

Interactive comment on “Ion-mediated nucleation as an important global source of tropospheric aerosols” by F. Yu et al.

F. Yu et al.

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The authors thank the referee for the useful and constructive comments. Our specific responses are given below (Comments of Anonymous Referee 3 in Italic).

1. *The relative importance of neutral and ion-induced nucleation has not been established yet. In fact, either of these two routes may be more important depending on the location and time. With this in mind, I think that the authors should avoid arguing about the potential importance of ion-induced nucleation at one single location (Hyytiälä, page 13600, lines 15-22), especially since the work of Yu and Turco (2007) has not been published yet.*

We agree that the relative importance of neutral and ion-induced nucleation has not been established yet. As we have emphasized in the paper, the relative importance

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of ion-mediated nucleation versus neutral nucleation under different atmospheric conditions needs to be further investigated (page 13600, lines 12-14). It is possible that either ion or neutral nucleation may be more important depending on location and time, as the referee notes. However, a physically based mechanism for neutral nucleation – one that has a true micro-physical and thermodynamic basis – has not yet been formulated, despite the fact that several empirical homogeneous nucleation models are presently in use. The ion-mediated nucleation model has remaining uncertainties (for example, we discuss these on page 13612, lines 13-19). Nevertheless, because of the nature of the physics of the molecular kinetics involving charged clusters, ion-mediated nucleation can be described more quantitatively in terms of available, reliable kinetic and thermodynamic data. Moreover, the site specific relevance of ion-mediated nucleation depends only on local conditions, which we have shown in a series of papers can be favorable at a wide range of locations. Thus, we are focusing on the contributions to particle formation due to ion-mediated processes, as opposed to directly comparing the contributions of ion versus neutral mechanisms.

We consider that the overcharging measurements taken at Hyytiälä to be critical because they provide the first direct observations regarding the relative contribution of ions to the overall particle formation rate. It has been stated that ion nucleation was not significant at the time these measurements were taken (page 13600, lines 17-19). However, we show that this interpretation is probably incorrect, owing to a limited analytical approach used in the original interpretation of the dataset (to estimate the relative importance of ion versus neutral nucleation). Indeed, we find that the tracking of charge on freshly nucleated particles is complicated, and cannot be determined accurately using a simple, but convenient, formulation, as was done earlier. In our revised paper, we will make these points more clearly.

2. *Since the sulfuric acid concentration driving the nucleation rate is expected to be directly proportional to the OH radical concentration, the authors should say something about the ability of the GEOS-Chem model to predict the global OH concentration field*

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(pages 13601-13602).

The ability of the GEOS-Chem model to predict the global OH concentration field has been evaluated independently in section 3.1 of Bey et al. (J. Geophys. Res., 106, 23,073, 2001). We will expand our discussion of this point in the revised version of the paper for clarification.

3. *In introducing the calculation procedure for ion-mediated nucleation (page 13604), it should be explicitly mentioned that only binary water-sulfuric acid IMN is being considered. The statement like JIMN can be accurately decided (page 13604, line 9) seems a little bit odd to me, given that theoretically calculated nucleation rates are practically always uncertain.*

We have explicitly noted that the current IMN model only considers binary $H_2SO_4 - H_2O$ system, and will emphasize this fact. When we say that "JIMN can be accurately decided", we mean that the JIMN values interpolated from the look-up tables are accurate (generally within a few percentage) when they are compared to the corresponding values calculated from a full IMN model. We will modify the sentence to clarify the statement.

4. *The modeled sulfuric acid concentrations should be compared briefly with measured concentrations (page 13605, lines 20-25). I understand that this comparison cannot be comprehensive due to the scarcity of measurement data. However, a few sentences demonstrating that modeled and measured concentrations are consistent with each other would strengthen the paper considerably.*

The main objective of this paper is to study the annual mean spatial pattern and overall contribution of IMN to new particle formation in the troposphere. In addition to the scarcity of available H_2SO_4 concentration data, the likely spatial inhomogeneities in H_2SO_4 concentrations are another issue when comparing model results at a grid resolution of 2x2.5 degree with those observed at specific locations. Nevertheless, we agree with the referee that the paper would be strengthened if we are able to demon-

strate the consistency between the model and observed H_2SO_4 concentrations at selected locations and time periods where and when data are available. In previous work – in developing and testing the ion-mediated mechanism – we had relied heavily on field experiments in which simultaneous H_2SO_4 and nanoparticle measurements were taken. Regarding the present analysis – we will certainly review the related publications for H_2SO_4 data. Unfortunately, we have not found data streams over long enough periods of time for meaningful comparisons to be made. If such data are available – and perhaps the referee can point us to relevant observations/publications for the simulation periods (7/2001-6/2006) – we will, for comparison, include new simulations in the revision as possible.

5. The authors state that nucleation in Arctic region is hindered due to Arctic haze. (page 13607, lines 1-3) This may be true during the winter/spring period but not during the summer when the Arctic region is very clean due to effective precipitation. As matter of fact, active particle new-particle production has been reported in several Arctic locations during the summer time. The authors should be more careful here in their statements.

We were trying to compare the difference in predicted nucleation rates between Arctic and Antarctic regions, and our results represent only annual mean values. Actually, our model did predict some nucleation during the summer season. It is also possible that GEOS-Chem overpredicted the condensation sink and thus underpredicted [H_2SO_4] and nucleation rates for the Arctic region. We will modify the statements to address the referee's concern. Could the referee provide us with the references in which active new particle production is reported in several Arctic locations? If such observations have been published, we will include them in Figure 2.

6. One cannot directly compare the ion-production rate and observed particle formation rate, since the vast majority of the ions are probably lost by pre-existing larger particles and oppositely-charged ions/particles before growing into observable size range of >3 nm (page 13607, lines 20-26).

The ambient ion-production rate defines the upper limit of the IMN particle formation rate. We have shown that this background ionization source is consistent with IMN theory and analysis as applied here. The fraction of ions that are lost before inducing nucleation, and the fraction of nucleated particles that are scavenged before growing to sizes $> 3\text{nm}$, depend on precursor vapor concentrations (growth rates), the surface areas of pre-existing particles, and other factors including temperature and humidity. All of these effects (that we are aware of) are explicitly treated in the IMN simulations, and are accounted for in the predictions and interpretations.

Table S1 below gives the ion-mediated nucleation rates at the critical size (J_{crit}) and at 3 nm ($J_{3\text{cm}}$, i.e., the "apparent" formation rates as observed) under a number of different combinations of sulfuric acid concentration and surface area of preexisting particles. The results were based on the simulations using a detailed kinetic model that takes into account the scavenging of ions and nucleated particles by pre-existing larger particles and oppositely-charged ions/particles (Yu, ACP, 6, 5193-5211). Condensation of organics is not considered in these results.

Table S1. Ion-mediated nucleation rates at critical size (J_{crit}) and 3 nm ($J_{3\text{cm}}$) under a number of different combinations of sulfuric acid concentration ($[H_2SO_4]$, read $1E7$ as 10^7cm^{-3}) and surface area of preexisting particles ($SA, \mu\text{m}^2\text{cm}^{-3}$). $T=280\text{K}$, $RH=50\%$, and ionization rate $Q = 5\text{ ion-pairs cm}^{-3}\text{s}^{-1}$. D_{crit} is the diameter (in nm) of critical clusters.

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SA	[H ₂ SO ₄]	Dcrit	Jcrit	J3nm	J3nm/Jcrit	J3nm/(2*Q)
50	5E6	1.6	0.22	0.032	15%	0.32%
51	1E7	1.45	1.82	0.68	37%	6.8%
64	5E7	1.37	5.64	3.47	62%	34.7%
100	1E8	1.35	5.95	4.05	68%	40.5%
224	5E7	1.37	4.1	1.63	40%	16.3%
260	1E8	1.35	5.06	2.87	57%	28.7%
606	1E8	1.35	3.1	1.05	34%	10.5%
742	2E8	1.34	4.3	1.96	46%	19.6%

While SA in polluted regions is quite large, the concentration of precursor gases can be very high as well. For example, the measured [H₂SO₄] can reach as high as $2 \times 10^8 \text{ cm}^{-3}$ in Atlanta, Georgia (McMurry et al., JGR, 110, D22S02, 2005) and $8.8 \times 10^7 \text{ cm}^{-3}$ in anthropogenic plumes advecting from Asia (Weber et al., JGR, 108, 8814, 2003). It is clear from Table S1 that a significant fraction of ions can lead to nucleation and a large fraction of the nucleated particles can grow into observable size range of > 3 nm.

It should be noted that certain organics may also contribute to the growth of nucleated particles. For example, Fiedler et al. (ACP, 5, 1773, 2005) showed that the measured [H₂SO₄] may only account for about 17% and 5% of observed growth rates of 1 – 3nm particles in Hyytiälä and Heidelberg, respectively. The enhanced growth rates as a result of organic condensation will increase the fraction of nucleated particles growing into observable range.

7. The authors should explicitly mention that in practically all heavily-polluted areas, observed nucleation rates are by far larger than what can be explained by ion production (page 13608, lines 1-3).

We do not agree with the referee on this point for the following reasons.

(1) The ion production rate in polluted urban areas is not well characterized. It is

possible that under certain conditions ion production rates may be much higher than the generally assumed values of 5-10 ion-pairs $cm^{-3}s^{-1}$. For example, as we noted in the paper (page 13608, lines 8-10), Dhanorkar and Kamra (1994) showed that ionization rates near the surface can exceed 100 ion-pairs $cm^{-3}s^{-1}$ due to the accumulation of radon gas in the nocturnal boundary layer. Recently, Vartiainen et al. (Boreal Env. Res., 12, 375, 2007) detected exceptionally high ion production rates of up to 30 ion-pairs $cm^{-3}s^{-1}$ in Russia due to 222-radon decay.

In urban zones, corona discharge may generate high concentrations of small ions as well. Small ion concentrations of up to $10^4 - 10^5 cm^{-3}$ have been observed near and downwind of high voltage Transmission lines (Carter and Johnson, IEEE Trans Power Delivery, 3, 2056, 1988; Suda and Sunaga, IEEE Trans Power Delivery, 5, 1426, 1990; Grabarczyk and Berlinski, J. Aerosol Sci., 35, 251, 2004). Engine combustion also emits large concentrations of ions due to chemiionization processes in the engine combustion zone (e.g., Yu et al., Atmos. Environ., 38, 1417-1423, 2004).

Table S2 and S3 show that Jcrit and J3nm can be very high when Q is large.

Table S2. Same as Table S1 except Q = 20 ion-pairs $cm^{-3}s^{-1}$

SA	[H ₂ SO ₄]	Dcrit	Jcrit	J3nm
260	1E8	1.35	17.2	9.0
606	1E8	1.35	11.4	3.7
740	2E8	1.34	15.5	6.6

Table S3. Same as Table S1 except Q = 50 ion-pairs $cm^{-3}s^{-1}$

SA	[H ₂ SO ₄]	Dcrit	Jcrit	J3nm
224	5E7	1.37	27.4	10.1
260	1E8	1.35	36.5	18.2

(2) The median observed formation rates of 3 nm particles in heavily polluted areas such as Pittsburgh and New Delhi are generally below $15 \text{ cm}^{-3} \text{ s}^{-1}$ (see Table 1 in the paper). Based on the discussions given in point (1) and our replying to comment 7, we think that IMN may be able to account for many of the observed nucleation events. Nevertheless, we acknowledge that situations also exist for which observed nucleation rates appear to be much larger than can be explained by local ion-production rates, and we offer several possible explanations for this in the paper (pages 13607-13608).

8. *The statement (4) on page 13608 (lines 10-12) is incorrect. How could mixing itself create larger particle number concentrations than what has been formed by nucleation? When air is mixing, it inevitably dilutes, as a result of which concentrations are decreased.*

In many nucleation events reported in the literature, apparent particle formation rates (for example J3nm) are calculated based on time series of the concentrations of freshly nucleated particles (for example, N_{3-20nm} , i.e. concentration of particles in the size range of 3 – 20 nm). This is a valid approach when the air mass during the nucleation period is spatially homogeneous. In such cases, the evolution of particle number size distributions shows a well defined "banana" shape (for example, see Fig. 1 in Kulmala et al., ACP, 4, 2553, 2004; Fig. 3a in Riipinen et al., ACP, 7, 1899, 2007; and Fig. 1 in Qian et al., Atmos. Environ., 41, 4119, 2007).

However, in many observations, particles in the size range of 3 - 20 nm appear simultaneously (i.e., no time delay in the appearance of the peak values of N3nm and N10nm), and the evolution of the particle size distribution has the "APPLE" shape rather than the "banana" shape (for example, see Fig. 3b in Wu et al., JGR, 112, D09209, 2007; Fig. 3 in Fiedler et al., ACP, 5, 1773, 2005; Fig. 10 in Mozurkewich et al., ACP, 4, 1047, 2004; Fig.5 in Petaja et al., ACP,7, 2705, 2007; Iida et al., JGR, 111, D23201, 2006; Fig. 6 in Eisele et al., JGR, 111, D04305). In these cases, the observed increases in N_{3-20nm} are likely a result of mixing or transport of particles nucleated somewhere else, and the particle formation rates derived from dN_{3-20nm}/dt

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may be significantly overestimated because the change of air mass is rapid.

Also see the comment of Referee 2 on this.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 13597, 2007.

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