

## ***Interactive comment on “Atmospheric sulphuric acid and neutral cluster measurements using CI-API-TOF” by T. Jokinen et al.***

### **Anonymous Referee #2**

Received and published: 29 January 2012

This manuscript reports measurement of atmospheric sulfuric acid and its clusters (including both naturally-charged and chemically-ionized) using coupled chemical ionization and time-of-flight mass spectrometry technique (CI-API-ToF). High resolution time-of-flight mass spectrometry is an extremely potent tool in differentiating nucleation-related compounds/clusters from interfered compounds especially organics in the complex Earth's atmosphere. Measurement of those nucleation-related compounds/clusters represents a very important topic in atmospheric research. Successful measurement of the precursors and nucleating clusters will help to unveil the nucleation mechanisms and to reconcile the discrepancies between laboratory experiments and field observations.

Specific comments:

1. The authors concluded that the measured sulfuric acid clusters are “mostly or purely” from naturally-charged clusters that are formed by ion-induced nucleation in the specific measurement site because “neutral clusters may not become charged in collision with nitrate ions” or insufficient neutral cluster concentrations (pg. 31994). The authors should give more details on how those naturally-charged clusters are formed in the atmosphere and the different mechanisms that govern the formation of naturally-charged clusters and the chemically-ionized clusters by the nitrate ions.

2. Related to 1, if those naturally-charged sulfuric acid clusters are formed by sequentially added sulfuric acid molecules, then the ion signals can be dominant over chemically-ionized signals due to the sufficient long reaction time for naturally-charged clusters compared to chemically-ionized ones that are neutrally origin. In an environment with low sulfuric acid concentration (but it is still high enough for “ion-induced” formation of naturally-charged clusters because of the long reaction time), concentrations of neutral sulfuric acid clusters are extremely low and the ion signals from neutral clusters are low due to low ionization efficiency. Then the ion signals from neutral can be overwhelmed by the naturally-charged ones. For example, if concentrations of the neutral clusters are in the order of  $1e4$  molecule / $cm^3$  and if the ionization efficiency is about 1% (can be much lower), then the charged concentration from chemical ionization will be about  $100 cm^3$  that can be lower than the corresponding naturally charged clusters. If this is the case, the naturally-charged ions must be removed in order to be able to measure neutral clusters.

3. Little was presented regarding the inlet of chemical ionization. Because inlet design is very important for measuring the very low concentrations of neutral clusters and it would also be beneficial to the chemical ionization community, detailed information on the CI inlet should be given, e.g., inlet diameter/material, ion source, how reagent is introduced, ion reaction time, flow rate, estimation of diffusion loss in the inlet, etc.

4. Why all the mass/charge (s) of sulfuric acid and its clusters are smaller than the corresponding nominal mass/charge (s), e.g., 97,195, 293 etc. (Fig. 2)? What are the

causes for those shifts? A detailed explanation should be given.

5. Figure 3 is too small and difficult to be visualized. For a lot of time periods, especially non-nucleation periods, the signals corresponding to neutral clusters (e.g. 293, 391) are higher than those from naturally-charged clusters, while during some event periods, they are lower than the naturally-charged clusters. There must be some changes by introducing chemical ionization in CI-API-ToF compared to API-ToF. How the detected sulfuric acid cluster ions are affected by introducing chemical ionization? What caution should be taken when comparing signals corresponding to sulfuric acid clusters from the two instruments because of the changes by introducing chemical ionization?

6. The assumption of the same calibration factors for sulfuric acid higher clusters as for sulfuric acid monomer is probably questionable because the loss of the clusters and sulfuric acid monomer in the inlet and vacuum are likely very different.

7. Other minor comments:

1) Abstract: “accompanied by ammonia”, using “accompanied by” seems “ammonia is still independent of tetramer” and “containing ammonia” sounds better; as what “cluster mass spectrometers” refer to here?

2) Introduction: Pg. 31985, line 3, “also” should be deleted; line 10, “accounting for” should be changed to “account for”; lines 11-13, please give Weber et al. (1996) credit when talking about the connection between sulfuric acid and atmospheric nucleation; there are a lot of “it’s” used as attributive and it should be “its” (e.g., pg. 31986, line 18); line 26, “mechanics” is better replaced by “mechanism”

3) Instrumentation: R1, the authors should state what all the terms in both hand sides stand for (pg. 31988)? Line 14, “The CI-A”Pi-TOF provides low signal-to-noise ratio”, here, “low” should be “high”?

4) Results and Discussion: pg. 31990, line 24, in “the same exact mass than”, “than” should be “as”;pg. 31991, “like seen” should be “as seen”.

Reference: Weber, R. J., J. J. Marti, P. H. McMurry, F. L. Eisele, D. J. Tanner, and A. Jefferson (1996), Measured atmospheric new particle formation rates: Implications for nucleation mechanisms, Chem. Eng. Commun., 151, 53–64, doi:10.1080/00986449608936541.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 31983, 2011.

ACPD

11, C14821–C14824,  
2012

---

Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

C14824

