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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Results from the CERN pilot CLOUD experiment" *by* J. Duplissy et al.

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Introduction

The review of referee #2 is included below, together with our replies (following, in italics, immediately below the corresponding comments of the referee).

Response

This manuscript reports initial 2006 results of the CLOUD experiment to understand the effect of cosmic rays on particle formation, using proton synchrotron beams in an environmental chamber. The main conclusion is that this pilot study has validated the experimental setup and from some of the initial experiments, the authors also claimed that they found evidence of ion-induced nucleation or ion-ion recombination processes for sulfuric acid particle formation at the typical atmospheric conditions.

The paper states "suggestive evidence" (Abstract l.21), which is a weaker claim than "evidence".

While this study intended to validate this new experimental setup,

No, it is not intended to validate the pilot experimental setup of the present paper paper but to "provide technical input for the CLOUD design" (Abstract, l.7), i.e. to shape some of the design principles of CLOUD.

Experiments shown in this manuscript were conducted in not well-controlled experimental conditions and the results are not reproducible.

This comment echoes the present text of the paper (e.g. p.18250, l.17: "Other runs taken under conditions similar to run 35 show either weak or even contradictory evidence for ion-induced nucleation...", and paragraph beginning p.18251, l.16 "In conclusion, therefore, the experimental variables were not well enough controlled..."

There is also some misinterpretation of experimental results.

We disagree with this comment. Would the referee kindly be more specific: where precisely are the experimental results misinterpreted?

And from these results, the main conclusion is not convincing.

Firstly, there is not one conclusion but two: 1) suggestive evidence for ion-induced nucleation, and 2) important lessons were learnt for the CLOUD design. The second item is a fact. In the case of the first item, the paper does not attempt to "convince" the reader of a particular conclusion, but to provide the reader with the experimental observations and their possible (but not definitive) interpretation. Conclusion 1 is rather mild, and we have gone to great care in wording the text carefully to express the limitations and uncertainties underlying the "suggestive evidence for ion-induced nucleation". We therefore suggest the reviewer should read the text once more with an open mind to see that we are not over-stating the significance of the observations.

A. Introduction.

The experiments shown in this manuscript were designed to study the cosmic ray effect on particle formation in the lower atmospheric region.

This is incorrect. The goals are more modest and are clearly stated in the second sentence of the abstract: "The purpose of the pilot experiment was firstly to carry out exploratory measurements of the effect of ionising particle radiation on aerosol formation from trace H2SO4 vapour and secondly to provide technical input for the CLOUD design.".

However, Introduction is confusing, considering the current understanding of the field. It is now relatively well recognized that ion-induced nucleation is important in the upper troposphere and lower stratosphere region (as opposed to lower troposphere) where ion production rates by cosmic rays are highest, as shown by [Lovejoy et al., 2004] IIN model predictions; this IIN model was vigorously tested and constrained by in-situ observation data of SO2, OH, H2SO4 and particle size distributions in this region provided by [Lee et al., 2003]. However, both [Lovejoy et al., 2004] (laboratory observations) and [Lee et al., 2003] (field observations) did not exclude the possibility of sulfuric acid binary or ternary nucleation processes in this region. Especially when temperatures are very low, nucleation barriers of even binary homogeneous nucleation can also disappear like in IIN [Yu, 2002]. So it is likely that cosmic rays have little or no effects on particle or cloud formation even in a global scale. A new article by [Carslaw, 2009] also states the same conclusion that the effect of cosmic rays on particle formation "is smaller than thought", by summarizing recent global aerosol modeling work. As another example, [Kulmala, 2009] also state in their title, "Atmospheric data over a solar cycle: no connection between galactic cosmic rays and new particle formation". The most important question here is, what will be the homogeneous nucleation processes in the lower temperature range and at low sulfuric acid concentrations (representative of upper troposphere and lower stratosphere where IIN is most effective), in comparison to IIN, rather than the effect of cosmic rays on particle or cloud formation at room

temperature.

We feel that the Introduction is not confusing, as stated by the reviewer, but represents a brief yet sufficient overview of the scientific interest and current experimental state of ion-induced nucleation. Furthermore, we do not agree with several of the points made above by the reviewer. However, given the modest scientific claims of the present paper, we feel it would be disproportionate to provide a more exhaustive review of the present scientific understanding of ion induced nucleation and so we believe that the level of detail in the present introduction is appropriate.

B. Interpretation of data.

1. The "evidence of ion-induced nucleation or ion-ion recombination for sulfuric acid particle formation" (Conclusions, page 18256) is not convincing.

We were unable to find this text in our Conclusions section. The closest text reads as follows (final sentence of the paper): "In summary, the exploratory measurements made with a pilot CLOUD experiment at the CERN Proton Synchrotron have validated the basic concept of the experiment, provided valuable technical input for the CLOUD design and instrumentation, and provided, in some of the experiments, suggestive evidence for ion-induced nucleation or ion-ion recombination as sources of aerosol particles from trace sulphuric acid vapour at typical atmospheric concentrations." We suggest that this sentence makes rather modest claims and correctly reflects the limitations of the data presented in the paper.

The authors used two criteria for IIN: a high fraction of charged particles and association of enhanced particle concentrations with beam intensities (Page 18248, 1st paragraph). However, the authors also stated that high fraction of charged particles does not necessary suggest IIN involvement but lack of charged particles also do not exclude IIN (Page 18248 3rd Paragraph; Page 18250, 4th paragraph). That is, this first criterion is not really useful.

No, it is useful, for the reason stated in the first paragraph of section 3.2.3: "Therefore the appearance of an "overcharged" aerosol distribution in the CPC battery - in which the charged aerosol fraction at 3nm threshold is larger than at 7.2nm threshold - is a fairly robust signature of ion-induced nucleation (Laakso et al., 2007). On the other hand, the absence of overcharging does not exclude contributions from ion-induced nucleation, since it may indicate either that the contribution is too small to be detected or else that the initially-charged aerosols have been partly neutralised by ion-aerosol attachment before reaching the 3nm size threshold for measurement." We were unable to find any contradiction to this statement in the text referred to by the reviewer (Page 18248 3rd Paragraph; Page 18250, 4th paragraph).

In fact, there are only 6 events showed overcharge out of 44 nucleation events (page 18248, 4th paragraph). With regard to the 2nd criterion, which is more straightforward, the experimental results do now show any consistent results (e.g., Figure 7; Section 3.2.4), except Run 35, which only showed some association of particle concentrations with beam intensities, but this Run 35 also did not have evidence of particle overcharge (Page 18250, 4th paragraph), on the other hand. From these data, it is difficult to conclude that IIN was actually involved in these nucleation events - it sounds rather that artifact particles were emitted or produced from unknown sources (likely form the wall) under uncontrolled experimental conditions (such as temperature fluctuations or by other species other than sulfuric acid).

As stated in the text, Run 35 did not show overcharging. So, according the previous comment, this neither supports nor excludes ion-induced nucleation. The observations of Run 35 show a nucleation rate that increases or decreases each time the particle beam increased or decreased, respectively. (We are careful to point out that the final transitions occurred during an increase of chamber temperature and so must be excluded due to the observed anomalous nucleation bursts from T increases.) The changes in nucleation rate occurred exactly (within a few minutes) after each beam transition. The chamber temperature is unaffected by the beam and was measured

throughout this run (and is displayed in Fig.4). So the proposal by the reviewer of "temperature fluctuations" is excluded by the experimental data. We are unsure what the reviewer has in mind for the "other species" that would have caused this nucleation. It is certainly possible that the nucleations are a combination of H2SO4 and other unknown contaminants such as organics or NH3. However, this cannot explain why these materials would suddenly become more or less abundant in the chamber at precisely the same time that the particle beam is increased or decreased respectively. We therefore fail to understand why it "sounds" to the reviewer that ion induced nucleation is not involved. We would be happy to hear of a plausible alternative explanation from the reviewer, because we have failed to find one.

2. While the authors claim that particle formation was seen at H2SO4 around e6 cm-3 or less - when beams were either on or off, in both cases (e.g., Table 1, Figures 4 and 5; page 18250, 1st paragraph). Note, the particle concentrations and nucleation rates reported here in both cases are very high at such low sulfuric acid conditions and the differences in particle concentrations between neutral and IIN processes are very small (e.g., 3,600 cm-3 vs 4,300 cm-3; Page 18250, 2nd paragraph). The authors then conclude that these results are consistent with Figure 2 in [Laaksonen et al., 2008] which summarized that field and laboratory studies show nucleation takes place in this H2SO4 range. [Laaksonen et al., 2008]'s conclusion is, however, that HSO5 radicals (which are not mentioned in the current manuscript) contribute to SO2 + OH reaction so homogeneous nucleation (without ions) to make sulfuric acid nucleation threshold very low. Also, Figure 2 of [Laaksonen et al., 2008] specifically showed that threshold of ion nucleation from the same SO2 + OH reaction by [Sorokin, 2007] is very high ((e9 cm-3) - on contrary to the current manuscript conclusion.

There is no conflict. The paper states that - even though not measured directly - organic contaminants were clearly present in the chamber (nucleations in the absence of UV light in the early stages of the campaign; growth rates that were too large to be due to HSO4 alone). The nucleation rates and corresponding H2SO4 concentrations may be

strongly influenced by low volatility organic vapour contaminants. These experimental uncertainties are sufficiently large that they preclude a meaningful contribution to the current debate on HS05 radicals and other possible mechanisms. So the paper can (and does) limit itself to rather qualitative statements about the H2SO4 concentrations corresponding to the measured J values.

Also, it is noted that even though using the same SO2 + OH reaction, other laboratory studies do not show this low threshold for H2SO4 nucleation [Benson et al., 2008; Benson, 2009; Young et al., 2008]. I also want to point out that formation of particles by IIN at 20-28 C temperatures with sulfuric acid around e6 cm-3 or less quite contradicts [Hanson and Lovejoy, 2006]'s cluster thermodynamics measurements and [Lovejoy et al., 2004] IIN laboratory observations. So either neutral or IIN nucleation is not explained well from these experiments - and this brings to technical issues such as not-controlled experimental conditions and reproducibility (also see Technical issues: C).

We are happy that the referee echoes our text, which clearly states that the pilot CLOUD experiment did not have sufficiently well-controlled experimental conditions and reproducibility.

3. Growth rates reported here in general are also much higher than those reported in most of atmospheric observations, except only one report (Iida et al., 2008) so the 1st paragraph in Section 3.2.2 is misleading.

No, the first paragraph of Section 3.2.2 is not misleading. It states, quite correctly: "During the 4-week run, 44 nucleation bursts were produced and recorded, with formation rates of particles above the 3nm detection threshold of between 0.1 and 100 cm-3s-1, and growth rates between 2 and 37 nmh-1. These values are similar to those observed in the atmosphere (Kulmala et al., 2004), e.g. growth rates of 1-2 nmh-1 in the boreal forest (Dal Maso et al., 2005), and 40 nmh-1 in Mexico City (Iida et al., 2008)."

Also with regard to this high growth rates, the authors state that artifact organic compounds (at 20 pptv levels) emitted from the chamber wall during temperature fluctuations are responsible (Section 3.2.2. 2nd paragraph).

No, we do not make this statement. What we say in Section 3.2.2. 2nd paragraph is as follows: "Although not directly measured, on the assumption that organic vapour contaminants were indeed responsible for the observed aerosol growth rates, we can estimate that their mixing ratios would need to be in the approximate range 1-20 pptv or larger (Joutsensaari et al., 2007)." This is a qualified statement, and an estimate not a measurement.

However, this 20 pptv of additional organic compounds still cannot explain 2-37 nm per hour growth rates.

Our estimate suggests otherwise.

In addition, most of organic compounds either do not participate in sulfuric acid nucleation at all [Berndt et al., 2006] or some HC alkene compounds can even completely suppress particle formation by consuming OH radicals [Kiendler-Scharr et al., 2009; Wolf, 2009].

We are unable to share the same conviction as the reviewer that organics do not participate in sulphuric acid nucleation. Moreover we know nothing of the identity of the organic contaminants in the present experiment.

C. Technical issues. Most of experiments shown in this manuscript lack proper controlling or monitoring of experimental condition.

Once again, we are happy that the referee echoes our text.

Considering nucleation is a highly non-linear process, under these conditions, it will be difficult to correctly evaluate and interpret experimental results.

1. Temperature was controlled only for the second half of the experiments and for the

first part, temperature varied from 20-28 C (Page 18254, Section 4.2, first paragraph), while IIN process is very sensitive to temperature [Lovejoy et al., 2004].

The variation of temperature and the sensitivity of J to temperature does not, by itself, invalidate the experimental measurements since the temperature was monitored during the entire run. So, for example, the data could, if necessary, be divided into restricted temperature intervals and the variation of J vs. T experimentally measured. However, what is important is the spurious nucleations caused by small T increases, a described in detail in the paper.

2. For the most of time (except the final 3 runs), SO2 background concentration in the chamber was between 0.1-0.2 ppb (similar to typical atmospheric conditions seen in rural, remote or less polluted environment), emitted from un-determined sources in the chamber. (Page 18252, last paragraph).

Once again, we are happy that the referee echoes our text.

3. For the final days when SO2 was raised, however, no H2SO4 measurements were available. Considering IIN is highly sensitive to H2SO4 concentrations ([Lee et al., 2003] SOM), without direct measurements of H2SO4, there will be large uncertainties in interpretation of the cosmic ray effect on particle formation via IIN. In addition, with regard to H2SO4 concentrations, the authors state that experiments were conducted typically at e6 cm-3 or less (Abstract), while they used a CIMS that can measure as low as 5e5 cm-3 (Section 2.3, 2nd paragraph).

The reviewer seems to be trying to extract quantitative results from the experimental measurements that go far beyond what the authors claim the data are capable of providing. The experimental conclusions of the paper, as we have stated previously, are modest and correctly match the quality of the experimental measurements. There seems little point to judge the paper to stronger experimental conclusions than claimed by the authors.

4. Ammonia contamination. While ammonia is not mentioned in this article, it is likely that there are also quite significant ammonia left in the chamber (some of the parts consisted of stainless steel which can absorb ammonia most efficiently below 40 C), considering even less-sticky SO2 gasses (sub-ppbv) remained in the chamber for the most of the part of experimental runs. Note, deionized water also produces high concentrations of ammonia even at low relative humidity (sub-ppbv level).

Yes, the contaminants certainly may include ammonia. However this alters none of the discussion in the paper of unmeasured contaminants that may influence the nucleation and growth rates.

5. Wall effects. Wall loss of aerosol precursors and vaporization of precursors and particles from the wall is tremendous for this kind of environmental chamber but it is not analyzed how sulfuric acid, ammonia or organic compounds are lost to the wall and how long these processes can be stabilized. Especially, sulfuric acid has high wall loss factors.

Wall loss rates will strongly affect calculated H2SO4 concentrations. However, no calculations are presented in this paper since the H2SO4 was measured by a CIMS, for part of the run, and then scaled to different SO2/O3 concentrations and UV intensities for other runs. The measurements automatically account for the H2SO4 loss rates to the wall, so this is not an issue. The contaminants were not measured but, in these cases, the walls were the source, not the sink, so the loss rates are not relevant. Aerosol loss rates to the walls were measured and accounted for in the calculated nucleation rates.

It is also not clear whether experiments were conducted in a steady state condition, especially considering poor reproducibility (also see B1).

All the quantitative results reported correspond to steady-state UV illumination (Section 4.20: "Since stable temperature conditions were not met for UV bursts during the pre-CLOUD experiment, we have not used UV burst data for quantitative studies presented

in this work, to avoid spuriously-generated nucleations."

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