

## ***Interactive comment on* “Chemical characteristics of cloud water and the impacts on aerosol properties at a subtropical mountain site in Hong Kong” by Tao Li et al.**

### **Anonymous Referee #1**

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The authors discuss data from cloud water and aerosol analysis at Mount Tai, Hong Kong. Their data set seems very unique not only for this location but also in general for the interpretation of sulfate and organic formation in clouds and the partitioning of organics. The manuscript is fairly well structured. However, I have numerous comments that should be addressed to clarify results and simplify the discussion. In addition, the scientific language could be improved for clarity at many places. Given the large number of my comments, I recommend a major revision.

#### Major comments

1) Terminology: Throughout the manuscript some ambiguous and unclear terminology

C1

Is used. It should be modified accordingly:

a) Cloud water organics: A large fraction of organics dissolved in cloud water is usually comprised of small volatile compounds, such as formaldehyde, formic and acetic acid etc which likely do not contribute to aqSOA; another large fraction is often not characterized on a molecular level; e.g. (Herckes et al., 2013). Thus, sentences such as ‘glyoxal is suggested to be the most likely precursor of cloud water organics’ do not seem correct.

b) In-cloud aerosols: Are you referring to aerosol particles that have been scavenged and that form cloud droplets? Or do you include interstitial particles as well? In the latter, chemical reactions might be possible to (cf the large body of literature on chemical processes in wet aerosols) but time scales, products and product distributions will be likely different due to limited water amounts and much higher ionic strengths.

c) Cloud processes: I assume that you mean ‘chemical reactions in cloud droplets’. ‘Cloud processes’ is too unspecific as it implies any physical, chemical, dynamical, meteorological . . . process related to clouds.

d) DOM (dissolved organic matter): What is ‘pre-cloud DOM’ and ‘in-cloud DOM’? Could their loading and composition simply differ because the latter includes organics that are dissolved in cloud water whereas the former only includes low volatility and semivolatile compounds whereas highly volatile but soluble compounds are not included because they resided in the gas phase during the pre-cloud periods?

e) aqueous-phase partitioning fraction: I think it would be sufficient to call it ‘aqueous phase fraction’ or ‘fraction that partitions to the aqueous phase’

2) Absolute vs relative numbers In several sections, mass fractions rather than absolute masses are discussed. This is sometimes misleading since, for example, a decreasing ratio might either indicate a decreasing numerator or an increasing denominator. I suggest adding absolute numbers where possible.

C2

a) p. 8, l. 13: What are the absolute masses of Na<sup>+</sup> and Cl<sup>-</sup> in E1 vs the marine cases? Or is the apparent increase in the fraction simply observed because other compounds (sulfate, organics etc) are less abundant?

b) p. 16, l. 15ff: This discussion is focused on the lower DOM/SO<sub>4</sub><sup>2-</sup> ratio under acidic conditions. As stated correctly, more sulfate leads to lower pH which leads to the trend of DOM/SO<sub>4</sub><sup>2-</sup> with pH as shown in Figure 8. However, I cannot follow the text in l. 19, that a lower pH leads then to decreased DOM rates. Does your data support this?

c) In Figure 9, you show clearly an increase in the DOM fraction between pre- and in-cloud aerosol. Why does the total sulfate mass apparently decrease in both cases and also organics in E.4 (sulfate from 60% x 10.7 ug/m<sup>3</sup> = 6.4 ug/m<sup>3</sup> to 31% x 15.8 ug/m<sup>3</sup> = 4.9 ug/m<sup>3</sup> during E.1 and from 5.4 ug/m<sup>3</sup> to 1 ug/m<sup>3</sup> during E.4, respectively).

### 3) Role of pH

I do not understand why the pH is included in Figures 3 and 5. In fact, I think it is rather distracting as no explanation is given for the possible influence. As stated in the discussion of Figure 5, pH is not included in the calculation of F<sub>p</sub>. Thus, there is no reason why F(the) should be color-coded. The relationship between LWC and pH, seems robust as it can be expected that at low LWC, droplets maybe on average smaller and thus more concentrated. However, the fact that high LWC causes high F<sub>p</sub> and high pH should not be presented as a correlation of F<sub>p</sub> and pH.

### 4) Previous studies

I appreciate the discussion of related studies. However, at many places the discussion is too brief to fully understand the previously discussed results. I suggest adding a few sentences to the places listed below.

a) p. 7, l. 7: I expect that the F/A ratio depends on potential precursors and their emission strength for formic and acetic acid. Was the study by Wang et al, 2011b performed at a similar location? Why can it be implied that formic acid is more efficiently

C3

formed to result in a higher F/A ratio?

b) p. 7, l. 15: What are the yields of glyoxal and methylglyoxal from oxidation of their known precursors. Can such differences indeed explain the differences in the relative abundances of glyoxal, methylglyoxal and formaldehyde at the various locations? Please also add the measured values at the various locations.

c) p. 7, l. 20 – 25: Add also the numbers for the metal concentrations as measured at the various locations.

d) p. 11, l. -18 – p. 12, l. 4: This discussion is confusing and distracting. The study by Waxman et al was performed on aerosol particles where the high ionic strength is indeed sufficiently high to cause salting-out effects. The study by Shen was performed on cloud water and thus the apparent higher solubility must have different reasons as those discussed by Waxman. If the authors decide to keep this text discussing these two studies, I suggest to start with the sentence on p. 12 (cloud water molality ... is far from high enough. ...) so that the reader knows immediately that salting-in/out does not play a role here. The last sentence (l. 4) contradicts both the previous one (salting-in/out not important in cloud water) and any reference to salting-out effects.

e) p. 11, l. 15: To what extent could oligomerization on droplet surfaces explain apparent supersaturation of less-soluble carbonyls in cloud water? If this effect indeed plays a role in the accumulation of carbonyl compounds, one might expect a stronger saturation at relatively larger drop surface areas. Can you comment on this idea? For example, do you have any measure of the drop surface area and/or drop surface-to-volume ratio in the different events? If nothing else available, one could use the aerosol particle concentration as a proxy for drop number.

f) p. 15, l. 25 ff: The relative increase of oxalate vs sulfate will depend also on the ratio of their precursors. Can you compare the SO<sub>2</sub>/VOC ratios at Mt Tai to those found by Sorooshian et al. (2007)?

C4

## 5) Partitioning

At several places, additional reactions in the aqueous phase are discussed as possible reasons for a deviation from the theoretically calculated aqueous phase fraction. I don't understand this argument since chemical reactions convert the respective species and thus it should not be included in the measured value. Or are you referring to experimental biases due to reactions in the cloud sample after collection?

a) p. 12, l. 5: The Henry's law constants in Table S3 are the effective Henry's law constants. Thus, they include hydration.

b) p. 12, l. 9: The potential of HMs- formation could be easily estimated based on the equilibrium constants available in the literature and the measured HCHO and SO<sub>2</sub> concentrations.

### Minor comments

p. 1, l. 14: Strictly, carboxylic acids are also carbonyl compounds. Maybe specify here aldehydes and acetone.

p. 1, l. 20: 'complicated effects of both physical and chemical processes' is very vague and does not add any information here. Given that you do not identify any of these processes in the discussion, I suggest removing this fragment.

p. 2, l. 19: 'cloud-free particles' should be reworded.

p. 2, l. 29: Not only the hydrolysis of sulfate and organonitrate formation leads to differences between aerosol and cloud water O/C. Also the differences in chemical composition due to dissolution of volatile organics might add to such differences (cf. Comment 1a and 1d).

p. 2, l. 31: There are many observational studies that have shown sulfate formation in clouds in the 1980 and 1990s. At least some should be referenced here.

p. 4, l. 3: Define AIM. Did you use the AIM model for any calculation? If so, for what?

C5

p. 5, l. 28: Here and throughout the manuscript: Numbers should be rounded to their significant digits. For example, here:  $96 \pm 3$ , instead of  $96.4 \pm 2.6$

p. 7, l. 22: Does this sentence refer to your analysis or to the one by Harris?

p. 10, l. 7-10: The discussion of the F/A ratios is redundant here and should be included either here or on p. 7 only.

p. 10, l. 17: Are the inverse-power fits empirical or do they have any physical meaning?

p. 11, l. 8 and 10: Add 'carbonyl' here to specify the species group.

p. 14, l. 15: Add a reference for non-radical oxidation of glyoxal.

p. 15, l. 20: Direct photolysis processes are likely less efficient. 'Photolysis reactions' should be replaced by 'photochemical reactions'.

p. 16, l. 5: Oligomer formation is most likely not important in clouds and thus not relevant here, e.g. (Lim et al., 2010)

p. 16, l. 1: During E.4, the sum of sulfate and DOM formation rates ( $0.52 + 0.45$  ug /m<sup>3</sup>/h) almost equal the total growth rate (1.07 ug/m<sup>3</sup>/h). However, during E.5 the discrepancy is much greater ( $0.05 + 0.03$  ug/m<sup>3</sup>/h vs 0.35 ug/m<sup>3</sup>/h). Can you comment on possible reasons?

p. 16, l. 14: Is this sentence a contradiction of the previous one where you discuss a decrease in DOM?

### Technical comments

p. 2, l. 18: 'contained' can be removed

p. 2, l. 19: ..was three times. . .

p. 4, l. 19: Text is unclear 'into 2 ml a high-pressure liquid chromatography (HPLC) grade acetonitrile'.

C6

p. 5, l. 12: average LWC

p. 5, l. 22: at many sites

p. 7, l. 29: Three-day back trajectories

Figure 1: The red cross is very hard to see. Replace by a different color with more contrast (e.g. black) and/or increase the symbol size.

p. 10, l. 19/20: These two sentences need some grammatical corrections.

p. 10, l. 22: ...each carbonyl compound ...

p. 14, l. 4: Ranges should be presented as  $0.72 < r < 0.94$  etc

p. 15, l. 2: 'unsaturation' should be 'subsaturation'

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