

# Ion-mediated Nucleation as an Important Source of Global Tropospheric Aerosols

Fangqun Yu<sup>1</sup>, Zifa Wang<sup>2</sup>, and Richard P. Turco<sup>3</sup>

**Abstract** Aerosol nucleation events have been observed at a variety of locations worldwide, and may have significant climatic and health implications. While ions have long been suggested as favorable nucleation embryos, their significance as a global source of particles has remained uncertain. Here, an ion-mediated nucleation (IMN) mechanism, which is supported by recent measurements of the overcharging of newly formed particles, has been integrated into a global chemical transport model to study ion mediated particle formation in the global troposphere. We show that predicted annual spatial patterns of particle nucleation agree well with land-, ship-, and aircraft-based observations throughout the troposphere. The ratio of particle number annual source strength due to IMN to those associated with primary particle emission suggests that IMN contribution is significant. This analysis represents the first confirmation of a significant, predictable global-scale source of new tropospheric aerosols.

**Keywords** Ion-mediated nucleation, tropospheric aerosols, global modeling

## Ion-Mediated Nucleation

New particle formation frequently observed at various locations worldwide is an important source of atmospheric aerosols. Measurements indicate that  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  are clearly involved in many nucleation events observed in the atmosphere. Due to the difficulty of  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  binary homogeneous nucleation (BHN) theory in explaining the observed particle formation rate, it has been

---

<sup>1</sup>Atmospheric Sciences Research Center, State University of New York, Albany, New York

<sup>2</sup>NZC/LAPC, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China

<sup>3</sup>Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, California

proposed that others species including ammonia,<sup>1</sup> ions,<sup>2</sup> and certain organic compounds<sup>3</sup> may enhance the  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  nucleation. Analysis of laboratory measurements shows that the contribution of ternary  $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$  homogeneous nucleation (THN) to the formation of new particles is also likely to be very limited.<sup>4</sup> While certain organics have been shown to be able to enhance  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  nucleation in the laboratory,<sup>3</sup> the level of enhancement is similar to that of ammonia, and the significance of organics in enhancing nucleation rates in the atmosphere is unclear.

Ions, which are generated continuously and ubiquitously in the atmosphere by cosmic radiation and radioactive decay, have long been known to promote nucleation. However, the recent availability of detailed field data on nanometer-sized particles during aerosol nucleation “events” led Yu and Turco<sup>2,5,6</sup> to develop a more comprehensive approach for studying nucleation processes involving ion clusters. They utilized a kinetic model that explicitly treats the complex interactions among small air ions, neutral and charged clusters of various sizes, precursor vapor molecules, and the preexisting aerosol. Compared to homogeneous nucleation, which involves the formation of small, transient neutral molecular clusters, nucleation onto ions is favored because: (1) small charged clusters are typically more stable thermodynamically than their neutral counterparts; (2) the initial growth rates of small ion clusters are enhanced by the dipole–charge interaction between the core ion and the strongly dipolar condensing molecules; and (3) there is a continuous and ubiquitous supply of stable, fast growing ionic embryos. Further, the properties of ions are well determined by extensive laboratory studies, unlike the situation with respect to their neutral counterparts. Yu and Turco<sup>2</sup> refer to the coupled formation and evolution of aerosol size distributions, including both charged and neutral clusters, under the influence of ionization, recombination, neutralization, condensation, evaporation, coagulation, and scavenging as ion-mediated nucleation (IMN). It is clear that the IMN mechanism is different from classical ion-nucleation theory<sup>7,8</sup> which is based on a simple modification of the free energy associated with the formation of a “critical nucleation embryo”.

Our understanding of the role of ions in atmospheric nucleation has advanced recently, both from experimental and theoretical points of view. Experimental progress includes measurements of the mobility spectra of atmospheric cluster ions beginning at molecular sizes, as well as the charged fraction of freshly nucleated nanoparticles.<sup>9–12</sup> The theoretical progress includes the quantification of the role of dipole–charge interaction in ion clustering thermodynamics<sup>13–16</sup> and the development of up-to-date IMN models incorporating recently available thermodynamic data and schemes.<sup>17</sup> The long-term (multiple years) measurements taken in Hyytiälä, Finland indicate that ions are involved in more than 90% of the particle formation days that can be clearly identified.<sup>11,12</sup> While Laakso et al.<sup>11</sup> concluded that the average contribution of ion nucleation to total nucleation rate is small, we find, based on a conservative analytical analysis and detailed kinetic simulations, that the same measurements presented in Laakso et al.<sup>11</sup> may actually indicate the dominance of IMN in the observed nucleation.

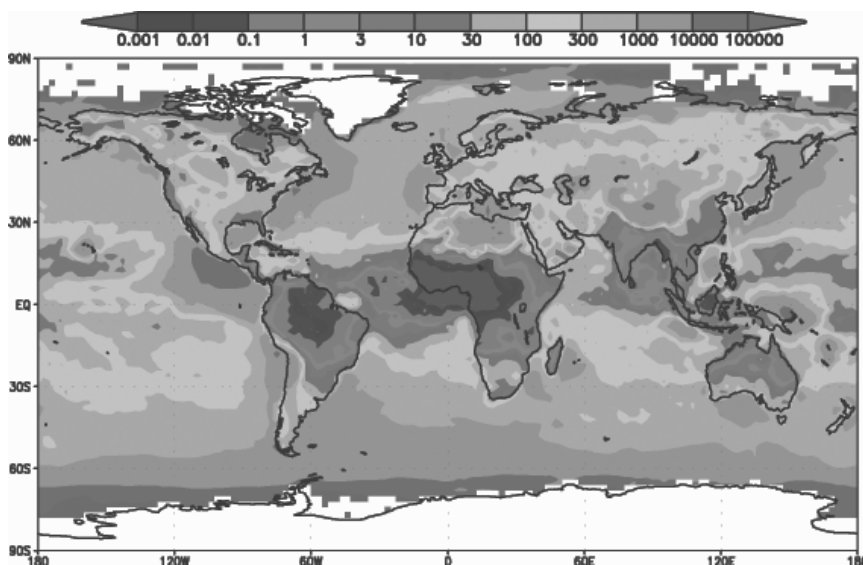
## Global Simulation of Ion-Mediated Nucleation

To study particle nucleation in the global atmosphere, we couple our nucleation sub-module to GEOS-Chem model which is a global 3D model of atmospheric composition driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling Assimilation Office (GMAO). Meteorological fields include surface properties, humidity, temperature, winds, cloud properties, heat flux, and precipitation. For the results presented in this paper, the GEOS-3 grid with  $2^\circ \times 2.5^\circ$  horizontal resolution and 30 vertical levels was used. The first 15 levels in the model are centered at approximately 10, 50, 100, 200, 330, 530, 760, 1,100, 1,600, 2,100, 2,800, 3,600, 4,500, 5,500, and 6,500 m above surface. A detailed description of the model (including the treatment of various emission sources, chemistry and aerosol schemes) can be found in the model web-page (<http://www.as.harvard.edu/chemistry/trop/geos/index.html>).

In order to study aerosol nucleation in the context of 3D models, the nucleation calculations must be simplified or parameterized to reduce computing costs. We have developed an efficient IMN nucleation module based on nucleation rate look-up tables that are derived from detailed nucleation model simulations (8 Yu, 2006c). The IMN nucleation rate (JIMN) depends on the ambient sulfuric acid vapor concentration ( $[\text{H}_2\text{SO}_4]$ ), temperature (T), relative humidity (RH), ionization rate Q, and the surface area of preexisting particles,  $S_0$  (i.e.,  $\text{JIMN} = f([\text{H}_2\text{SO}_4], T, \text{RH}, Q, S_0)$ ). For a given set of conditions, JIMN is determined from the look-up table using an efficient multiple-variable interpolation scheme.

We run the GEOS-Chem coupled with nucleation model for 1 year from July 1, 2001 to June 30, 2002. The time step for transport is 15 min and for chemistry (and nucleation) is 60 min. We have compared our simulated annual spatial patterns of particle nucleation with land-, ship-, and aircraft-based observations relevant of particle formation and found that the agreement is quite well. The generally good agreement strongly supports the important role of IMN in generating new particles in global troposphere.

Figure 1 gives the ratio of annual mean IMN rates integrated in the lowest 3 km of atmosphere above surface (e.g., source strength due to IMN  $\text{SS}_{\text{IMN0-3}}$ ,  $\#/ \text{cm}^2 \text{day}$ ) to the annual mean number emission of primary aerosols (e.g., source strength due to primary particle emission  $\text{SS}_{\text{primary}}$ ,  $\#/ \text{cm}^2 \text{day}$ ). Figure 1 clearly indicates that IMN is a significant source of particle number in the lower troposphere. At high latitude (30N–90N, 30S–90S),  $\text{SS}_{\text{IMN0-3}}$  to  $\text{SS}_{\text{primary}}$  ratio is above 300 over oceans and between 30 and 300 over land. In the tropic regions (30S–30N),  $\text{SS}_{\text{IMN0-3}} / \text{SS}_{\text{primary}}$  is above 10 over Pacific Ocean and relatively small over continentals, Atlantic and Indian Oceans. It should be noted that the diameters of nucleated particles are only a few nanometer while those of primary particles are generally above 50 nm. The fraction of nucleated particles survives and is able to grow to CCN size depend on the growth rates (and hence precursor gas concentrations) and the concentration of preexisting particles. Pierce and Adams (2006) found that the probability of a nucleated particles generating a CCN varies from  $<0.1\%$  to  $>90\%$



**Figure 1** The ratio of annual mean IMN rates integrated in the lowest 3 km of atmosphere above surface (e.g., source strength due to IMN  $SS_{\text{IMNO-3}}$ ,  $\#/\text{cm}^2/\text{day}$ ) to the annual mean number emission of primary aerosols (e.g., source strength due to primary particle emission  $SS_{\text{primary}}$ ,  $\#/\text{cm}^2/\text{day}$ ). The primary aerosols considered in GEOS-Chem and the corresponding assumed (fixed) sizes (radius) are: dust (4 sizes: 0.7, 1.5, 2.5, 4  $\mu\text{m}$ ), sea salt (3 sizes: 0.732, 5.67  $\mu\text{m}$ , and ultrafine sea salt mode with radius of 40 nm), black carbons (39 nm), and organic carbons (70 nm)

in different regions of the atmosphere and is between 5% and 40% for a large fraction of nucleated particles in the boundary layer. Clearly IMN is likely to be a significant source of particles that can have important climatic impacts.

**Acknowledgments** This study is supported by the NOAA/DOC under grant NA05OAR4310103 and NSF under grant 0618124. Z.W. acknowledges the support of National 973 Project (2005CB422205). The GEOS-Chem model is managed by the Atmospheric Chemistry Modeling Group at Harvard University with support from the NASA Atmospheric Chemistry Modeling and Analysis Program.

## References

1. Weber, R.J. et al., *Chem. Eng. Comm.*, **151**, 53–62 (1996).
2. Yu, F. and Turco, R.P., *Geophys. Res. Lett.*, **27**, 883–886 (2000).
3. Zhang, R. et al., *Science*, **304**, 1487–1490 (2004).
4. Yu, F., *J. Geophys. Res.*, **111**, D01204, doi:10.1029/2005JD005968 (2006).
5. Yu, F. and Turco, R.P., *Geophys. Res. Lett.*, **24**, 1927–1930 (1997).
6. Yu, F. and Turco, R.P., *J. Geophys. Res.*, **106**, 4797–4814 (2001).
7. Hamill, P., Turco, R.P., Kiang, C.S., Toon, O.B., and Whitten, R.C., *J. Aerosol Sci.*, **13**, 561–585 (1982).
8. Raes, F., Augustin, J., and Vandingenen, R., *J. Aerosol Sci.*, **17**, 466–470 (1986).

9. Vana, M. et al., *Atmos. Res.*, **82**, 536–546 (2006).
10. Iida, K. et al., *J. Geophys. Res.*, **111**, D23201, doi:10.1029/2006JD007167 (2006).
11. Laakso, L. et al., *Atmos. Chem. Phys. Discuss.*, **7**, 1333–1345 (2007).
12. Hirsikko, A. et al., *Atmos. Chem. Phys. Discuss.*, **7**, 201–210 (2007).
13. Nadykto, A., Makela, J., Yu, F., Kulmala, M., Laaksonen, A., *Chem. Phys. Letts.*, **382**/1–2, 6 (2003).
14. Nadykto A. and Yu, F., *J. Geophys. Res.*, **108**, 4717, doi:10.1029/2003JD003664 (2003).
15. Nadykto, A. and Yu, F., *Phys. Rev. Letts.*, **93**, 016101 (2004).
16. Yu, F., *J. Chem. Phys.*, **122**, 084503 (2005).
17. Yu, F., *Atmos. Chem. Phys.*, **6**, 5193–5211 (2006).
18. Pierce, J.R. and Adams, P.J., *Atmos. Chem. Phys.*, **7**, 1367–1379 (2007).