



Contribution of particle formation to global cloud condensation nuclei concentrations

Dominick V. Spracklen,¹ Kenneth S. Carslaw,¹ Markku Kulmala,² Veli-Matti Kerminen,³ Sanna-Liisa Sihto,² Ilona Riipinen,² Joonas Merikanto,¹ Graham W. Mann,¹ Martyn P. Chipperfield,¹ Alfred Wiedensohler,⁴ Wolfram Birmili,⁴ and Heikki Lihavainen³

Received 20 December 2007; revised 17 January 2008; accepted 12 February 2008; published 29 March 2008.

[1] We use a global aerosol microphysics model to predict the contribution of boundary layer (BL) particle formation to regional and global distributions of cloud condensation nuclei (CCN). Including an observationally derived particle formation scheme, where the formation rate of molecular clusters is proportional to gas-phase sulfuric acid to the power one, improves modeled particle size distribution and total particle number concentration at three continental sites in Europe. Particle formation increases springtime BL global mean CCN (0.2% supersaturation) concentrations by 3–20% and CCN (1%) by 5–50%. Uncertainties in particle formation and growth rates must be reduced before the accuracy of these predictions can be improved. These results demonstrate the potential importance of BL particle formation as a global source of CCN. **Citation:** Spracklen, D. V., et al. (2008), Contribution of particle formation to global cloud condensation nuclei concentrations, *Geophys. Res. Lett.*, 35, L06808, doi:10.1029/2007GL033038.

1. Introduction

[2] Aerosols absorb and scatter radiation and influence the properties of clouds through a subset of the aerosol population, which act as cloud condensation nuclei (CCN). Both primary and secondary (nucleated) aerosol particles are potential sources of CCN number, but the relative contribution of each to regional and global CCN is unknown.

[3] Boundary Layer (BL) particle formation events have been observed at many locations around the world ranging from the sub-Arctic through boreal forests to polluted industrial and coastal regions [Kulmala et al., 2004b]. Particles nucleated at nanometer sizes must undergo considerable growth before they can act as CCN, and the loss by various scavenging processes limits the number that grow that large [Pierce and Adams, 2007]. Nevertheless, formation events have been shown to make an important contribution to local CCN concentrations through examination of observed aerosol size distributions before and after a nucleation event [Lihavainen et al., 2003; Kerminen et al., 2005; Laaksonen et al., 2005]. Regional models have shown that particle formation (from a ternary NH₃-H₂SO₄-H₂O nucleation mechanism) can increase CCN concentrations

(at 1% supersaturation) locally over parts of Europe by 40–100% and regionally by 1–10% over a 3 day period [Sotiropoulou et al., 2006]. In Spracklen et al. [2006] we used a global aerosol model to show that nucleation events enhance total particle number concentrations in the remote continental BL by a factor of 2–8 greater than concentrations from primary sources and upper tropospheric (UT) nucleation alone. Here, we extend this analysis to explore the contribution of BL particle formation to regional and global CCN concentrations.

2. Model Description

[4] We use the GLOMAP aerosol microphysics model [Spracklen et al., 2005a, 2005b] which is an extension to the TOMCAT 3-D chemical transport model [Chipperfield, 2006]. GLOMAP has a horizontal resolution of ~2.8° by ~2.8°, 31 vertical levels between the surface and 10 hPa and is forced by ECMWF analyses. GLOMAP includes sulfate (SU), sea-salt (SS), elemental carbon (EC) and organic carbon (OC). We treat two externally mixed distributions, each described by a two-moment sectional scheme with 20 sections spanning 3 nm to 25 μm dry diameter. One distribution, representing freshly emitted primary carbonaceous aerosol, contains OC and EC, is treated as hydrophobic and is not wet scavenged. The other distribution contains SU, SS, EC and OC, is hydrophilic and is wet scavenged. We assume that the first-stage oxidation products of monoterpenes [Guenther et al., 1995] form hydrophilic secondary organic aerosol (SOA) with a yield of 13% [Spracklen et al., 2006]. This yield is important for particle growth to CCN sizes and is increased in a sensitivity study. Hydrophobic particles age to become hydrophilic through condensation of soluble gas-phase species and coagulation with hydrophilic particles.

[5] Implementation of the nucleation scheme in GLOMAP is described by Spracklen et al. [2006]. The formation rate of 1 nm molecular clusters is given by

$$j_1 = A[H_2SO_4] \quad (1)$$

where [H₂SO₄] is the gas-phase sulfuric acid concentration and A is an empirical activation coefficient [Kulmala et al., 2006]. The formation rate of 3 nm particles is calculated using the expression of Kerminen and Kulmala [2002], which takes into account loss of 1 nm clusters onto the existing particles during growth. Particles at 3 nm are added to the smallest size bin of the model. As in the work by Spracklen et al. [2006], we restrict this mechanism to the BL and at higher levels use the binary homogeneous

¹School of Earth and Environment, University of Leeds, Leeds, UK.

²Department of Physical Sciences, University of Helsinki, Helsinki, Finland.

³Finnish Meteorological Institute, Helsinki, Finland.

⁴Leibniz Institute for Tropospheric Research, Leipzig, Germany.

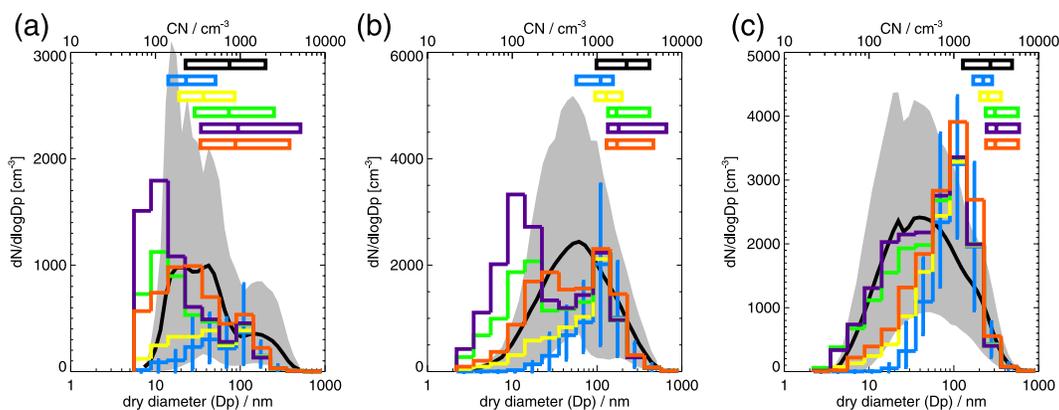


Figure 1. Monthly-mean number-size distributions and total particle number concentrations at (a) Pallas ($67^{\circ}57'N$, $24^{\circ}17'E$); (b) Hyytiälä ($61^{\circ}51'N$, $24^{\circ}7'E$) and (c) Hohenpeissenberg ($47^{\circ}48'N$, $11^{\circ}E$) in April 2000. Observations from CREATE (black), model without (blue) and with BL particle formation (yellow: activation coefficient $A = 2 \times 10^{-8} \text{ s}^{-1}$; green: $A = 2 \times 10^{-7} \text{ s}^{-1}$; purple: $A = 2 \times 10^{-6} \text{ s}^{-1}$, red: $A = 2 \times 10^{-6} \text{ s}^{-1}$ and SOA yield from monoterpenes increased from 13% to 65%). The 10th to 90th percentile variability is shown for the observations (shading) and model (vertical bars). Horizontal boxes show 5th, 50th and 95th percentiles of total particle number concentration, plotted against upper x-axis.

nucleation rate of *Kulmala et al.* [1998]. Evaluation of observed nucleation events suggests that A varies spatially and temporally by over an order of magnitude. In Hyytiälä, Finland (during March–April), calculated values of A varied from $3.3 \times 10^{-8} \text{ s}^{-1}$ to $6.0 \times 10^{-6} \text{ s}^{-1}$ whereas in Heidelberg, Germany (February–April), A varied from $3.2 \times 10^{-6} \text{ s}^{-1}$ to $3.5 \times 10^{-4} \text{ s}^{-1}$ [Sihto et al., 2006; Riipinen et al., 2007]. The reasons for this variability are not understood. Here, we investigate the sensitivity of CCN formation to this uncertainty by varying A between $2 \times 10^{-9} \text{ s}^{-1}$ and $2 \times 10^{-4} \text{ s}^{-1}$. We restrict our study to Northern Hemisphere springtime (March–May), which is the time of year for which extensive evaluation of formation events has occurred.

3. Results

[6] Figure 1 shows number size distributions and total particle number concentrations at 3 surface sites in Europe (Pallas, Finland [Tunved et al., 2003]; Hyytiälä [Tunved et al., 2003]; and Hohenpeissenberg, Germany [Birmili et al., 2003]). Observations are from the CREATE database (<http://www.nilu.no/projects/ccc/create/database.htm>) recorded using Differential Mobility Particle Sizers (DMPS). At Pallas the observed size range is 7–530 nm, Hyytiälä 3–550 nm and Hohenpeissenberg 3–730 nm. Model values are plotted for the same size range as the observations.

[7] The model without BL particle formation, where aerosol is from primary sources and UT nucleation, underpredicts total particle number concentration at all the sites due to an underprediction at diameters less than 100 nm. With BL particle formation the model better reproduces both the median and variability in total particle number concentrations. At Hohenpeissenberg, overprediction of the accumulation mode may be due to problems with primary particle emissions. At Pallas and Hyytiälä the model underpredicts the growth of small particles, probably due to underprediction of SOA which can contribute significantly

to particle growth [Tunved et al., 2006]. The modeled size distribution at these boreal forest sites is improved (Figure 1, red line) by increasing the SOA yield from terpenes by a factor of 5 (from 13% to 65%). The impact of uncertainty in SOA is explored below. The value of activation coefficient A that results in the best match with observations is between $2 \times 10^{-7} \text{ s}^{-1}$ and $2 \times 10^{-6} \text{ s}^{-1}$, consistent with values calculated from individual particle formation events [Riipinen et al., 2007].

[8] Simulated CCN concentrations are calculated using the modeled particle dry diameter and composition and a hygroscopicity parameter, κ [Petters and Kreidenweis, 2007]. We assume that the hydrophobic distribution does not contribute to CCN formation. For the hydrophilic distribution we take values of κ from Petters and Kreidenweis [2007]: SU $\kappa = 0.61$ (assuming ammonium sulfate), SS $\kappa = 1.28$, EC $\kappa = 0.0$, OC $\kappa = 0.1$ (assuming SOA from α -pinene). Simulated surface CCN concentrations without BL particle formation at 0.2% (1.0%) supersaturations are typically $50\text{--}200 \text{ cm}^{-3}$ ($100\text{--}500 \text{ cm}^{-3}$) over oceans and between $100\text{--}1000 \text{ cm}^{-3}$ ($300\text{--}2000 \text{ cm}^{-3}$) over land (Figure 2a and b) with a global surface mean value of 250 cm^{-3} (380 cm^{-3}) respectively. Modeled CCN concentrations are typically within a factor of 2–3 of observations (Figures 2a and 2b).

[9] Two model runs, with and without BL particle formation, are used to quantify the effect of particle formation on CCN (Figures 2c and 2d). All model runs include particle growth due to SOA. With an activation coefficient $A = 2 \times 10^{-6} \text{ s}^{-1}$, particle formation increases the global BL springtime (March–May) CCN (0.2%) concentration by 9% and CCN (1%) by 20% over concentrations predicted from primary sources and UT nucleation. CCN enhancements of 10–50% over Scandinavia and large regions of boreal Asia and larger enhancements over parts of the continental US, Australia and southern Africa are simulated. It is worth noting that the regional changes can be negative where particle formation rates are high and growth of these particles alters the condensation sink, thereby reducing the condensational growth of exist-

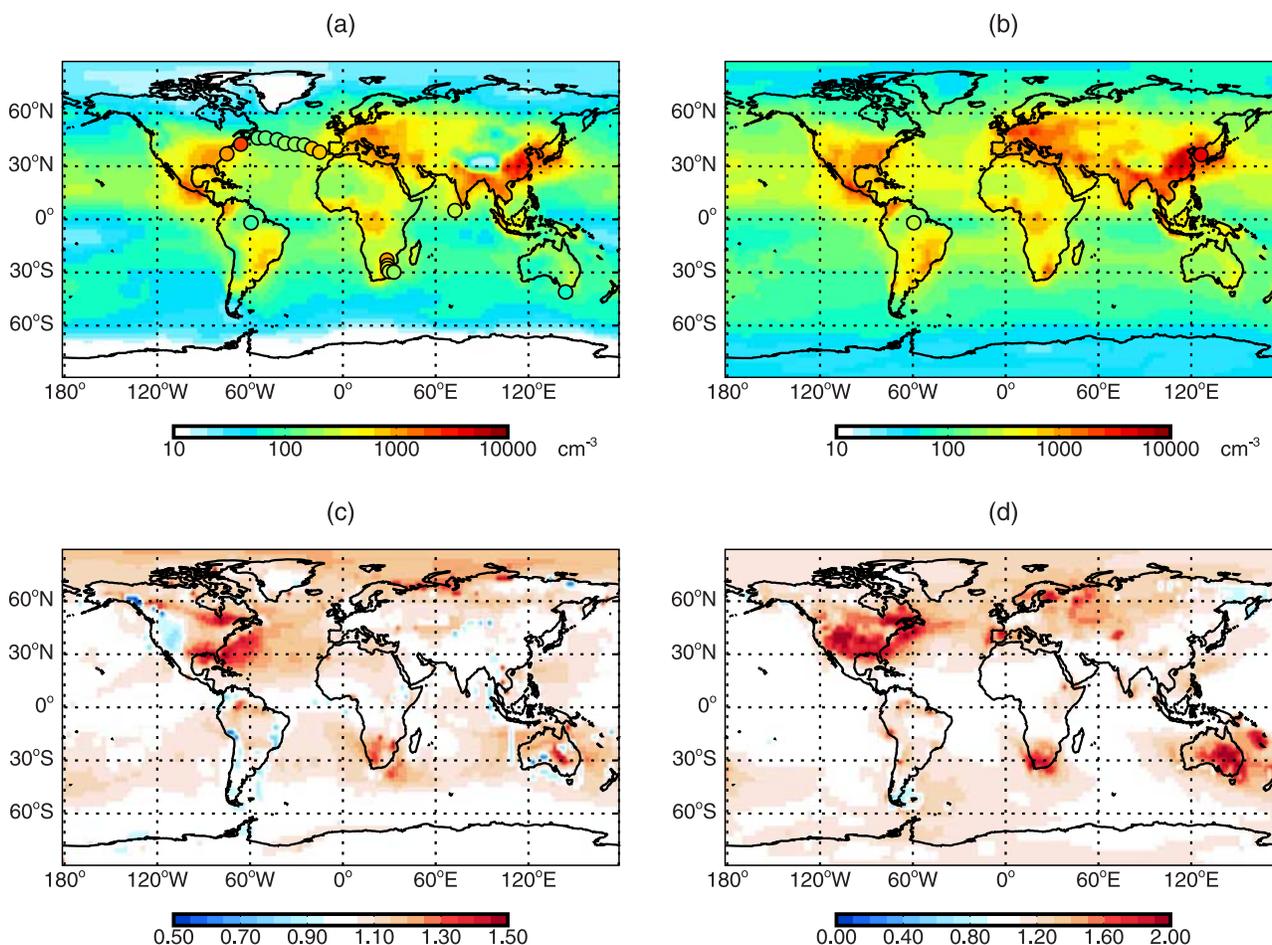


Figure 2. Surface CCN concentrations (cm^{-3}) at (a) 0.2% and (b) 1.0% supersaturation. Model results (background, average for March–May 2000 without BL particle formation) are compared against observations (circles) from Cape Grim (0.23%, March–May) [Ayers *et al.*, 1997], Atlantic Ocean (0.16%, May 1997) [Hoppel, 1979], Indian Ocean (0.23%, February–March 1998) [Cantrell *et al.*, 2000], southern Africa (0.3%, March–April 2001) [Ross *et al.*, 2003], Amazonia (0.3% and 1%, May 1999) [Roberts *et al.*, 2003] and Korea (1%, May 2004) [Yum *et al.*, 2005]. Ratio of simulated surface CCN concentrations with BL particle formation (activation coefficient $A = 2 \times 10^{-6} \text{ s}^{-1}$) to without at (c) 0.2% and (d) 1.0% supersaturation.

ing primary particles to CCN sizes (as simulated over the western US). The enhancement is temporally highly variable. For example, at Hyytiälä the mean enhancement to CCN at 0.2% (1%) supersaturation is 15% (30%) whereas the maximum enhancement is a factor 2 (3). In Hohenpeissenberg the mean enhancement is 6% (30%) and maximum enhancement is a factor of 2.5 (4). These modeled short-term enhancements are of similar magnitude to the increase in CCN observed directly after particle formation events in Finland [Lihavainen *et al.*, 2003].

[10] The sensitivity of predicted CCN concentrations to uncertainty in the activation coefficient A is shown in Figure 3. Increasing A from $2 \times 10^{-8} \text{ s}^{-1}$ to $2 \times 10^{-4} \text{ s}^{-1}$ (approximately the observed range) increases the enhancement of CCN (0.2%) from 3 to 20% and of CCN (1%) from 5% to 50% (global mean). For $A = 2 \times 10^{-9} \text{ s}^{-1}$ CCN enhancement both regionally and globally is <1%.

[11] SOA plays an important role in particle formation but the global budget is very uncertain [Goldstein and Galbally, 2007]. Our analysis of particle size distributions

(Figure 1) suggests that in springtime at boreal forest sites, SOA needs to be increased by a factor of 5 to match observed particle growth rates. This may be due to underestimation of monoterpene emissions from boreal forests during the spring [Haapanala *et al.*, 2007] or condensed product yields from monoterpenes may be greater than the 13% assumed here. In addition, anthropogenic organics contribute to SOA [Volkamer *et al.*, 2006] as may isoprene [Kroll *et al.*, 2006]. Here we make a simple evaluation of this uncertainty by increasing the yield of SOA from monoterpenes by a factor of 5 (from 13% to 65%). The vertical bars in Figure 3 show the effect of increased SOA on nucleation-derived CCN calculated as the ratio (CCN with BLN and increased SOA)/(CCN without BLN but with increased SOA). The effect is variable, resulting in increased or decreased enhancements depending on location and nucleation rate. Note that where simulated CCN enhancements with increased SOA are less than with baseline SOA, this is not a reduction in overall CCN concentrations (which always increase with increased

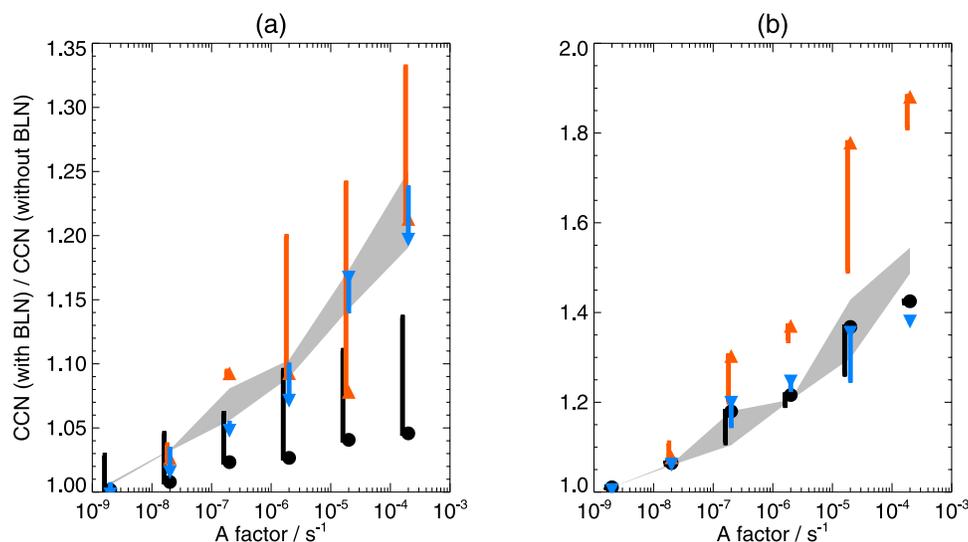


Figure 3. Ratio of simulated BL CCN concentrations with BL particle formation to without in April 2000 at (a) 0.2% and (b) 1.0% supersaturation for a range of activation coefficients A . Global (shading) and regional (symbols) ratios are shown. Central Europe (45° – 55° N, 5° – 30° E): circles, Southern Finland (60° – 66° N, 22° – 30° E): upward triangle, Boreal Asia (55° – 65° N, 80° – 100° E): downward triangle. The range of CCN enhancement due to particle formation when SOA from monoterpenes is increased by a factor of 5 is shown by shading and vertical bars (see text).

SOA), but a reduction in the enhancement to CCN due to particle formation. The effect on CCN enhancement can be quite large: over Europe and southern Finland a factor 5 increase in SOA causes a factor of 3 increase in the CCN (0.2%) enhancement due to particle formation. SOA contributes to the growth of newly formed particles, which increases the number of these particles that grow to CCN sizes, but also increases the existing aerosol condensation sink, which will act to quench formation events [Spracklen *et al.*, 2006]. The results indicate that impact of SOA on CCN enhancement from nucleation is likely to be complex.

4. Implications and Conclusions

[12] Although recent progress has been made [Kulmala *et al.*, 2007], the mechanism behind particle formation is not fully understood. We have assumed that sulfuric acid controls the nucleation rate, as observed, and have used an empirical activation coefficient derived from two sites in Europe.

[13] The observed variability in the activation coefficient [Riipinen *et al.*, 2007] suggests that additional factors are important that we do not account for here. We have explored the sensitivity of our results to uncertainty in the nucleation rate (within the limits derived from analyzed observations). A four-order-of-magnitude change in nucleation coefficient results in a factor of 5–10 change in the predicted enhancement to CCN concentrations. We also explored the uncertainty due to poorly constrained SOA. Varying the SOA yield from monoterpenes by a factor of 5 leads to up to a factor of 3 change in the predicted enhancement to CCN from particle formation. Improving the estimated contribution of particle formation to CCN

requires improved understanding of the factors that control particle formation and growth rates.

[14] We have shown that BL particle formation is an important global source of CCN, increasing global BL CCN (0.2%) concentrations by 3–20% and CCN (1%) by 5–50%. Our regional monthly mean CCN enhancements of $\sim 30\%$ are similar to those of Sotiropoulou *et al.* [2006] using a regional model and a different nucleation mechanism, and our localized short-term enhancements of a factor of 3–4 are similar to the observed enhancements of Lihavainen *et al.* [2003]. A combination of widespread observations with regional and global models is needed to understand the variability in CCN production from nucleation. It will also be necessary to understand the role of natural ecosystems, such as boreal forests, in particle formation [Kurten *et al.*, 2003] and potentially important climate feedbacks [Kulmala *et al.*, 2004a]. The previously identified coupling between primary and secondary aerosol [Spracklen *et al.*, 2006] suggests that CCN concentrations may vary non-linearly with changes in primary emissions and gas-phase aerosol precursors. To accurately account for the long term historical change in aerosol direct and indirect forcing, a better understanding and treatment of particle formation events is required.

[15] **Acknowledgments.** This work was supported by NERC grant NE/D01395X/1, Royal Society (2005/R4-JP), the Finnish Academy and APPRAISE.

References

- Ayers, G., *et al.* (1997), Atmospheric sulfur and cloud condensation nuclei in marine air in the southern hemisphere, *Philos. Trans. R. Soc. London Ser. B*, 352, 203–211.
 Birmili, W., *et al.* (2003), The Hohenpeissenberg aerosol formation experiment (HAFEX): A long-term study including size-resolved aerosol,

- H₂SO₄, OH, and monoterpenes measurements, *Atmos. Chem. Phys.*, **3**, 361–376.
- Cantrell, W., et al. (2000), Relationships between cloud condensation nuclei spectra and aerosol particles on a south-north transect of the Indian Ocean, *J. Geophys. Res.*, **105**, 15,313–15,320.
- Chipperfield, M. (2006), New version of the TOMCAT/SLIMCAT off-line chemical transport model: Intercomparison of stratospheric tracer experiments, *Q. J. R. Meteorol. Soc.*, **132**(617), 1179–1203.
- Goldstein, A., and I. Galbally (2007), Known and unexplored organic constituents in the Earth's atmosphere, *Environ. Sci. Technol.*, **41**(5), 1514–1521.
- Guenther, A., et al. (1995), A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, **100**, 8873–8892.
- Haapanala, S., et al. (2007), Boundary layer concentrations and landscape scale emissions of volatile organic compounds in early spring, *Atmos. Chem. Phys.*, **7**, 1869–1878.
- Hoppel, W. (1979), Measurement of the size distribution and CCN supersaturation spectrum of submicron aerosols over the ocean, *J. Atmos. Sci.*, **36**, 2006–2015.
- Kerminen, V.-M., and M. Kulmala (2002), Analytical formulae connecting the 'real' and the apparent nucleation rate and the nuclei number concentration for atmospheric nucleation events, *J. Aerosol Sci.*, **33**, 609–622.
- Kerminen, V.-M., H. Lihavainen, M. Komppula, Y. Viisanen, and M. Kulmala (2005), Direct observational evidence linking atmospheric aerosol formation and cloud droplet activation, *Geophys. Res. Lett.*, **32**, L14803, doi:10.1029/2005GL023130.
- Kroll, J., et al. (2006), Secondary organic aerosol formation from isoprene photooxidation, *Environ. Sci. Technol.*, **40**(6), 1869–1877.
- Kulmala, M., A. Laaksonen, and L. Pirjola (1998), Parameterizations for sulfuric acid/water nucleation rates, *J. Geophys. Res.*, **103**, 8301–8307.
- Kulmala, M., et al. (2004a), A new feedback mechanism linking forests, aerosol and climate, *Atmos. Chem. Phys.*, **4**, 557–562.
- Kulmala, M., et al. (2004b), Formation and growth rates of ultrafine atmospheric particles: A review of observations, *J. Aerosol Sci.*, **35**, 143–176.
- Kulmala, M., et al. (2006), Cluster activation theory as an explanation of the linear dependence between formation rate of 3 nm particles and sulfuric acid concentration, *Atmos. Chem. Phys.*, **6**, 787–793.
- Kulmala, M., et al. (2007), Toward direct measurement of atmospheric nucleation, *Science*, **318**, 89–92.
- Kurten, T., et al. (2003), Estimation of different forest-related contributions to the radiative balance using observations in southern Finland, *Boreal Environ. Res.*, **8**, 275–285.
- Laaksonen, A., A. Hamed, J. Joutsensaari, L. Hiltunen, F. Cavalli, W. Junkermann, A. Asmi, S. Fuzzi, and M. C. Facchini (2005), Cloud condensation nucleus production from nucleation events at a highly polluted region, *Geophys. Res. Lett.*, **32**, L06812, doi:10.1029/2004GL022092.
- Lihavainen, H., V.-M. Kerminen, M. Komppula, J. Hatakka, V. Aaltonen, M. Kulmala, and Y. Viisanen (2003), Production of "potential" cloud condensation nuclei associated with atmospheric new-particle formation in northern Finland, *J. Geophys. Res.*, **108**(D24), 4782, doi:10.1029/2003JD003887.
- Petters, M. D., and S. M. Kreidenweis (2007), A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, *Atmos. Chem. Phys.*, **7**, 1961–1971.
- Pierce, J. R., and P. J. Adams (2007), Efficiency of cloud condensation nuclei formation from ultrafine particles, *Atmos. Chem. Phys.*, **7**, 1367–1379.
- Riipinen, I., et al. (2007), Connections between atmospheric sulphuric acid and new particle formation during QUEST III-IV campaigns in Heidelberg and Hyytiälä, *Atmos. Chem. Phys.*, **7**, 1899–1914.
- Roberts, G. C., A. Nenes, J. H. Seinfeld, and M. O. Andreae (2003), Impact of biomass burning on cloud properties in the Amazon Basin, *J. Geophys. Res.*, **108**(D2), 4062, doi:10.1029/2001JD000985.
- Ross, K. E., S. J. Piketh, R. T. Bruintjes, R. P. Burger, R. J. Swap, and H. J. Anegarn (2003), Spatial and seasonal variations in CCN distribution and the aerosol-CCN relationship over southern Africa, *J. Geophys. Res.*, **108**(D13), 8481, doi:10.1029/2002JD002384.
- Sihto, S.-L., et al. (2006), Atmospheric sulphuric acid and aerosol formation: Implications from atmospheric measurements for nucleation and early growth mechanisms, *Atmos. Chem. Phys.*, **6**, 4079–4091.
- Sotiropoulou, R., et al. (2006), Modeling new particle formation during air pollution episodes: Impacts on aerosol and cloud condensation nuclei, *Aerosol Sci. Technol.*, **40**(7), 557–572, doi:10.1080/02786820600714346.
- Spracklen, D., et al. (2005a), A global off-line model of size-resolved aerosol microphysics: I. Model development and prediction of aerosol properties, *Atmos. Chem. Phys.*, **5**, 2227–2252.
- Spracklen, D., et al. (2005b), A global off-line model of size-resolved aerosol microphysics: II. Identification of key uncertainties, *Atmos. Chem. Phys.*, **5**, 3233–3250.
- Spracklen, D., et al. (2006), The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales, *Atmos. Chem. Phys.*, **6**, 7323–7368.
- Tunved, P., et al. (2003), One year boundary layer aerosol size distribution data from five nordic background stations, *Atmos. Chem. Phys.*, **3**, 2183–2205.
- Tunved, P., et al. (2006), Is nucleation capable of explaining observed aerosol integral number increase during southerly transport over Scandinavia?, *Tellus*, **58B**, 129–140.
- Volkamer, R., J. L. Jimenez, F. San Martini, K. Dzepina, Q. Zhang, D. Salcedo, L. T. Molina, D. R. Worsnop, and M. J. Molina (2006), Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, *Geophys. Res. Lett.*, **33**, L17811, doi:10.1029/2006GL026899.
- Yum, S. S., J. G. Hudson, K. Y. Song, and B.-C. Choi (2005), Springtime cloud condensation nuclei concentrations on the west coast of Korea, *Geophys. Res. Lett.*, **32**, L09814, doi:10.1029/2005GL022641.

K. S. Carslaw, M. P. Chipperfield, G. W. Mann, J. Merikanto, and D. V. Spracklen, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK. (dominick@env.leeds.ac.uk)

M. Kulmala, I. Riipinen, and S.-L. Sihto, Department of Physical Sciences, POB 64, University of Helsinki, FIN-00014 Helsinki, Finland.

V.-M. Kerminen and H. Lihavainen, Finnish Meteorological Institute, P.O. BOX 503, FIN-00101 Helsinki, Finland.

A. Wiedensohler and W. Birmili, Leibniz Institute for Tropospheric Research, Permoserstrasse 15, D-04318 Leipzig, Germany.