

Interactive comment on “In situ chemical measurement of individual cloud residue particles at a mountain site, South China” by Qinhao Lin et al.

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In their manuscript "In situ chemical measurement of individual cloud residue particles at a mountain site, South China", Qinhao Lin and co-workers report on the analysis of single particles from cloud residues using a single particle aerosol mass spectrometer. They observed a high fraction of EC-containing particle in the residuals and detected amines with a high variability. Nitrate was found to be increased in residuals compared to ambient particles, while sulfate showed a dependency on the chemical composition of the residues. The topic of the paper is well suited for ACP, and the data itself are interesting, because single particle measurements of cloud residuals are still sparse. However, the manuscript suffers from many unclear statements and some severe un-

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certainties regarding the analysis of interstitial particles. I have many points where more information is needed or where I disagree. None of these points alone would be a "major" comment, but the multitude of my remarks and questions suggest to require a major revision and to reconsider the manuscript after my comments listed below have been addressed.

Comments and remarks:

Title: I suggest to change the title to "In situ chemical composition measurement of individual cloud residue particles at a mountain site, South China"

Page 4, lines 64 – 68:

More references are needed here to discuss the anthropogenic influence on cloud particles, not just two papers on single particle analysis.

Page 5, line 79:

Replace "Nf of sulfate" by "NF of sulfate-containing particles"

Page 5, line 80:

Replace "other study" by "other studies"

Page 7, line 122:

Was the humidity measured in the evaporation chamber? How do you make sure that all water evaporates?

Page 8, lines 147-149:

Did you do the size calibration on the mountain top station? What was the ambient pressure during the measurements and during the calibration? Did you check the inlet flow or the pressure inside the aerodynamic lens?

Page 8, line 161:

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The SMPS does not measure the cloud droplet concentration but the cloud residue concentration. Cloud droplets would have to be measured outside in the cloud (by FSSP or similar instrumentation).

Page 9, line 171:

As I will outline in more detail below, I doubt the existence of interstitial particles in this size range.

Page 9 lines 184-185 and Figure 2:

More info on the trajectories is needed: How did the vertical evolution look like? How well is the mountain represented in the model? Is 1800 m the best altitude that represents the mountain site? Please add also the most important megacities to the map to help estimating the influence of anthropogenic emissions.

Page 10, line 207:

I suggest moving Figure S3 to the main paper.

Page 11, lines 221-222:

But Roth et al. found a clear enhancement of amines in residues compared to the background aerosol (9% to about 2%).

Page 12, lines 235-237:

I agree that dust is found more frequently in the coarse particle size range, but then I would expect to see an increase of the dust fraction in the residues with increasing diameter. This is not seen in Figure S3. Is the identification of dust reliable? What about the Fe-containing particles? They might be dust as well.

Page 12, lines 238-243:

What could be the source of these Pb- and Fe-containing particles? See also comment above. Can the Fe-containing particles belong to the dust-type?

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Page 12, lines 244-252:

If these particles were from sea salt, they should contain chloride ions. That is hard to see in Figure 3. Are these Na-rich particles correlated with air masses coming from the ocean?

Page 13, line 259 and Figure 5:

How do you distinguish between sulfuric acid and sulfate? Besides, spelling (sulfate, sulphuric acid) should be consistent ("f" or "ph").

Page 13, lines 265-267:

What other forms of nitrate do you suggest to be present on the Na-rich and dust residues? What about uptake of nitric acid from the gas-phase by the cloud droplets?

How certain is the identification of ammonium? Which peak was used? Page 13, lines 268-272:

The stability of ammonium nitrate depends also on the humidity. In the book by Seinfeld and Pandis (2nd edition, Wiley and Sons, 2006, Chapter 10.4.3) it is shown that at 30% RH ammonium nitrate does not exist above 30°C. I would assume that the dry carrier gas in the evaporation section is below 30%RH. Thus, it may well be that NH₄NO₃ evaporates in your system.

Page 13, lines 275-276:

The sentences "The presence of abundant sulfate in aged EC cloud residues was considered to be a good CCN species before activation. . ." needs rephrasing. It is not clear to me what you want to say. Do you mean "aged EC particles mixed with sulfate are good CCN"?

Page 13, line 279:

Ammonium will most likely play a key role in the form of ammonium sulfate or ammo-

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niium nitrate. In organic particles, amines may play that role (methylamines). Again: how do you identify ammonium and how do you distinguish between amines and ammonium?

Page 14, line 281 (and Figure 5):

Why does oxalate not correlate with OC?

Page 14, lines 284-285:

What do you mean by "enrichment of TMA in amine cloud residuals"? You observe that in 93% of those cloud residuals that are assigned to the "amine" type contain TMA. That is not surprising, more surprising is that it's not 100%. But that's inside the measurement uncertainties, to my opinion.

Page 14, lines 294-295:

"This may result in 33% by number to the Amine residues containing oxalate." Please rephrase, not clear what you want to say.

Page 14, line 298:

What does "unscaled" mean? These are absolute particle numbers.

Page 14, lines 302-303:

You say that the air masses change from northerly on 18 Jan to southwesterly on 19 Jan, but the particles remain similar from 17 Jan (around noon) to 20 Jan (noon). On the other hand, the change in particle types is very abrupt from cloud residuals to ambient on Jan 17.

Page 15, lines 322-325:

Do verify the possible transport of biomass burning particles to the site, the vertical history of the trajectories is required.

Page 16, lines 337-229:

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"Note that after the activation of amine particles, the partitioning of the gas amine on cloud droplets may further contribute to the enhanced Amine cloud residues". That is true, but holds also for other species, as nitrate (HNO₃) or water-soluble OC.

Section 3.5

Here I have a major concern: You report interstitial particles containing sulfate and nitrate in the size range between 200 and 1300 nm. It is very hard to believe (not to say impossible) that such large particles are not activated in a cloud.

Later (page 17, lines 366-368) you write " However, few studies have focused on this issue, in part because interstitial particles show a smaller size than that detected by single-particle mass spectrometry (Roth et al., 2016)." Since the SPAMS has a very similar lower detection size range as the ALABAMA used by my group in Roth et al., 2016), you can not expect that you detect non-activated interstitial particles which should be in the size range below 200 nm.

My suspicion is: The clouds became thinner, and entrainment of cloud-free air has mixed "normal" aerosol particles into the cloud. But such particles cannot be referred to as "interstitial". As long as you don't have cloud microphysics (number and size of cloud droplets) or at least liquid water content (Particle Volume Monitor) available, I would suggest to remove this chapter on interstitial particles.

Page 17, line 358 / Table 1:

I would prefer a graph with bars or pie charts. I also strongly recommend showing the SMPS size distributions from residues, ambient and interstitial. That might help to identify the issues with the large interstitial particles.

Page 18, lines 374-375 / Figure 7 & 8:

How are the difference mass spectra of Figure 7 and 8 calculated? Is it ambient - residues and interstitial - residues? Or vice versa? How were the spectra normalized? Please explain.

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Page 18, lines 376-382:

Why not? I drew the same conclusion as Hayden et al. (2008) in my 2017 paper (Schneider et al., 2017, please note the update from ACPD 2016 to ACP 2017). HNO₃ uptake may not be the source of the particles but explains the high amount of nitrate found on many particles, also on the Na-rich and dust particles discussed above.

Page 18, lines 384-386:

I agree with that, but wouldn't that support the idea of uptake of HNO₃ from the gas phase? If the nitrate content does not play the major role in the activation, but more nitrate is found in the residues, that's an argument for HNO₃ uptake.

Page 18, lines 387-388:

Can intensity simply be compared like this? What about size effects and matrix effects? But again, an explanation how Figures 7 and 8 were calculated might help here.

Page 18, lines 391-392:

"Compared with interstitial particles, sulfate enhanced in the Fe cloud residues." I think an "is" is missing here.

Page 19, lines 398-399:

Better: "The in-cloud process has been reported to be an important pathway..."

Page 20, lines 421-422:

The Jungfraujoch is a station located mostly in the free troposphere and in a remote region, so the biomass burning contribution can be expected to be lower than at other sites.

Figures

Figure 3: Please improve resolution. Labels can't be read upon zooming in.

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Figure 6: The ambient particle time series (b) are broader than the corresponding gaps in (a). Please make the Figure broader. You can move the legend with the particle types to above or below the graphs, plus the legend is only needed once.

References:

Roth, A., Schneider, J., Klimach, T., Mertes, S., van Pinxteren, D., Herrmann, H., and Borrmann, S.: Aerosol properties, source identification, and cloud processing in orographic clouds measured by single particle mass spectrometry on a central European mountain site during HCCT-2010, *Atmos. Chem. Phys.*, 16, 505-524, doi:10.5194/acp-16-505-2016, 2016.

Schneider, J., Mertes, S., van Pinxteren, D., Herrmann, H., and Borrmann, S.: Uptake of nitric acid, ammonia, and organics in orographic clouds: mass spectrometric analyses of droplet residual and interstitial aerosol particles, *Atmos. Chem. Phys.*, 17, 1571-1593, doi:10.5194/acp-17-1571-2017, 2017.

Seinfeld, J. H., and Pandis, S. N.: *Atmospheric chemistry and physics: from air pollution to climate change* John Wiley and Sons, Hoboken, NJ, 2006.

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