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Atmospheric
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Discussions

Interactive comment on “Aerosol nucleation over oceans and the role of galactic cosmic rays” *by* J. Kazil et al.

J. Kazil et al.

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We would like to thank the referees for their thoughtful review of our manuscript. The referees agree on two main objections which we address in the section ”Reply to all Referees”. In the subsequent sections we reply to the individual referee comments.

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Reply to all Referees

Preexisting aerosol

The main objection brought forward against the validity of our approach is that we start our simulations with zero aerosol concentrations and thus fail to account for the limiting effect of preexisting aerosol on nucleation, which may result in an overestimation of the ability of a given atmospheric region to produce new aerosol. This objection weighs most with regard to the high nucleation in the tropical upper troposphere, and least with regard to the marginal nucleation in the tropical MBL predicted by our model. However, it is based on this striking difference that we argue for the tropical upper troposphere as the likely origin for non-sea salt sulfate aerosol in the tropical MBL. Starting the simulations with zero aerosol concentrations does not affect our findings concerned with the response of clouds and radiative forcing to changes in GCR ionization. That's because we estimate the upper limit of the effect: Any preexisting aerosol reduces gas phase sulfuric acid concentrations, and in turn the response of supercritical aerosol and consequently of CCN populations to a change in ionization [Kazil and Lovejoy (2004)].

The question to answer is therefore "Can a vigorous nucleation be expected in the tropical upper troposphere in the presence of actual aerosol concentrations?" As the referees point out, specifying actual aerosol concentrations (or their average and variability) is not straightforward. A comprehensive survey of aerosol observations in the marine troposphere has been published by [Clarke and Kapustin (2002)]. Their compilation shows that for both polluted and clean air, the aerosol surface area decreases with altitude: Lower tropospheric average surface area concentrations amount to approximately 45 μm^2 cm^{-3} in polluted and 10 μm^2 cm^{-3} in clean conditions. Above 7 km, average surface area concentrations are less than 10 μm^2 cm^{-3} in both polluted and clean conditions. These surface area concentrations are given in STP (which is ambiguous owing to the various definitions of STP, but using the IUPAC values, 1000

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hPa and 273.15 K, would seem appropriate), hence the actual decrease of surface area concentration with altitude is steeper than these numbers indicate. The variability of individual measurements around the average values is substantial.

As suggested by the referees we have conducted a sensitivity study to investigate the effect of preexisting aerosol on nucleation: We ran our model with different initial aerosol surface area concentrations between 0 and 20 μm^2 cm^{-3} (in ambient temperature and pressure) for March, June, September and December 21, using solar maximum ionization rates, at the 925, 700, 550, and 300 hPa pressure levels. We will discuss the change of the $>$ 3 nm diameter particle concentration from 0 h to 24 h of March 21: Comparing the concentrations of supercritical aerosol particles is not meaningful here, as the size of the neutral critical cluster depends on gas phase H_2SO_4 concentration, which again depends on the preexisting aerosol concentration, the parameter varied in the sensitivity study. Also, 3 nm is the smallest particle diameter that can be detected with current experimental techniques. Results for June, September and December 21 are qualitatively similar to those for the of March 21.

2.5 μm^2 cm^{-3}: The presence of this comparably low preexisting aerosol surface area concentration suppresses particle formation in most of the tropical lower and middle troposphere. The upper troposphere exhibits a vigorous particle production.

5 μm^2 cm^{-3}: A preexisting aerosol surface area concentration of 5 μm^2 cm^{-3} suppresses particle formation in most of the lower troposphere and large areas of the middle troposphere, while in the upper troposphere, particle formation is still proceeding at formidable rates.

$\geq$ 10 μm^2 cm^{-3}: The production of $>$ 3 nm diameter particles is increasingly reduced to pockets around polluted coastal areas in the northern hemisphere in the lower and middle troposphere. The upper troposphere on the other hand is capable of a widespread $>$ 3 nm diameter particle production at 10 μm^2 cm^{-3}, but loses vigor at 15 μm^2 cm^{-3}, and is nearly absent at 20 μm^2 cm^{-3}.

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Therefore, the question posed above can be answered in the affirmative: Indeed, a vigorous nucleation can be expected in the tropical upper troposphere in the presence of actual aerosol concentrations. More specifically, the sensitivity study can be summarized as follows for the purpose of elucidating the origin of tropical MBL non-sea salt aerosol: In the adopted average conditions and for the nucleation mechanisms accounted for in our model,

- particle formation in the tropical upper troposphere is much less sensitive to the presence of preexisting aerosol compared with the tropical middle and lower troposphere.
- the tropical upper troposphere can maintain particle formation at preexisting aerosol surface area concentrations well above observed average values, while the middle and lower troposphere require removal of preexisting aerosol below observed average values to produce new particles, and produce no aerosol over extended regions at all.

Thus in contrast to the tropical upper troposphere, sulfate aerosol nucleation in the middle and lower tropical troposphere requires reduced aerosol surface area concentrations, increased SO_2 concentrations, presence of ammonia or other aerosol precursors, reduced temperatures, or increased RH. These results supports our finding on the role of nucleation related to convective lifting of boundary layer air into the upper troposphere over the oceans as a source of MBL aerosols. This sensitivity study is presented in the revised manuscript, together with the corresponding plots.

H_2SO_4

The referees suggest to present distributions of gas phase H_2SO_4 calculated with our model and to compare them with observations. This is done in the revised manuscript.

Reply to Referee 1

Referee: *The authors start their simulation from an aerosol-free atmosphere. This assumption, while understandable when considering the large uncertainties associated with explicitly simulating the whole atmospheric aerosol population, leads to a few incorrect statements and conclusions throughout the paper.The authors should definitely do something for these points.*

Authors: See ”Reply to all Referees”.

Referee: *First, in the beginning of section 4.1 (page 5549, lines 11-12) it is stated that*

”..., and allow us to compare the potential of different regions in the troposphere to produce aerosol”.

I do not agree on this statement. In their nucleation mechanisms, the concentration of gaseous sulfuric acid plays a central role in determining the nucleation rate. The sulfuric acid concentration, in turn, is directly proportional to its production term (effectively SO_2 *times OH concentration) and inversely proportional to its sink term (pre-existing aerosol surface area). Since the pre-existing aerosol surface area varies by several orders of magnitude in the atmosphere, starting the simulations from an aerosol free atmosphere does not give a fair ranking between different tropospheric regions in their potential for forming new aerosol particles.*

Authors: This is correct. For a precise ranking, averaging the nucleation rate over a representative set of environmental conditions, weighted with their probability of occurrence would be required, while our approach only gives a ranking in terms of nucleation in average conditions, in the absence of preexisting aerosol. We replaced the sentence

”The resulting aerosol concentrations are thus an upper limit in the adopted conditions, and allow us to compare the potential of different regions in the troposphere to produce

aerosol.”

with

”The resulting supercritical aerosol concentrations are thus an upper limit in the adopted average conditions.”

Referee: *Second, given the importance of gaseous sulfuric acid in their nucleation mechanisms, it is surprising that the authors do not provide pictures of simulated global sulfuric acid concentration, while doing so for SO_2, OH and ionization rate (Figs 1, 2 and 4). I would recommend the author to add such a figure and to make a brief overview on how the predicted sulfuric acid compare with available atmospheric measurements.*

Authors: See ”Reply to all Referees”.

Referee: *Third, it is stated that ternary nucleation in the marine boundary layer is suppressed by the lack of ammonia (abstract, page 5561). I am not convinced that this is true. It is more likely that the large aerosol surface area provided by sea-salt particles suppresses nucleation in the MBL by acting as an effective sink for both gaseous sulfuric acid and nanometer-size nuclei.*

Authors: We agree that the mentioned passage of the abstract

”Neutral nucleation contributes only marginally to aerosol production in our simulations. This highlights the importance of charged binary and of ternary nucleation involving ammonia for aerosol formation. In clean marine regions however, ammonia concentrations seem too low to support ternary nucleation, making binary nucleation from ions a likely pathway for sulfate aerosol formation.”

wrongly suggests that ammonia concentrations are generally too low in marine regions to support neutral ternary nucleation. This is only so in the cases reported by [Weber et al.(2001)], who measured high H_2SO_4 in the MBL during PEM-Tropics B without new particle formation. Obviously, in these cases, neither ammonia nor ions triggered nucleation. On the other hand, [Brock et al. (1995)] analyzed upper tropospheric aerosol and concluded that its composition is consistent with H_2O and H_2SO_4 only in tropical regions, while additionally containing a non-volatile component, possibly ammonium, at extra-tropical locations. Similarly, [Yamato and Tanaka (1994)] found that in the unpolluted free marine troposphere, sulfuric acid aerosol particles are neutralized by ammonia at a small degree, while in marine air masses originating from land, ammoniated particles dominate over sulfuric acid particles. These results show that ternary nucleation involving ammonia is not necessarily involved in new particle formation in the unpolluted marine troposphere. We therefore revised the above passage as follows:

”Neutral binary nucleation contributes only marginally to aerosol production in our simulations. This highlights the importance of other mechanisms, including charged binary and ternary, and neutral ternary nucleation for aerosol formation.”

The other instances in the manuscript has been changed accordingly, from

”... observations suggest that in clean marine areas such as in the tropical Pacific, nucleation does not proceed even at very high H_2SO_4 concentrations [Weber et al.(2001)], indicating that ammonia concentrations are insufficient for ternary nucleation to occur there. The absence of ternary nucleation in clean marine areas is also supported by the results of [Brock et al. (1995)], who analyzed the volatility of aerosol in the upper troposphere, and concluded that it consists of H_2O and H_2SO_4 in tropical regions, while additionally containing ammonium at extra-tropical locations. A recent model study using an experimentally constrained kinetic model of neutral ternary nucleation [Yu (2005)] indicates a negligible contribution of this mechanism to new particle formation in the tropospheric boundary layer. Hence in the clean tropical marine environment, where deep convection would lift boundary layer air and initiate

nucleation in the upper troposphere, ammonia may be not involved.”

to

”... a recent experimentally constrained kinetic model of neutral ternary nucleation [Yu (2005)] indicates a negligible contribution of this mechanism to new particle formation in the tropospheric boundary layer. Observations show that in clean marine areas such as in the tropical Pacific, nucleation needs not to proceed even at very high H_2SO_4 concentrations [Weber et al.(2001)]. Moreover, [Brock et al. (1995)] analyzed upper tropospheric aerosol and concluded that its composition is consistent with H_2O and H_2SO_4 only in tropical regions, while additionally containing a non-volatile component, possibly ammonium, at extra-tropical locations. Similarly, [Yamato and Tanaka (1994)] found that in the unpolluted free marine troposphere, sulfuric acid aerosol particles are neutralized by ammonia at a small degree, while in marine air masses originating from land, ammoniated particles dominate over sulfuric acid particles. These examples illustrate that ternary neutral nucleation involving ammonia is not necessarily involved in new particle formation in the unpolluted marine troposphere. Nonetheless, efficient neutral ternary nucleation cannot be ruled out, in particular over and near the continents, where ammonia concentrations are elevated [Dentener and Crutzen (1994)].”

and from

”Nonetheless, in clean marine regions, in particular those with strong convection responsible for upper tropospheric nucleation, ammonia concentrations seem not sufficient to warrant ternary nucleation, making binary nucleation from ions a likely pathway for sulfate aerosol formation.”

to

”Nonetheless, observations show that in clean marine regions, ammonia is not necessarily involved in new particle formation, making contributions from ions likely.”

Referee: *Finally, the authors could easily estimate how sensitive their results are to* *pre-existing aerosols by making a sensitivity study in which an additional sink term for gaseous sulfuric acid (imitating the effect of pre-existing particles) would be present. These sink terms do not need to be accurate, single values representing ”typical” condensation sinks in different tropospheric regions (MBL, middle and upper free troposphere) would be enough.*

Authors: See ”Reply to all Referees”.

Referee: *Minor/technical comments The global OH concentration field is calculated with a photochemical model (Figure 2). How well this model performs when compared to observations/empirical estimates of global OH concentrations?*

Authors: [Spivakovsky et al. (2000)] discuss uncertainties and possible errors in the modeled OH, which we summarize here: The global OH distributions are consistent within a few percent with the chlorinated and fluorinated hydrocarbon budgets at the time of the generation of the OH data. Tests by [Spivakovsky et al. (2000)] did not establish significant errors in the OH concentrations, except for a possible underestimation of the OH concentration in winter by 15-20 % in the northern and by 10-15 % in the southern tropics, and an overestimation by $\sim$ 25 % in the southern extratropics.

Referee: *Satellites are able to ”see” only particles that are much larger than those formed recently in the atmosphere. Therefore, relations obtained from satellite measurement (like aerosol column number concentrations) may not be applicable at all when trying to estimate the climatic effects of aerosols formed by atmospheric nucleation.*

Authors: While it is true that satellite observations are limited to aerosols above a given size, we do not consider this a constraint to our reasoning: We aim at estimating an upper limit to the effect on clouds of a response of CCN concentrations to a change in GCR ionization. For this purpose we assume that the maximum effect occurs when the CCN (which are "visible" to satellites) carry the same response to a change in ionization as the small, supercritical aerosol particles that nucleated recently in conditions that maximize the response. This is equivalent to assuming that each of these CCN particles evolved from one of the recently nucleated supercritical aerosol particles. In a few words, we do not apply a relation obtained from satellite observations of large aerosol to small aerosol, but to large particles under the assumption that all of these large particles evolved from small particles that formed due to neutral and charged nucleation. This is discussed in the revised version of the manuscript.

Referee: *The order of pictures in Figures 1, 2, 4, 5 and 6 is strange.*

Authors: Corrected.

Reply to Referee 2

Referee: *Specific comments: i) Previous studies have shown that surface area of preexisting aerosol particles is important factor influencing the formation processes of new aerosol particles. In present study, the authors start their model with no preexisting aerosol, which certainly leads away from real conditions and wrong conclusions can be made easily.*

Authors: See ”Reply to all Referees”.

Referee: *The authors have aimed to obtain an upper limit of effects. However, the authors should investigate the sensitivity of model results to preexisting aerosol and add some discussion what happens by adding this parameter into model. Of course, this is not easy, as concentration of aerosol particles can vary several orders of magnitude at different locations.*

Authors: See ”Reply to all Referees”.

Referee: *ii) In the paper we can see plots for global OH and SO_2 concentrations. The production rate of sulfuric acid is calculated using parameterization of SO_2 and OH. I think that readers would be interested to see model results about gas phase concentra-*

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tion of H_2SO_4. The authors should consider adding such figure for H_2SO_4 like Figures 1 and 2.

Authors: See ”Reply to all Referees”.

Referee: *iii) The model computes the aerosol size distribution at given times from SO_2 concentration, the concentration of the hydroxyl radical OH, ionization rate, relative humidity, temperature, and pressure. In what size range we get the size distribution?*

Authors: The sectional (”bin”) scheme of our model covers particle sizes up to approximately 900 nm in diameter. The peak of a freshly nucleated aerosol mode is located between 2 and 10 nm in diameter at noon, depending on temperature, RH, and on the availability of gas phase H_2SO_4.

Referee: *I recommend adding quantitative values about the size of calculated aerosol particle, and also estimations about charging efficiencies or charged fraction of the freshly nucleated particles.*

Authors: Typical particle sizes in the freshly nucleated aerosol mode, such as given above, are given in the revised manuscript. Extracting the charging efficiency from our model results is straightforward, however, discussing it in the manuscript would require a compelling reason.

Referee: *What is the size limit for the supercritical aerosol particles which concentrations we can see in Figure 5?*

Authors: The aerosol concentrations seen in Figure 5 were obtained by integrating the aerosol size distribution starting at particles that contain one H_2SO_4 molecule more than the neutral critical cluster, up to about 900 nm in diameter. However, no 900 nm particles form in the 24 h of our simulations. Practically speaking, the concentrations seen in Figure 5 of the manuscript represent particles with diameters between about 2 and 30 nm.

Referee: *Technical corrections: Figures 1, 2, 4, 5 and 6 would be better readable if* *they are ordered so that plots (a) and (b) are located in the upper row, and plots (c) and (d) in the lower row, like in Figure 8.*

Authors: Corrected.

Referee: *In page 5561 line 14, there is one extra ”not” in expression: ”we cannot not rule out...”.*

Authors: Corrected.

Reply to Referee 3

Referee: *As mentioned by two other referees, assumption of particle-free atmosphere is somewhat problematic and I hope the authors follow the suggestions made by referees 1 and 2.*

Authors: See ”Reply to all Referees”.

Referee: *I would like to see the authors to discuss about the importance of ion-ion recombination as a source of new particles (e.g. [Turco et al. (1998)]).*

Authors: This is a point that deserves attention indeed. Ion-ion recombination is an important process in ion-induced nucleation, and accounted for in our model. However, we represent the cations summarily by $H_3O^+(H_2O)_4$. Heavier cations which recombine less rapidly could allow more negative sulfuric acid/water clusters to grow to supercritical sizes before being neutralized, and complex cations, containing compounds other than water, could contribute to nucleation by recombination [Turco et al. (1998)]. This possibility is supported by the observations of [Eichkorn et al. (2002)], who measured massive positive ions in the upper troposphere, although only in 4 % of the observations. Positive H_2SO_4 clusters e.g., while less potent to promote nucleation compared with their negative counterparts [Froyd and Lovejoy (2003)] might thus enhance production of neutral supercritical sulfate aerosol in the upper troposphere by recombination. This is discussed in the revised manuscript.

Referee: *In the model of [Lovejoy et al. (2004)], ion-ion recombination produces neutral particles which are able to grow if they are larger than the critical size. However, in the atmosphere, there are several compounds that may stabilize the neutral clusters, and thus ion-ion recombination can lead to a large number of clusters, which may grow to larger sizes. I would like the authors discuss also this possibility, together with more realistic background aerosol populations. How would this change the conclusions?*

Authors: Regarding more realistic background aerosol populations, see ”Reply to all Referees”.

A stabilization of subcritical neutral clusters would reduce the barrier for neutral nucleation and increase its contribution to aerosol formation.

A stabilization of negative clusters by a third compound (e.g. ammonia) in addition to water and sulfuric acid (charged ternary nucleation) could lead to a stronger contribution from ions to aerosol formation. This possibility is addressed in the manuscript.

Abundant complex cations in the atmosphere (as opposed to the simple proton hydrate which represents the cation population in our model) could lead to a stronger contribution of ion recombination to aerosol formation. This possibility is discussed in the revised manuscript (see also above).

Referee: *Small technical corrections: Order of pressure levels in subplots is strange.*

Authors: Corrected.

Referee: *Right axis of Figure 7 should be corrected.*

Authors: Corrected.

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