718 (1999).

10. D. R. Benson, J. H. Yu, A. Markovich, S.-H. Lee, Ternary homogeneous nucleation of H_2SO_4, NH_3, and H_2O under conditions relevant to the lower troposphere, *Atmospheric Chemistry and Physics* **11**, 4755–4766 (2011).

11. R. Makkonen, A. Asmi, H. Korhonen, H. Kokkola, S. Järvenoja, P. Räisänen, K. E. J. Lehtinen, A. Laaksonen, V.-M. Kerminen, H. Järvinen, U. Lohmann, R. Bennartz, J. Feichter, M. Kulmala, Sensitivity of aerosol concentrations and cloud properties to nucleation and secondary organic distribution in ECHAM5-HAM global circulation model, *Atmospheric Chemistry and Physics* **9**, 1747– 1766 (2009).

12. P. J. Adams, J. H. Seinfeld, Predicting global aerosol size distributions in general circulation models, *Journal of Geophysical Research: Atmospheres* **107**, AAC 4-1–AAC 4-23 (2002).

13. D. V. Spracklen, K. J. Pringle, K. S. Carslaw, M. P. Chipperfield, G. W. Mann, A global off-line model of size-resolved aerosol microphysics: I. model development and prediction of aerosol properties, *Atmospheric Chemistry and Physics* **5**, 2227-2252 (2005).

14. S.-H. Lee, J. M. Reeves, J. C. Wilson, D. E. Hunton, A. A. Viggiano, T. M. Miller, J. O. Ballenthin, L. R. Lait, Particle formation by ion nucleation in the upper troposphere and lower stratosphere, *Science* **301**, 1886–1889 (2003).

15. J. Kazil, P. Stier, K. Zhang, J. Quaas, S. Kinne, D. O'Donnell, S. Rast, M. Esch, S. Ferrachat, U. Lohmann, J. Feichter, Aerosol nucleation and its role for clouds and Earth's radiative forcing in the aerosol-climate model ECHAM5-HAM, *Atmospheric Chemistry and Physics* **10**, 10733-10752 (2010).

16. M. Kulmala, H. Vehkamäki, T. Petäjä, M. Dal Maso, A. Lauri, V.-M. Kerminen, W. Birmili, P. H. McMurry, Formation and growth rates of ultrafine atmospheric particles: a review of observations, *Journal of Aerosol Science* **35**, 143–176 (2004).

17. H. Svensmark, E. Friis-Christensen, Variation of cosmic ray flux and global cloud coverage-a missing link in solar-climate relationships, *Journal of Atmospheric and Solar-Terrestrial Physics* **59**, 1225-1232 (1997).

18. G. Bond, B. Kromer, J. Beer, R. Muscheler, M. N. Evans, W. Showers, S. Hoffmann, R. Lotti-Bond, I. Hajdas, G. Bonani, Persistent solar influence on North Atlantic climate during the Holocene, *Science* **294**, 2130-2136 (2001).

19. U. Neff, S. J. Burns, A. Mangini, M. Mudelsee, D. Fleitmann, A. Matter, Strong coherence

between solar variability and the monsoon in Oman between 9 and 6 kyr ago, *Nature* **411**, 290-293 (2001).

20. K. S. Carslaw, R. G. Harrison, J. Kirkby, Cosmic rays, clouds, and climate, *Science* **298**, 1732-1737 (2002).
21. J. Kirkby, Cosmic rays and climate, *Surveys in Geophysics* **28**, 333-375 (2007).
22. R. Zhang, I. Suh, J. Zhao, D. Zhang, E. C. Fortner, X. Tie, L. T. Molina, M. J. Molina, Atmospheric new particle formation enhanced by organic acids, *Science* **304**, 1487-1490 (2004).
23. M. Chen, M. Titcombe, J. Jiang, C. Jen, C. Kuang, M. L. Fischer, F. L. Eisele, J. I. Siepmann, D. R. Hanson, J. Zhao, P. H. McMurry, Acid-base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer, *Proceedings of the National Academy of Sciences* **109**, 18713-18718 (2012).
24. J. Almeida, S. Schobesberger, A. Kürten, I. K. Ortega, O. Kupiainen-Määttä,, A. P. Praplan, A. Adamov, A. Amorim, F. Bianchi, M. Breitenlechner, A. David, J. Dommen, N. M. Donahue, A. Downard, E. Dunne, J. Duplissy, S. Ehrhart, R. C. Flagan, A. Franchin, R. Guida, J. Hakala, A. Hansel, M. Heinritzi, H. Henschel, T. Jokinen, H. Junninen, M. Kajos, J. Kangasluoma, H. Keskinen, A. Kupc, T. Kurtén, A. N. Kvashin, A. Laaksonen, K. Lehtipalo, M. Leiminger, J. Leppa, V. Loukonen, V. Makhmutov, S. Mathot, M. J. McGrath, T. Nieminen, T. Olenius, A. Onnela, T. Petaja, F. Riccobono, I. Riipinen, M. Rissanen, L. Rondo, T. Ruuskanen, F. D. Santos, N. Sarnela, S. Schallhart, R. Schnitzhofer, J. H. Seinfeld, M. Simon, M. Sipilä, Y. Stozhkov, F. Stratmann, A. Tomé, J. Tröstl, G. Tsagkogeorgas, P. Vaattovaara, Y. Viisanen, A. Virtanen, A. Vrtala, P. E. Wagner, E. Weingartner, H. Wex, C. Williamson, D. Wimmer, P. Ye, T. Yli-Juuti, K. S.

Carslaw, M. Kulmala, J. Curtius, U. Baltensperger, D. R. Worsnop, H. Vehkamäki, J. Kirkby, Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature* **502**, 359–363 (2013). Letter.

25. F. Riccobono, S. Schobesberger, C. E. Scott, J. Dommen, I. K. Ortega, L. Rondo, J. a. Almeida, A. Amorim, F. Bianchi, M. Breitenlechner, A. David, A. Downard, E. M. Dunne, J. Duplissy, S. Ehrhart, R. C. Flagan, A. Franchin, A. Hansel, H. Junninen, M. Kajos, H. Keskinen, A. Kupc, A. Kürten, A. N. Kvashin, A. Laaksonen, K. Lehtipalo, V. Makhmutov, S. Mathot, T. Nieminen, A. Onnela, T. Petäjä, A. P. Praplan, F. D. Santos, S. Schallhart, J. H. Seinfeld, M. Sipilä, D. V. Spracklen, Y. Stozhkov, F. Stratmann, A. Tom, G. Tsagkogeorgas, P. Vaattovaara, Y. Viisanen, A. Vrtala, P. E. Wagner, E. Weingartner, H. Wex, D. Wimmer, K. S. Carslaw, J. Curtius, N. M. Donahue, J. Kirkby, M. Kulmala, D. R. Worsnop, U. Baltensperger, Oxidation products of biogenic emissions contribute to nucleation of atmospheric particles, *Science* **344**, 717-721 (2014).

26. H. Vehkamäki, M. Kulmala, I. Napari, K. E. J. Lehtinen, C. Timmreck, M. Noppel, A. Laaksonen, An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions, *Journal of Geophysical Research: Atmospheres* **107**, AAC 3-1–AAC 3-10 (2002). 4622.

27. I. Napari, M. Noppel, H. Vehkamäki, M. Kulmala, Parametrization of ternary nucleation rates for $H_2SO_4 - NH_3 - H_2O$ vapors, *Journal of Geophysical Research* **107**, 6 (2002).

28. S. D. D'Andrea, S. A. K. Häkkinen, D. M. Westervelt, C. Kuang, E. J. T. Levin, V. P. Kanawade, W. R. Leaitch, D. V. Spracklen, I. Riipinen, J. R. Pierce, Understanding global secondary organic aerosol amount and size-resolved condensational behavior, *Atmospheric Chemistry and Physics* **13**, 11519–11534 (2013).

29. J. Jung, C. Fountoukis, P. J. Adams, S. N. Pandis, Simulation of in situ ultrafine particle formation in the eastern United States using PMCAMx-UF, *Journal of Geophysical Research: Atmospheres* **115**, D03203 (2010).

30. L. K. Peters, A. A. Jouvanis, Numerical simulation of the transport and chemistry of CH_4 and CO in the troposphere, *Atmospheric Environment* **13**, 1443 - 1462 (1979).

31. H. Rodhe, I. Isaksen, Global distribution of sulfur compounds in the troposphere estimated in a height/latitude transport model, *Journal of Geophysical Research: Oceans* **85**, 7401–7409 (1980).

32. J. Duplissy, J. Merikanto, A. Franchin, G. Tsagkogeorgas, J. Kangasluoma, D. Wimmer, H. Vuollekoski, S. Schobesberger, K. Lehtipalo, R. C. Flagan, D. Brus, N. M. Donahue, H. Vehkamäki, J. Almeida, A. Amorim, P. Barmet, F. Bianchi, M. Breitenlechner, E. M. Dunne, R. Guida, H. Henschel, H. Junninen, J. Kirkby, A. Kürten, A. Kupc, A. Määttänen, V. Makhmutov, S. Mathot, T. Nieminen, A. Onnela, A. P. Praplan, F. Riccobono, L. Rondo, G. Steiner, A. Tome, H. Walther, U. Baltensperger, K. S. Carslaw, J. Dommen, A. Hansel, T. Petäjä, M. Sipilä, F. Stratmann, A. Vrtala, P. E. Wagner, D. R. Worsnop, J. Curtius, M. Kulmala, Effect of ions on sulfuric acid-water binary particle formation: 2. Experimental data and comparison with QC-normalized classical nucleation theory, *Journal of Geophysical Research: Atmospheres* **121**, 1752–1775 (2016). 2015JD023539.

33. A. Kürten, F. Bianchi, J. Almeida, O. Kupiainen-Määttä, E. M. Dunne, J. Duplissy, C. Williamson, J. Hakala, A. Hansel, M. Heinritzi, L. Ickes, T. Jokinen, J. Kangasluoma, J. Kim, J. Kirkby, A. Kupc, K. Lehipalo, M. Leiminger, V. Makhmutov, A. Onnela, I. Ortega, T. Petäjä, A. Praplan, F. Riccobono, M. P. Rissanen, L. Rondo, R. Schnitzhofer,

A. Tomé, J. Tröstl, G. Tsagkogeorgas, P. Wagner, D. Wimmer, P. Ye, U. Baltensperger, K. Carslaw, M. Kulmala, J. Curtius, Experimental particle formation rates spanning tropospheric sulfuric acid and ammonia abundances, ion production rates, and temperatures, *Journal of Geophysical Research: Atmospheres* **121** (2016).

34. A. Franchin, S. Ehrhart, J. Leppä, T. Nieminen, S. Gagné, S. Schobesberger, D. Wimmer, J. Duplissy, F. Riccobono, E. M. Dunne, L. Rondo, A. Downard, F. Bianchi, A. Kupc, G. Tsagkogeorgas, K. Lehtipalo, H. E. Manninen, J. Almeida, A. Amorim, P. E. Wagner, A. Hansel, J. Kirkby, A. Kürten, N. M. Donahue, V. Makhmutov, S. Mathot, A. Metzger, T. Petäjä, R. Schnitzhofer, M. Sipilä, Y. Stozhkov, A. Tomé, V.-M. Kerminen, K. Carslaw, J. Curtius, U. Baltensperger, M. Kulmala, Experimental investigation of ion–ion recombination under atmospheric conditions, *Atmospheric Chemistry and Physics* **15**, 7203–7216 (2015).

35. S. Schobesberger, A. Franchin, F. Bianchi, L. Rondo, J. Duplissy, A. Kürten, I. K. Ortega, A. Metzger, R. Schnitzhofer, J. Almeida, A. Amorim, J. Dommen, E. M. Dunne, M. Ehn, S. Gagné, L. Ickes, H. Junninen, A. Hansel, V.-M. Kerminen, J. Kirkby, A. Kupc, A. Laaksonen, K. Lehtipalo, S. Mathot, A. Onnela, T. Petäjä, F. Riccobono, F. D. Santos, M. Sipilä, A. Tomé, G. Tsagkogeorgas, Y. Viisanen, P. E. Wagner, D. Wimmer, J. Curtius, N. M. Donahue, U. Baltensperger, M. Kulmala, D. R. Worsnop, On the composition of ammonia–sulfuric–acid–ion clusters during aerosol particle formation, *Atmospheric Chemistry and Physics* **15**, 55–78 (2015).

36. S. Schobesberger, H. Junninen, F. Bianchi, G. Lönn, M. Ehn, K. Lehtipalo, J. Dommen, S. Ehrhart, I. K. Ortega, A. Franchin, T. Nieminen, F. Riccobono, M. Hutterli, J. Duplissy, J. Almeida, A. Amorim, M. Breitenlechner, A. J. Downard, E. M. Dunne, R.

C. Flagan, M. Kajos, H. Kesk- inen, J. Kirkby, A. Kupc, A. Kürten, T. Kurtén, A. Laaksonen, S. Mathot, A. Onnela, A. P. Pra- plan, L. Rondo, F. D. Santos, S. Schallhart, R. Schnitzhofer, M. Sipilä, A. Tomé, G. Tsagkogeorgas, H. Vehkamäki, D. Wimmer, U. Baltensperger, K. S. Carslaw, J. Curtius, A. Hansel, T. Petäjä, M. Kul- mala, N. M. Donahue, D. R. Worsnop, Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules, *Proceedings of the National Academy of Sciences* **110**, 17223-17228 (2013).

37. J. D. Crounse, L. B. Nielsen, S. Jørgensen, H. G. Kjaergaard, P. O. Wennberg, Autoxidation of organic compounds in the atmosphere, *The Journal of Physical Chemistry Letters* **4**, 3513–3520 (2013).
38. M. Ehn, J. A. Thornton, E. Kleist, M. Sipilä, H. Junninen, I. Pullinen, M. Springer, F. Rubach, R. Tillmann, B. Lee, F. Lopez-Hilfiker, S. Andres, I-H. Acir, M. Rissanen, T. Jokinen, S. Schobesberger, J. Kangasluoma, J. Kontkanen, T. Nieminen, T. Kurtén, L. B. Nielsen, S. Jorgensen, H. G. Kjaergaard, M. Canagaratna, M. Dal Maso, T. Berndt, T. Petäjä, A. Wahner, V-M. Kerminen, M.Kulmala, D. R. Worsnop, J. Wildt, and T. F. Mentel, A large source of low-volatility secondary organic aerosol, *Nature* **506**, 476–479 (2014). Letter.
39. M. E. Erupe, A. A. Viggiano, S.-H. Lee, The effect of trimethylamine on atmospheric nucleation involving H_2SO_4, *Atmospheric Chemistry and Physics* **11**, 4767–4775 (2011).
40. C. N. Jen, P. H. McMurry, D. R. Hanson, Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, *Journal of Geophysical Research: Atmospheres* **119**, 7502–7514 (2014).
41. T. Bergman, A. Laaksonen, H. Korhonen, J. Malila, E. Dunne, T. Mielonen, K. Lehtinen,

T. Kühn, A. Arola, H. Kokkola, Geographical and diurnal features of amine-enhanced boundary layer nucleation, *Journal of Geophysical Research: Atmospheres* **120**, 9606–9624 (2015).

42. X. Ge, A. S. Wexler, S. L. Clegg, Atmospheric amines – Part II. Thermodynamic properties and gas/particle partitioning, *Atmospheric Environment* **45**, 561 - 577 (2011).

43. J. Zhao, J. N. Smith, F. L. Eisele, M. Chen, C. Kuang, P. H. McMurry, Observation of neutral sulfuric acid-amine containing clusters in laboratory and ambient measurements, *Atmospheric Chemistry and Physics* **11**, 10823–10836 (2011).

44. D. V. Spracklen, K. S. Carslaw, J. Merikanto, G. W. Mann, C. L. Reddington, S. Pickering, J. A. Ogren, E. Andrews, U. Baltensperger, E. Weingartner, M. Boy, M. Kulmala, L. Laakso, H. Li- havainen, N. Kivekäs, M. Komppula, N. Mihalopoulos, G. Kouvarakis, S. G. Jennings, C. O'Dowd, W. Birmili, A. Wiedensohler, R. Weller, J. Gras, P. Laj, K. Sellegri, B. Bonn, R. Krejci, A. Laaksonen, A. Hamed, A. Minikin, R. M. Harrison, R. Talbot, J. Sun, Explaining global surface aerosol number concentrations in terms of primary emissions and particle formation, *Atmospheric Chemistry and Physics* **10**, 4775–4793 (2010).

45. A. D. Clarke, V. N. Kapustin, A Pacific aerosol survey, Part I: A decade of data on particle production, transport, evolution, and mixing in the troposphere, *Journal of the Atmospheric Sciences* **59**, 363–382 (2002).

46. A. D. Clarke, J. Varner, F. Eisele, R. Mauldin, D. Tanner, M. Litchy, Particle production in the remote marine atmosphere: Cloud outflow and subsidence during ACE 1, *Journal of Geophysical Research: Atmospheres* **103**, 16397–16409 (1998).

47. A. D. Clarke, F. Eisele, V. N. Kapustin, K. Moore, D. Tanner, L. Mauldin, M. Litchy, B. Lienert, M. Carroll, G. Albercook, Nucleation in the equatorial free troposphere: Favorable environments during PEM-Tropics, *Journal of Geophysical Research: Atmospheres* **104**, 5735–5744 (1999).

48. L. A. Lee, K. J. Pringle, C. L. Reddington, G. W. Mann, P. Stier, D. V. Spracklen, J. R. Pierce, K. S. Carslaw, The magnitude and causes of uncertainty in global model simulations of cloud condensation nuclei, *Atmospheric Chemistry and Physics* **13**, 8879–8914 (2013).

49. K. S. Carslaw, L. A. Lee, C. L. Reddington, G. W. Mann, K. J. Pringle, The magnitude and sources of uncertainty in global aerosol, *Faraday Discuss.* **165**, 495-512 (2013).

50. J. Kazil, K. Zhang, P. Stier, J. Feichter, U. Lohmann, K. O'Brien, The present-day decadal solar cycle modulation of Earth's radiative forcing via charged H_2SO_4/H_2O aerosol nucleation, *Geophysical Research Letters* **39**, 5 (2012).

51. J. R. Pierce, P. J. Adams, Can cosmic rays affect cloud condensation nuclei by altering new particle formation rates? *Geophysical Research Letters* **36**, L09820 (2009).

52. A. F. Bouwman, D. Lee, W. Asman, F. Dentener, K. Van Der Hoek, J. Olivier, A global high-resolution emission inventory for ammonia, *Global Biogeochemical Cycles* **11**, 561–587 (1997).

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

54. U. Cubasch, D. Wuebbles, D. Chen, M. Facchini, D. Frame, N. Mahowald, J.-G. Winther,

Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the IPCC: Introduction (Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013), book section 1, p. 119158.

55. F. Yu, G. Luo, R. P. Turco, J. A. Ogren, R. M. Yantosca, Decreasing particle number concentrations in a warming atmosphere and implications, *Atmospheric Chemistry and Physics* **12**, 2399–2408 (2012).

56. P. Paasonen, A. Asmi, T. Petaja, M. K. Kajos, M. Aijala, H. Junninen, T. Holst, J. P. D. Abbatt, A. Arneth, W. Birmili, H. D. van der Gon, A. Hamed, A. Hoffer, L. Laakso, A. Laaksonen, W. R. Leaitch, C. Plass-Dulmer, S. C. Pryor, P. Raisanen, E. Swietlicki, A. Wiedensohler, D. R. Worsnop, V.-M. Kerminen, M. Kulmala, Warming-induced increase in aerosol number concentration likely to moderate climate change, *Nature Geosci* **6**, 438–442 (2013). Letter.

57. R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O_X, HO_X, NO_X and SO_X species, *Atmospheric Chemistry and Physics* **4**, 1461–1738 (2004).

58. A. Kupc and A. Amorim and J. Curtius and A. Danielczok and J. Duplissy and S. Ehrhart and H. Walther and L. Ickes and J. Kirkby and A. Kürten and J.M. Lima and S. Mathot and P. Minginette and A. Onnela and L. Rondo and P.E. Wagner, A fibre-optic UV system for H_2SO_4 production in aerosol chambers causing minimal thermal effects, *Journal of Aerosol Science* **42**, 532 - 543 (2011).

59. J. Voigtländer, J. Duplissy, L. Rondo, A. Kürten, F. Stratmann, Numerical simulations of

mixing conditions and aerosol dynamics in the CERN CLOUD chamber, *Atmospheric Chemistry and Physics* **12**, 2205–2214 (2012).

60. F. L. Eisele, D. Tanner, Measurement of the gas phase concentration of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, *Journal of Geophysical Research: Atmospheres* **98**, 9001–9010 (1993).

61. A. Kürten, L. Rondo, S. Ehrhart, J. Curtius, Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid, *Journal of Physical Chemistry A* **116**, 6375–6386 (2012).

62. T. Jokinen, M. Sipilä, H. Junninen, M. Ehn, G. Lönn, J. Hakala, T. Petäjä, R. L. Mauldin III, M. Kulmala, D. R. Worsnop, Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF, *Atmospheric Chemistry and Physics* **12**, 4117–4125 (2012).

63. A. Kürten, S. Münch, L. Rondo, F. Bianchi, J. Duplissy, T. Jokinen, H. Junninen, N. Sarnela, S. Schobesberger, M. Simon, M. Sipilä, J. Almeida, A. Amorim, J. Dommen, N. M. Donahue, E. M. Dunne, R. C. Flagan, A. Franchin, J. Kirkby, A. Kupc, V. Makhmutov, T. Petäjä, A. P. Praplan, F. Riccobono, G. Steiner, A. Tomé, G. Tsagkogeorgas, P. E. Wagner, D. Wimmer, U. Baltensperger, M. Kulmala, D. R. Worsnop, J. Curtius, Thermodynamics of the formation of sulfuric acid dimers in the binary (H_2SO_4-H_2O) and ternary (H_2SO4-H_2O-NH_3) system, *Atmospheric Chemistry and Physics* **15**, 10701–10721 (2015).

64. S. Saunders, M. Jenkin, R. Derwent, M. Pilling, World wide web site of a master chemical mechanism (MCM) for use in tropospheric chemistry models, *Atmospheric*

Environment **31**, 1249 - (1997).

65. F. Bianchi, J. Dommen, S. Mathot, U. Baltensperger, On-line determination of ammonia at low pptv mixing ratios in the CLOUD chamber, *Atmospheric Measurement Techniques* **5**, 1719–1725 (2012).

66. A. P. Praplan, F. Bianchi, J. Dommen, U. Baltensperger, Dimethylamine and ammonia measurements with ion chromatography during the CLOUD4 campaign, *Atmospheric Measurement Tech- niques* **5**, 2161–2167 (2012).

67. F. Bianchi, A. P. Praplan, N. Sarnela, J. Dommen, A. Kürten, I. K. Ortega, S. Schobesberger, H. Junninen, M. Simon, J. Tröstl, T. Jokinen, M. Sipilä, A. Adamov, A. Amorim, J. Almeida, M. Breitenlechner, J. Duplissy, S. Ehrhart, R. C. Flagan, A. Franchin, J. Hakala, A. Hansel, M. Heinritzi, J. Kangasluoma, H. Keskinen, J. Kim, J. Kirkby, A. Laaksonen, M. J. Lawler, K. Lehtipalo, M. Leiminger, V. Makhmutov, S. Mathot, A. Onnela, T. Petäjä, F. Riccobono, M. P. Rissanen, L. Rondo, A. Tom, A. Virtanen, Y. Viisanen, C. Williamson, D. Wimmer, P. M. Winkler, P. Ye, J. Curtius, M. Kulmala, D. R. Worsnop, N. M. Donahue, U. Baltensperger, Insight into acid–base nucleation experiments by comparison of the chemical composition of positive, negative, and neutral clusters, *Environmental Science & Technology* **48**, 13675-13684 (2014).

68. D. Wimmer, K. Lehtipalo, T. Nieminen, J. Duplissy, S. Ehrhart, J. Almeida, L. Rondo, A. Franchin, F. Kreissl, F. Bianchi, H. E. Manninen, M. Kulmala, J. Curtius, T. Petäjä, Technical Note: Using DEG-CPCs at upper tropospheric temperatures, *Atmospheric Chemistry and Physics* **15**, 7547–7555 (2015).

69. V.-M. Kerminen, M. Kulmala, Analytical formulae connecting the ‘real’ and the ‘apparent’ nucle- ation rate and the nuclei number concentration for atmospheric nucleation

events, *Journal of Aerosol Science* **33**, 609-622 (2002).

70. S. Mirme, A. Mirme, The mathematical principles and design of the NAIS - a spectrometer for the measurement of cluster ion and nanometer aerosol size distributions, *Atmospheric Measurement Techniques* **6**, 1061–1071 (2013).

71. A. Kürten, C. Williamson, J. Almeida, J. Kirkby, J. Curtius, On the derivation of particle nucleation rates from experimental formation rates, *Atmospheric Chemistry and Physics* **15**, 4063–4075 (2015).

72. J. J. Moré, *Numerical analysis* (Springer, 1978), pp. 105–116.

73. I. K. Ortega, O. Kupiainen, T. Kurtén, T. Olenius, O. Wilkman, M. J. McGrath, V. Loukonen, H. Vehkamäki, From quantum chemical formation free energies to evaporation rates, *Atmospheric Chemistry and Physics* **12**, 225–235 (2012).

74. I. K. Ortega, T. Olenius, O. Kupiainen-Määttä, V. Loukonen, T. Kurtén, H. Vehkamäki, Electrical charging changes the composition of sulfuric acid–ammonia/dimethylamine clusters, *Atmospheric Chemistry and Physics* **14**, 7995–8007 (2014).

75. G. Brasseur, A. Chatel, *Presented at 9th Ann. Meeting of the European Geophys. Soc. Leeds, Great Britain, Aug. 1982* (1983), vol. 1.

76. V.-M. Kerminen, A. S. Wexler, Particle formation due to SO_2 oxidation and high relative humidity in the remote marine boundary layer, *Journal of Geophysical Research: Atmospheres* **99**, 25607– 25614 (1994).

77. M. J. McGrath, T. Olenius, I. K. Ortega, V. Loukonen, P. Paasonen, T. Kurtén, M. Kulmala, H. Vehkamäki, Atmospheric cluster dynamics code: a flexible method for solution of the birth-death equations, *Atmospheric Chemistry and Physics* **12**, 2345–2355 (2012).

78. T. Olenius, S. Schobesberger, O. Kupiainen- Määttä, A. Franchin, H. Junninen, I. K. Ortega, T. Kurtén, V. Loukonen, D. R. Worsnop, M. Kulmala, H. Vehkamäki, Comparing simulated and experimental molecular cluster distributions, *Faraday Discuss.* **165**, 75-89 (2013).

79. D. V. Spracklen, K. J. Pringle, K. S. Carslaw, M. P. Chipperfield, G. W. Mann, A global offline model of size-resolved aerosol microphysics: II. Identification of key uncertainties, *Atmospheric Chemistry and Physics* **5**, 3233-3250 (2005).

80. M. P. Chipperfield, New version of the TOMCAT/SLIMCAT off-line chemical transport model: Intercomparison of stratospheric tracer experiments, *Quarterly Journal of the Royal Meteorological Society* **132**, 1179-1203 (2006).

81. P. T. Manktelow, K. S. Carslaw, G. W. Mann, D. V. Spracklen, The impact of dust on sulfate aerosol, CN and CCN during an East Asian dust storm, *Atmospheric Chemistry and Physics* **10**, 365–382 (2010).

82. A. J. Kettle, M. O. Andreae, Flux of dimethylsulfide from the oceans: A comparison of updated data sets and flux models, *Journal of Geophysical Research* **105**, 26793–26808 (2000).

83. P. D. Nightingale, G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, R. C. Upstill-Goddard, In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochemical Cycles* **14**, 373 (2000).

84. J. Cofala, M. Amann, Z. Klimont, K. Kupiainen, L. Höglund-Isaksson, Scenarios of global anthropogenic emissions of air pollutants and methane until 2030, *Atmospheric*

Environment **41**, 8486– 8499 (2007).

85. A. Guenther, C. N. Hewitt, D. Erickson, R. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W. A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, P. Zimmerman, A global model of natural volatile organic compound emissions, *Journal of Geophysical Research* **100**, 8873 (1995).

86. F. Dentener, S. Kinne, T. Bond, O. Boucher, J. Cofala, S. Generoso, P. Ginoux, S. Gong, J. J. Hoelzemann, A. Ito, L. Marelli, J. E. Penner, J.-P. Putaud, C. Textor, M. Schulz, G. R. van der Werf, J. Wilson, Emissions of primary aerosol and precursor gases in the years 2000 and 1750 prescribed data-sets for AeroCom, *Atmospheric Chemistry and Physics* **6**, 4321–4344 (2006).

87. E. Mårtensson, E. Nilsson, G. de Leeuw, L. Cohen, H.-C. Hansson, Laboratory simulations and parameterization of the primary marine aerosol production, *Journal of Geophysical Research: Atmospheres* **108** (2003).

88. E. C. Monahan, D. E. Spiel, K. L. Davidson, *Oceanic whitecaps* (Springer, 1986), pp. 167–174.

89. S. L. Gong, A parameterization of sea-salt aerosol source function for sub- and super-micron particles, *Global Biogeochemical Cycles* **17**, 7 (2003).

90. J. Ovadnevaite, A. Manders, G. de Leeuw, D. Ceburnis, C. Monahan, A.-I. Partanen, H. Korhonen, C. D. O'Dowd, A sea spray aerosol flux parameterization encapsulating wave state, *Atmospheric Chemistry and Physics* **14**, 1837–1852 (2014).

91. R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr (Chairman), J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement III:

IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *Journal of Physical and Chemical Reference Data* **18**, 881-1097 (1989).

92. R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, IUPAC Subcommittee, Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II: gas phase reactions of organic species, *Atmospheric Chemistry and Physics* **6**, 3625–4055 (2006).

93. P. Tunved, H. Korhonen, J. Ström, H.-C. Hansson, K. E. J. Lehtinen, M. Kulmala, A pseudo- Lagrangian model study of the size distribution properties over Scandinavia: transport from Aspvreten to Värriö, *Atmospheric Chemistry and Physics Discussions* **4**, 7757–7794 (2004).

94. G. W. Mann, K. S. Carslaw, D. V. Spracklen, D. A. Ridley, P. T. Manktelow, M. P. Chipperfield, S. J. Pickering, C. E. Johnson, Description and evaluation of GLOMAP-mode: a modal global aerosol microphysics model for the UKCA composition-climate model, *Geoscientific Model Development* **3**, 519-551 (2010).

95. F. Benduhn, G. W. Mann, K. J. Pringle, D. O. Topping, G. McFiggans, K. S. Carslaw, Size-resolved simulations of the aerosol inorganic composition with the new hybrid dissolution solver HyDiS-1.0 – Description, evaluation and first global modelling results, *Geoscientific Model Development Discussions* **2016**, 1–54 (2016).

96. D. Topping, D. Lowe, G. McFiggans, Partial Derivative Fitted Taylor Expansion: An efficient method for calculating gas-liquid equilibria in atmospheric aerosol particles: 1. Inorganic compounds, *Journal of Geophysical Research: Atmospheres* **114**, D04304 (2009).

97. S. Krupa, Effects of atmospheric ammonia (NH3) on terrestrial vegetation: a review, *Environmental Pollution* **124**, 179 - 221 (2003).

98. K. von Bobrutzki, C. F. Braban, D. Famulari, S. K. Jones, T. Blackall, T. E. L. Smith, M. Blom, H. Coe, M. Gallagher, M. Ghalaieny, M. R. McGillen, C. J. Percival, J. D. Whitehead, R. Ellis, J. Murphy, A. Mohacsi, A. Pogany, H. Junninen, S. Rantanen, M. A. Sutton, E. Nemitz, Field intercomparison of eleven atmospheric ammonia measurement techniques, *Atmospheric Measurement Techniques* **3**, 91–112 (2010).

99. F. Hilton, R. Armante, T. August, C. Barnet, A. Bouchard, C. Camy-Peyret, V. Capelle, L. Clarisse, C. Clerbaux, P.-F. Coheur, A. Collard, C. Crevoisier, G. Dufour, D. Edwards, F. Faijan, N. Fourrié, A. Gambacorta, M. Goldberg, V. Guidard, D. Hurtmans, S. Illingworth, N. Jacquinet-Husson, T. Kerzenmacher, D. Klaes, L. Lavanant, G. Masiello, M. Matricardi, A. McNally, S. Newman, E. Pavelin, S. Payan, E. Péquignot, S. Peyridieu, T. Phulpin, J. Remedios, P. Schlüssel, C. Serio, L. Strow, C. Stubenrauch, J. Taylor, D. Tobin, W. Wolf, D. Zhou, Hyperspectral Earth observation from IASI: Five years of accomplishments, *Bulletin of the American Meteorological Society* **93**, 347–370 (2012).

100. L. Clarisse, C. Clerbaux, F. Dentener, D. Hurtmans, P.-F. Coheur, Global ammonia distribution derived from infrared satellite observations, *Nature Geoscience* **2**, 479–483 (2009).

101. M. Van Damme, L. Clarisse, C. L. Heald, D. Hurtmans, Y. Ngadi, C. Clerbaux, A. J. Dolman, J. W. Erisman, P. F. Coheur, Global distributions, time series and error characterization of atmospheric ammonia (NH3) from IASI satellite observations, *Atmospheric Chemistry and Physics* **14**, 2905– 2922 (2014).

102. I. G. Usoskin, G. A. Kovaltsov, I. A. Mironova, Cosmic ray induced ionization model CRAC:CRII: An extension to the upper atmosphere, *Journal of Geophysical Research* **115**, 6 (2010).

103. A. C. Fraser-Smith, Centered and eccentric geomagnetic dipoles and their poles, 16001985, *Re- views of Geophysics* **25**, 1–16 (1987).

104. K. Zhang, J. Feichter, J. Kazil, H. Wan, W. Zhuo, A. D. Griffiths, H. Sartorius, W. Zahorowski, L. Ramonet, M. Schmidt, C. Yver, R. E. M. Neubert, E. G. Brunke, Radon activity in the lower troposphere and its impact on ionization rate: a global estimate using different radon emissions, *Atmospheric Chemistry and Physics* **11**, 7817-7838 (2011).

105. B. A. Tinsley, The global atmospheric electric circuit and its effects on cloud microphysics, *Reports on Progress in Physics* **71**, 066801 (2008).

106. R. G. Harrison, The global atmospheric electrical circuit and climate, *Surveys in Geophysics* **25**, 441–484 (2004).

107. M. Kulmala, A. Laaksonen, L. Pirjola, Parameterizations for sulfuric acid/water nucleation rates, *Journal of Geophysical Research* **103**, 8301–8307 (1998).

108. M. D. Petters, S. M. Kreidenweis, A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, *Atmospheric Chemistry and Physics* **7**, 1961–1971 (2007).

109. C. E. Scott, A. Rap, D. V. Spracklen, P. M. Forster, K. S. Carslaw, G. W. Mann, K. J. Pringle, L. Kivekäs, M. Kulmala, H. Lihavainen, P. Tunved, The direct and indirect radiative effects of biogenic secondary organic aerosol, *Atmospheric Chemistry and*

Physics **14**, 447–470 (2014).

110. A. Nenes, J. H. Seinfeld, Parameterization of cloud droplet formation in global climate models, *Journal of Geophysical Research: Atmospheres* **108**, 4415 (2003).

111. C. Fountoukis, A. Nenes, Continued development of a cloud droplet formation parameterization for global climate models, *Journal of Geophysical Research: Atmospheres* **110**, D11212 (2005).

112. R. Morales, A. Nenes, H. Jonsson, R. C. Flagan, J. H. Seinfeld, Evaluation of an entraining droplet activation parameterization using in situ cloud data, *Journal of Geophysical Research: Atmospheres* **116**, D15205 (2011).

113. J. M. Edwards, A. Slingo, Studies with a flexible new radiation code. I: Choosing a configuration for a large-scale model, *Quarterly Journal of the Royal Meteorological Society* **122**, 689–719 (1996).

114. A. Rap, C. E. Scott, D. V. Spracklen, N. Bellouin, P. M. Forster, K. S. Carslaw, A. Schmidt, G. Mann, Natural aerosol direct and indirect radiative effects, *Geophysical Research Letters* **40**, 3297–3301 (2013).

115. W. B. Rossow, R. A. Schiffer, Advances in understanding clouds from ISCCP, *Bulletin of the American Meteorological Society* **80**, 2261–2287 (1999).

116. A. Schmidt, K. S. Carslaw, G. W. Mann, A. Rap, K. J. Pringle, D. V. Spracklen, M. Wilson, P. M. Forster, Importance of tropospheric volcanic aerosol for indirect radiative forcing of climate, *Atmospheric Chemistry and Physics* **12**, 7321–7339 (2012).

117. F. Yu, G. Luo, Modeling of gaseous methylamines in the global atmosphere: impacts of

oxidation and aerosol uptake, *Atmospheric Chemistry and Physics* **14**, 12455–12464 (2014).

118. X. Ge, A. S. Wexler, S. L. Clegg, Atmospheric amines- Part I. A review, *Atmospheric Environment* **45**, 524 - 546 (2011).

119. D. V. Spracklen, K. S. Carslaw, M. Kulmala, V. M. Kerminen, G. W. Mann, S. L. Sihto, The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales, *Atmospheric Chemistry and Physics* **6**, 5631-5648 (2006).

120. D. V. Spracklen, K. J. Pringle, K. S. Carslaw, G. W. Mann, P. Manktelow, J. Heintzenberg, Evaluation of a global aerosol microphysics model against size-resolved particle statistics in the marine atmosphere, *Atmospheric Chemistry and Physics* **7**, 2073-2090 (2007).

121. D. V. Spracklen, K. S. Carslaw, M. Kulmala, V.-M. Kerminen, S.-L. Sihto, I. Riipinen, J. Merikanto, G. W. Mann, M. P. Chipperfield, A. Wiedensohler, W. Birmili, H. Lihavainen, Contribution of particle formation to global cloud condensation nuclei concentrations, *Geophysical Research Letters* **35**, L06808 (2008).

122. C. L. Reddington, K. S. Carslaw, D. V. Spracklen, M. G. Frontoso, L. Collins, J. Merikanto, A. Minikin, T. Hamburger, H. Coe, M. Kulmala, P. Aalto, H. Flentje, C. Plass-Dülmer, W. Birmili, A. Wiedensohler, B. Wehner, T. Tuch, A. Sonntag, C. D. O'Dowd, S. G. Jennings, R. Dupuy, U. Baltensperger, E. Weingartner, H.-C. Hansson, P. Tunved, P. Laj, K. Sellegri, J. Boulon, J.-P. Putaud, C. Gruening, E. Swietlicki, P. Roldin, J. S. Henzing, M. Moerman, N. Mihalopoulos, G. Kouvarakis, V. Ždímal, N. Zíková, A. Marinoni, P.

Bonasoni, R. Duchi, Primary versus secondary contributions to particle number concentrations in the European boundary layer, *Atmospheric Chemistry and Physics* **11**, 12007–12036 (2011).

123. A. D. Clarke, S. Howell, P. Quinn, T. Bates, J. Ogren, E. Andrews, A. Jefferson, A. Massling, O. Mayol-Bracero, H. Maring, D. Savoie, G. Cass, INDOEX aerosol: A comparison and summary of chemical, microphysical, and optical properties observed from land, ship, and aircraft, *Journal of Geophysical Research: Atmospheres* **107**, 8033 (2002).

124. H. Singh, W. Brune, J. Crawford, D. Jacob, P. Russell, Overview of the summer 2004 Intercontinental Chemical Transport Experiment–North America (INTEX-A), *Journal of Geophysical Research: Atmospheres* **111** (2006).

125. I. Faloona, S. Conley, B. Blomquist, A. Clarke, V. Kapustin, S. Howell, D. H. Lenschow, A. R. Bandy, Sulfur dioxide in the tropical marine boundary layer: dry deposition and heterogeneous oxidation observed during the Pacific Atmospheric Sulfur Experiment, *Journal of Atmospheric Chemistry* **63**, 13–32 (2009).

126. D. J. Jacob, J. H. Crawford, H. Maring, A. D. Clarke, J. E. Dibb, L. K. Emmons, R. A. Ferrare, C. A. Hostetler, P. B. Russell, H. B. Singh, A. M. Thompson, G. E. Shaw, E. McCauley, J. R. Pederson, J. A. Fisher, The Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) mission: design, execution, and first results, *Atmospheric Chemistry and Physics* **10**, 5191–5212 (2010).

127. R. Wood, C. R. Mechoso, C. S. Bretherton, R. A. Weller, B. Huebert, F. Straneo, B. A. Albrecht, H. Coe, G. Allen, G. Vaughan, P. Daum, C. Fairall, D. Chand, L. Gallardo

Klenner, R. Garreaud, C. Grados, D. S. Covert, T. S. Bates, R. Krejci, L. M. Russell, S. de Szoeke, A. Brewer, S. E. Yuter, S. R. Springston, A. Chaigneau, T. Toniazzo, P. Minnis, R. Palikonda, S. J. Abel, W. O. J. Brown, S. Williams, J. Fochesatto, J. Brioude, K. N. Bower, The VAMOS Ocean-Cloud-Atmosphere-Land Study Regional Experiment (VOCALS-REx): goals, platforms, and field operations, *Atmospheric Chemistry and Physics* **11**, 627–654 (2011)

128. G. W. Mann, K. S. Carslaw, C. L. Reddington, K. J. Pringle, M. Schulz, A. Asmi, D. V. Spracklen, D. A. Ridley, M. T. Woodhouse, L. A. Lee, K. Zhang, S. J. Ghan, R. C. Easter, X. Liu, P. Stier, Y. H. Lee, P. J. Adams, H. Tost, J. Lelieveld, S. E. Bauer, K. Tsigaridis, T. P. C. van Noije, A. Strunk, D. Vignati, N. Bellouin, M. Dalvi, C. E. Johnson, T. Bergman, H. Kokkola, K. von Salzen, F. Yu, G. Luo, A. Petzold, J. Heintzenberg, A. Clarke, J. A. Ogren, J. Gras, U. Baltensperger, U. Kaminski, S. G. Jennings, C. D. O'Dowd, R. M. Harrison, D. C. S. Beddows, M. Kulmala, Y. Viisanen, V. Ulevicius, N. Mihalopoulos, V. Ždímal, M. Fiebig, H.-C. Hansson, E. Swietlicki, J. S. Henzing, Intercomparison and evaluation of global aerosol microphysical properties among AeroCom models of a range of complexity, *Atmospheric Chemistry and Physics* **14**, 4679–4713 (2014).

129. H. E. Manninen, T. Nieminen, E. Asmi, S. Gagné, S. Häkkinen, K. Lehtipalo, P. Aalto, M. Vana, A. Mirme, S. Mirme, U. Hõrrak, C. Plass-Dülmer, G. Stange, G. Kiss, A. Hoffer, N. Törö, M. Moerman, B. Henzing, G. de Leeuw, M. Brinkenberg, G. N. Kouvarakis, A. Bougiatioti, N. Mihalopoulos, C. O'Dowd, D. Ceburnis, A. Arneth, B. Svenningsson, E. Swietlicki, L. Tarozzi, S. Decesari, M. C. Facchini, W. Birmili, A. Sonntag, A. Wiedensohler, J. Boulon, K. Sellegri, P. Laj, M. Gysel, N. Bukowiecki, E. Weingartner, G. Wehrle, A. Laaksonen, A. Hamed, J. Joutsensaari, T. Petäjä, V. M. Kerminen, M. Kulmala,

EUCAARI ion spectrometer measurements at 12 European sites analysis of new particle formation events, *Atmospheric Chemistry and Physics* **10**, 7907-7927 (2010).

130. F. Yu, G. Luo, S. C. Pryor, P. R. Pillai, S. H. Lee, J. Ortega, J. J. Schwab, A. G. Hallar, W. R. Leaitch, V. P. Aneja, J. N. Smith, J. T. Walker, O. Hogrefe, K. L. Demerjian, Spring and summer contrast in new particle formation over nine forest areas in North America, *Atmospheric Chemistry and Physics* **15**, 13993–14003 (2015).

131. J.-P. Pietikäinen, S. Mikkonen, A. Hamed, A. I. Hienola, W. Birmili, M. Kulmala, A. Laaksonen, Analysis of nucleation events in the European boundary layer using the regional aerosol-climate model REMO-HAM with a solar radiation-driven OH-proxy, *Atmospheric Chemistry and Physics* **14**, 11711–11729 (2014).

132. P. Paasonen, T. Nieminen, E. Asmi, H. E. Manninen, T. Petäjä, C. Plass-Dülmer, H. Flentje, W. Birmili, A. Wiedensohler, U. Hõrrak, A. Metzger, A. Hamed, A. Laaksonen, M. C. Facchini, V.-M. Kerminen, M. Kulmala, On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation, *Atmospheric Chemistry and Physics* **10**, 11223–11242 (2010).

133. G. R. Van Der Werf, J. T. Randerson, G. J. Collatz, L. Giglio, Carbon emissions from fires in tropical and subtropical ecosystems, *Global Change Biology* **9**, 547–562 (2003).

134. P. Stier, J. Feichter, S. Kinne, S. Kloster, E. Vignati, J. Wilson, L. Ganzeveld, I. Tegen, M. Werner, Y. Balkanski, M. Schulz, O. Boucher, A. Minikin, A. Petzold, The aerosol-climate model ECHAM5- HAM, *Atmospheric Chemistry and Physics* **5**, 1125–1156 (2005).

135. T. C. Bond, D. G. Streets, K. F. Yarber, S. M. Nelson, J.-H. Woo, Z. Klimont, A technology-based global inventory of black and organic carbon emissions from combustion, *Journal of Geophysical Research: Atmospheres* **109** (2004).

136. R. Andres, A. Kasgnoc, A time-averaged inventory of subaerial volcanic sulfur emissions, *Journal of Geophysical Research: Atmospheres* **103**,