Response to Referee #1

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.

Response: We thank the reviewer for the helpful comments on our manuscript. We have made all of the suggested changes and clarifications. The reviewer's comments are in black and our responses are in blue, and the changes in the manuscript are in *italic*.

Major comments

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

Response: Thanks for pointing out the issue. We agree with this comment that a large fraction of cloud water organics such as highly oxidized materials are not characterized. We have clarified this and revised the relevant parts. The revised texts are as follows,

'*The abundant glyoxal showed positive correlations with all measured carboxylic acids and DOM.*'

'*…glyoxal should be of great importance in the secondary organic matters formation in cloud water at Mt. TMS.*'

'*…for which abundant glyoxal likely played an important role given its significant correlations with carboxylic acids and DOM.*'

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.

Response: The 'in-cloud aerosol' in the present study refers to the fine aerosols sampled during cloud event by an aerosol sampler, equipped with a 10-µm cut-size inlet and a 2.5-µm cut-size selective impactor. Since most of the cloud droplets are larger than 3 µm, the aerosols sampled during the cloud event were interstitial aerosols, together with some residual particles of smaller droplets <3 µm. To clarify, we have revised the text to include this information in the methodology and also revised the relevant terms in other parts.

'Daily *fine aerosol samples* were collected on quartz filters (47 mm diameter, Pall Inc.) using a four-channel sampler (Thermo Anderson, RAAS-400, USA) with *a size-selective inlet remove* *particles/droplets larger than 2.5 µm*, with a flow rate of 16.7 L min^{-1} and sampling duration of 23 hours. The sample filters were then refrigerated at -20 °C before laboratory analysis. An ambient ion monitor (URG 9000) *with a 2.5 µm cut-size cyclone inlet* was used to measure the hourly concentrations of water-soluble ions in $PM_{2.5}$. *During the cloud event, the collected fine aerosols were most of interstitial aerosols, together with some residual particles of smaller droplets < 3 µm.*'

'…the major water-soluble components in *pre-cloud aerosols* and *in-cloud interstitial aerosols (size < 2.5 µm)* are compared in Figure 9.'

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.

Response: We have revised the text to clarify this. The '*cloud processing*' is used when we discuss the combined effects of physical and chemical processes, and '*chemical cloud processing*' is used to refer to the chemical reactions in cloud droplets.

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?

Response: We are sorry for the misleading statement. We think the relevant discussion that the reviewer mentioned is in Section 3.4.2. As described in previous comment, we have clarified the relevant terms, the DOM now refer to the dissolved organic matter in cloud waters, while 'water-soluble organic matter (WSOM)' is used to represent the OM measured in aerosols. Many previous studies have indicated the significant changes in chemical composition of aerosol organics by cloud processing. In this study, due to the lack of speciation information in aerosol organic composition, we can only compare the differences of WSOM in bulk concentrations and mass fractions between pre-cloud aerosols and in-cloud interstitial aerosols to examine the apparent effects of cloud processing on aerosol organics.

The revised text reads,

'Meanwhile, the mass fraction of *WSOM in aerosols* was elevated from 20% (pre-cloud) to 30% (*in-cloud interstitial*), and nitrate increased from 4% to 19%, probably due to the large increase in NO_2 (over 4-fold). For the mixed case E.4, *WSOM mass fraction in the interstitial aerosols* was twice of that in pre-cloud aerosols, consistent with the increasing trend of DOM in cloud water shown in Figure 7.'

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'

Response: Agree. 'Aqueous-phase partitioning fraction' was replaced by the more concise '*aqueous phase fraction'* in the revised manuscript.

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.

Response: Thanks for the suggestion. Some absolute numbers have been added as suggested.

a) p. 8, l. 13: What are the absolute masses of Na+ and Cl- 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?

Response: It should be noted that the special cloud event 1 was highly polluted by continental sources and anthropogenic emissions during the passage of a cold front, so the absolute concentrations of most cloud water components in E.1 were the highest and the LWC was lowest at 0.08 g m^{-3}. In contrast, the clean marine E.6 with the highest LWC of 0.35 g m^{-3} generally had the lowest solute concentrations. The figure below compares the absolute concentrations of major components in cloud water among different events, and has been added as Figure S2 in the revised SI.

The absolute mass concentrations of Na$^+$ and Cl$^-$ in cloud water are 3.0 and 10 mg L^{-1} for continental polluted E.1, respectively, which are much more abundant than the Na$^+$ (0.2 mg L^{-1}) and Cl$^-$ (1.0 mg L^{-1}) in cloud water for continental E.2. However, the mass fractions of Na$^+$ and Cl$^-$ between E.1 and E.2 are comparable, with 1% for Na$^+$ and 3% for Cl$^-$ in E.1 vs. 0.4% and 2% in E.2. So the variation of absolute concentrations of other major compounds seems to have little effect on mass fractions of Na$^+$ and Cl$^-$, possibly because these main components were contributed by similar (continental) sources and changed synchronously. In comparison, the concentrations of Na$^+$ and Cl$^-$ in cloud water in marine E.5 were 2.5 and 5.9 mg L^{-1}, accounting for 5% and 11% of total mass, respectively. Their fractions are close to those for other marine-related cloud events, although the absolute concentrations also varied.

We have added the absolute mass concentration and revised the text, as follows,

‘The concentration and distributions of major components in cloud water during six cloud events are compared in Figure 2a *and Figure S2*.’

‘For example, continental E.1, *which was heavily polluted by anthropogenic emissions within the passage of a cold front (Table S2 and Figure S2)*, exhibited the largest amount of major components (393.9 mg L^{-1}) whereas marine E.6 had the least (15.7 mg L^{-1}).’

‘Influenced by marine air masses, *the concentration (and proportions) of Cl$^-$ and Na$^+$ notably increased from 0.2 mg L^{-1}(0.4%) and 1.0 mg L^{-1} (2%) in continental cloud water (E.2) to 2.5 mg L^{-1} (5%) and 5.9 mg L^{-1} (11%) in the marine one (E.5), respectively*.’

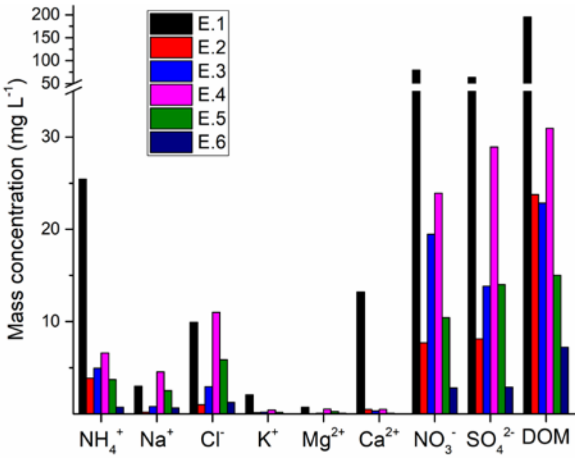

Figure S2. *Absolute mass concentrations of major components in cloud water for case E.1-6.*

b) p. 16, l. 15ff: This discussion is focused on the lower DOM/SO42- ratio under acidic conditions. As stated correctly, more sulfate leads to lower pH which leads to the trend of DOM/SO42- 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?

Response: Yes, as the reviewer stated, more sulfate leads to lower pH, but it doesn't necessarily lead to the lower DOM/SO_4^{2-} ratio at lower pH. As the DOM and sulfate in cloud water showed good correlation because of their common in-cloud aqueous production, the DOM concentrations in the high sulfate and lower pH cases were also much higher than the higher pH cases. It is well known that the in-cloud oxidation of S(IV) by H_2O_2 is the predominant pathway for sulfate formation at pH less than ~5, within which the oxidation rate is independent of pH. If the DOM aqueous formation is also independent of acidity, the DOM/SO_4^{2-} ratio would also show no clear dependence on pH. However, the observation showed that the DOM/sulfate ratios clearly decreased at lower pH, implying less DOM production compared to sulfate in the lower pH condition. We have revised the Figure 8 and the text to make it clear.

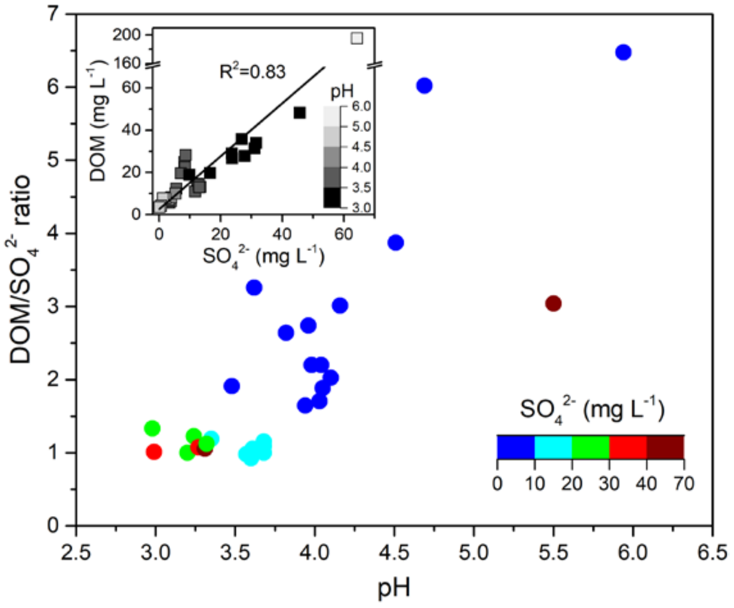

Figure 8. *DOM/SO_4^{2-} ratio as a function of cloud water pH. The embedded graph shows the relationship between DOM and SO_4^{2-}. SO_4^{2-} concentrations and pH values are both indicated by color scales.*

'Figure 8 shows the DOM/SO_4^{2-} ratio as a function of pH values and the significantly positive relationship between DOM and sulfate, *which indicates their common source of in-cloud aqueous production. The increased sulfate leads to more acidic conditions (i.e. lower pH), except the most polluted case E.1. Although the DOM also showed higher concentration in lower pH condition, the DOM/SO_4^{2-} ratios clearly decreased at lower pH range. It is well known that the in-cloud oxidation of S(IV) by H_2O_2 is the predominant pathway for sulfate formation at pH<5, within which the oxidation rate is independent of pH (Seinfeld and Pandis, 2006; Shen et al., 2012).The reduced DOM/SO_4^{2-} ratios with pH suggest that DOM production was reduced compared to the sulfate in the more acidic condition. It is consistent with a previous study which found that* oxalic acid production was more efficient relative to sulfate in the larger size and less acidic droplets (Sorooshian et al., 2007). Laboratory studies also found that the uptake of both glyoxal and methylglyoxal by acidic solutions increased with decreasing acid concentration, contributing to the formation of organic aerosols more efficiently *(Gomez et al., 2015; Zhao et al., 2006). Additionally, the possibility of competition for H_2O_2 between carbonyl* *compounds and S(IV) can be excluded because substantial H_2O_2 is usually found in cloud water (Shen et al., 2012). Although the influence mechanism of cloud water acidity on organics production remained unclear, the observed DOM/SO_4^{2-} dependent trend on pH suggests that the in-cloud formation of DOM is likely more efficient under less acidic conditions.'*

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/m3 -= 6.4 ug/m3 to 31% x 15.8 ug/m3 = 4.9 ug/m3 during E.1 and from 5.4 ug/m3 to 1 ug/m3 during E.4, respectively).

Response: We are sorry for the unclear terminology that may mislead the reviewer on this issue. As we discussed in the previous response (#1b), the in-cloud aerosol here we discussed in Fig 9 was the interstitial aerosols. Because of the cloud scavenging effects, many species in the pre-cloud aerosols were scavenged, especially the sulfate. Therefore, the total sulfate mass decreased in both cases, and the organics decreased in E.4. The highly polluted E.1 case, which showed increase in mass concentrations of aerosol DOM, nitrate, and ammonium, was exceptional. Due to the short cloud duration (~2 h) and low LWC (0.08 g m^{-3}) of cloud event E.1, the cloud scavenging of aerosol particles was ineffective. On the other hand, the intrusion of much-elevated air pollutants (including NO_x, SO_2, aged aerosols, etc.) carried by cold front passage (Figure S1 and Table S2) could lead to an increase in the mass of aerosol compositions.

We have updated the Fig 9 to make the terminology clearer and also included a figure with absolute mass concentrations in SI.

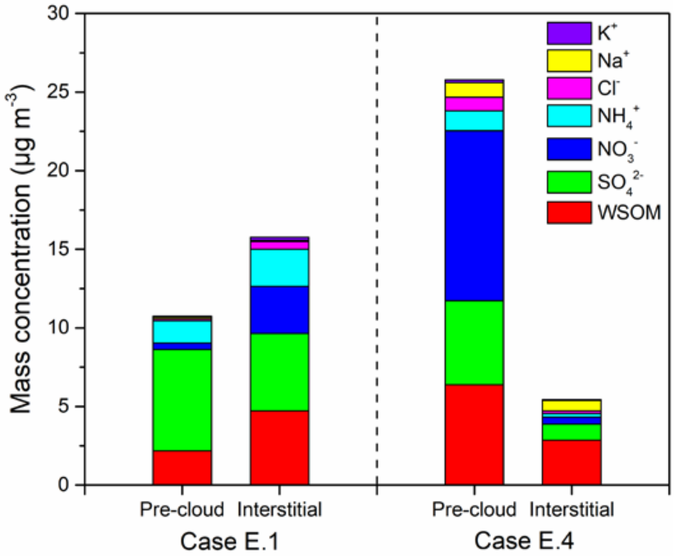

***Figure S6.** Absolute mass concentration of major water-soluble components in the pre-cloud aerosols and in-cloud interstitial aerosols for cloud events E.1 and E.4.*

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 in Figure 5, pH is not included in the calculation of Fp. 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 Fp and high pH should not be presented as a correlation of Fp and pH.

Response: As previous studies suggested, the phase partitioning and chemical reactions were both affected by the pH and LWC (Tilgner et al., 2005). In cloud droplets, acidity is generally related to soluble ions and can affect the solute composition in many ways, e.g., promoting the dissolution of trace metals, affecting uptake of trace gases and formation of aqueous organics (Cini et al., 2002; Deguillaume et al., 2005; Benedict et al., 2012; Sorooshian et al., 2007; Gomez et al., 2015; Straub, 2017). In Figure 3b, we intended to show the particular relationships between individual carbonyls and pH, which are quite different from the inverse-power fits for soluble ions, DOM, carboxylic acids and trace metals, and try to link the discussion in the respect of aqueous partitioning of carbonyls in Section 3.2. To make it clearer, we have revised the Fig 3 by moving the Fig 3b to SI, and include the pH dependence pattern as colored in Fig 3, as shown below.

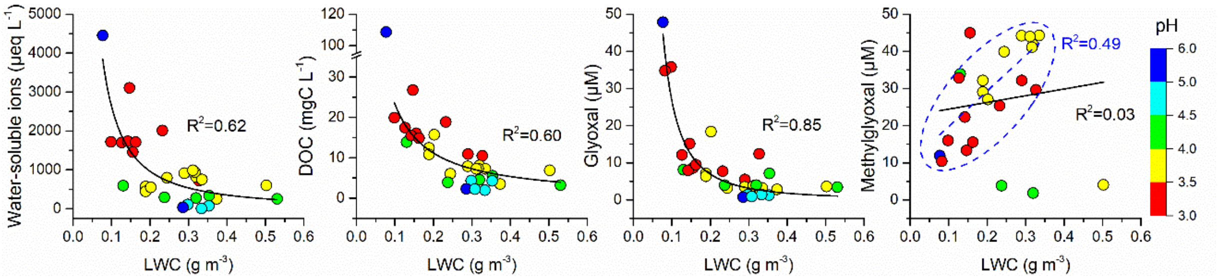

Figure 3. *Relationships of water-soluble ions, dissolved organic carbon (DOC), glyoxal and methylglyoxal with liquid water content (LWC). Color scale represents the pH range. Solid lines are empirical inverse-power fits to the data. Methylglyoxal has better linear fitting curves for samples within blue dashed circles.*

The text was also revised as follows,

'Similar inverse-power relationships of water-soluble ions, DOC and carboxylic acids with pH were also found *(Figure 3 and Figure S4)*. Increased air pollution and secondary acid ions formation likely made the cloud water more acidic, in turn promoting the dissolution of trace metals (Li et al., 2017). *Unexpectedly, individual carbonyl compounds showed different relationships with LWC and pH. For instance, as LWC and pH increased, glyoxal concentrations decreased in a power function while methylglyoxal tended to increase linearly.*'

Regarding Fig 5, we agree that the theoretical partitioning fraction F_{theo} should not be colored. The F_{theo} was updated by gray circle in the revised manuscript.

It is true that smaller droplets with low LWC are usually more concentrated and acidic. However, the pH is fundamentally determined by the relative amounts of anions and cations rather than the absolute total amounts of solutes. Although F_{me} generally increases with higher LWC in Figure 5, the gaps between F_{me} and F_{theo} vary differently for individual carbonyls, suggesting influences from unknown factors. As laboratory studies show that solution acidity is able to affect the reactive uptake of dicarbonyls (Gomez et al., 2015; Zhao et al., 2006), the cloud water acidity could be a possible factor influencing the actual partitioning of carbonyls, leading to the largely different gaps between F_{me} and F_{theo}. So we think that it is better to mark pH values to imply the possible effects of acidity on actual aqueous partitioning of carbonyls in addition to LWC, though the mechanism is currently unclear.

The text is also revised, as follows,

‘For dicarbonyls, the F_{me} of glyoxal slightly decreased at higher pH and showed a larger departure from F_{theo}, while the F_{me} of methylglyoxal far exceeded the theoretical values around pH of 3.0–3.5. *Previous studies have found that the solution acidity can largely affect the reactive uptake of dicarbonyls (Gomez et al., 2015; Zhao et al., 2006). The cloud water acidity may also influence the partitioning of carbonyls, and to some extent contribute to the different gaps between F_{me} and F_{theo} in the present study.*’

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.

Response: As suggested, the discussions have been revised or added.

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 formed to result in a higher F/A ratio?

Response: Carboxylic acids in the atmosphere mainly come from direct emissions (e.g., anthropogenic sources and biomass burning) and secondary formation through photochemical reactions in the gas phase. The F/A ratio was first proposed as a marker of the relative importance of these two sources for carboxylic acids in the gas phase (Talbot et al., 1988), and then was extended to the rainwater (Fornaro and Gutz, 2003) and cloudwater (Wang et al., 2011). Direct anthropogenic emission of acetic acid by vehicles is higher than of formic acid, which results in F/A ratios much less than 1.0, whereas photochemical oxidation of natural hydrocarbons in remote areas likely leads to higher concentrations of formic acid than acetic acid and thus the increase in F/A ratios (> 1.0) (Talbot et al., 1988; Fornaro and Gutz, 2003). Therefore, the F/A ratio is a robust and feasible method to infer the dominant sources of carboxylic acids and has been used in those previous studies. Unlike the gas phase, F/A ratio in the liquid phase (rainwater or cloudwater) is expected to be higher than that in the gas phase at equilibrium conditions, and is dictated by Henry’s law constants, dissociation constants of formic and acetic acids and pH. The F/A ratio in the gas phase can be calculated from the corresponding liquid phase, and can be used for roughly evaluating the dominant sources.

The study by Wang et al, 2011b was performed at Mt. Heng (1269 m) in south-central China, which is about 550 km north to the coastal Mt. Tai Mo Shan in Hong Kong. Both sites represent the regional atmospheric background environment surrounded by vegetation. Therefore, we think the F/A ratio method is applicable to this study.

We have revised manuscript by adding more discussions and relocating the relevant discussion to Section 3.1.2 on Page 10, according to this and below comments.

‘The formic-to-acetic acid (F/A) ratio has been suggested to be a useful indicator of sources of carboxylic acids from direct emissions (e.g., anthropogenic sources, biomass burning) or secondary photochemical formation, in the gas phase (Talbot et al., 1988), rainwater (Fornaro and Gutz, 2003) and cloudwater (Wang et al., 2011b). Direct anthropogenic emission of acetic acid from vehicle-related sources is higher than of formic acid, resulting in F/A ratios much less than 1.0, whereas photochemical oxidation of natural hydrocarbons leads to higher concentrations of formic acid than acetic acid, and therefore the increase in F/A ratios (> 1.0) (Talbot et al., 1988; Fornaro and Gutz, 2003). The F/A ratio in the liquid phase (rainwater or cloudwater) is expected to be higher than in the gas phase at equilibrium conditions, which is dictated by Henry’s law constants, dissociation constants of formic

and acetic acids and pH. So the corresponding gas-phase F/A ratio can be calculated from the aqueous concentrations to evaluate the dominant sources. In this study, a remarkable correlation between formic and acetic acid ($r = 0.97$, $p < 0.01$) suggests their similar sources or formation pathways. The high F/A ratios (1.2–1.9) than 1.0 for E.2–5 (Table S2) indicates the more important secondary formation for carboxylic acids in cloud water. In contrast, the F/A ratios in E.1 and E.6 were 0.4 and 0.5, respectively, suggesting the significant contributions from direct emissions during these two events. In addition, despite the decrease of total concentrations, the proportion of oxalic acid notably increased from 5% to 58% under more influence of marine air masses.'

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.

Response: The measured values at previous studies were added in Table S1, and more discussions were added in the revised text. According to Ervens et al. (2011) and Nishino et al. (2010), the glyoxal and methylglyoxal yields from isoprene at high NO_x level were round 0.05 and 0.20, respectively. While the two yields from toluene are approximately equal (0.14 and 0.12, respectively, at high NO_x level), methylglyoxal yields from xylene exceed the ones of glyoxal by a factor of 5 (0.08 and 0.47 respectively) (Nishino et al., 2010). Glyoxal and methylglyoxal are not only first, but also second-generation products in the oxidation of isoprene and, thus, their concentration ratio changes over time depending on the availability of oxidants. In general, the overall yields of these aldehydes from isoprene are much more uncertain, but are expected much lower than those from the oxidation of aromatics (Ervens et al., 2013), and the latter also contributes to higher yields of methylglyoxal than glyoxal. The high aromatics concentration at Mt. TMS (Table S1) and different precursors ratios compared to other studies, likely lead to the observed different pattern of methylglyoxal and glyoxal.

Table S1 below lists the measured values at various locations and is added in the SI.

Table S1. Comparison of glyoxal and methylglyoxal in cloud water [μM] and their gas-phase precursors [ppb] as well as pollutants concentrations [ppb] at Mt. TMS and other sites.

	Glyoxal	Methylglyoxal	Isoprene	Benzene	Toluene	Xylene	NO_x	O_3	References
Mt. TMS	6.7	19.1	0.16	0.5	2.3	0.9	3	31	this study
Whistler, Canada	0.6-1.8	0.5-7.4	0.6	0.05	0.1		4	25	(Ervens et al., 2013)
Davis, USA	1.3-8.7	0.1-0.9	0.2	2	4		20	70	(Ervens et al., 2013)
Mt. Schmücke, Germany	0.8-11.3	0.4-3.3							(van Pinxteren et al., 2005)
Puy de Dôme, France	0.13-0.89	0.01-0.22		up to 1.1[a]					(Deguillaume et al., 2014; Barbet et al., 2016)

[a] sum of observed benzene, toluene and ethylbenzene (Barbet et al., 2016)

The text is also revised, as follows,

'The nearly triple abundance of methylglyoxal than glyoxal at Mt. TMS differed from the previous observations at Puy de Dôme, France (Deguillaume et al., 2014), Mt. Schmücke, Germany (van Pinxteren et al., 2005), and Davis, USA (Ervens et al., 2013), where glyoxal concentrations were 2 to 10 times higher than methylglyoxal, but was similar to the results observed at Whistler, Canada (Ervens

et al., 2013) where the methylglyoxal/glyoxal ratio was much higher. These different patterns could partially be attributed to the large differences in precursors at various locations (Table S1) and also the availability of oxidants. Generally, the overall yields of these aldehydes from isoprene are much lower than those from the oxidation of aromatics (Ervens et al., 2013), and the latter also contributes to higher yields of methylglyoxal than glyoxal (Ervens et al., 2011). For example, the glyoxal and methylglyoxal yields from toluene are approximately equal (0.14 and 0.12, respectively, at high NO_x *level), and methylglyoxal yields from xylene exceed the ones of glyoxal by a factor of 5 (0.08 and 0.47, respectively) (Nishino et al., 2010; Ervens et al., 2011). The higher aromatics concentrations (toluene of 2.3 ppb, xylene of 0.9 ppb) than the biogenic isoprene (0.16 ppb) measured at Mt. TMS are expected to be the important precursors of these aldehydes and lead to the different ratio observed in the cloud water.*

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

Response: Added as suggested, as shown below,

'Aluminium (131.9 μg L^{-1}) dominated the cloud water trace metals, of which the concentration was comparable to that measured at other mountain sites in China *(99.7 to 157.3 μg* L^{-1}*)* (Li et al., 2017). *Transition metals of Fe, Cu and Mn, which play important roles in the heterogeneous catalytical formation of sulfate (Harris et al., 2013), were also found to be abundant in the cloud water, with mean concentrations of 50.6, 10.0 and 5.9 μg* L^{-1}*, respectively*. The toxic Pb concentration in cloud water (18.7 μg L^{-1}) was tens of times higher than *that observed at sites in Europe (1.4 μg* L^{-1}*) (Fomba et al., 2015) and America (0.6 μg* L^{-1}*)* (Straub et al., 2012), probably due to traffic emissions from the surrounding city-cluster.'

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.

Response: It should be noted that the study by Shen et al. (2018) was performed on ambient aerosol particles in urban Beijing, China, rather than on cloud water. As suggested, we simplified these sentences and started immediately with the statement that salting effects were not important in cloud water. The revised text is as follows:

'*The cloudwater sulfate molality (~0.1 mol* kg^{-1} *LWC on average) at Mt. TMS should be far from high enough to cause significant salting-in/out effect (i.e. an increased/decreased solubility of organics by higher salt concentrations) to remarkably alter the solubility of carbonyls in the dilute cloud water,* although the salting-in/out effect is of particular importance in the effective uptake of carbonyl compounds by concentrated solutions (Waxman et al., 2015) *and ambient particles (Shen et al., 2018).*'

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.

Response: As the literature suggested (e.g., Li et al., 2008), the oligomerization on droplet surface may not occur due to the low solubility for these carbonyls (formaldehyde, acetaldehyde and acetone). Djikaev and Tabazadeh (2003) had proposed an uptake model to account for the gas adsorption at the droplet surface, in which several adsorption parameters (e.g., Γ, b and K) are needed to perform the calculation. However, these parameters for the species studied in the present work were not well quantified, and the drop surface area or drop surface-to-volume was not measured in the present work. Thus it is impossible to perform a quantitative estimation on the oligomerization and adsorption effects. According to simulations with some example organic species (e.g., acetic acid, methanol and butanol) by Djikaev and Tabazadeh (2003), the 'overall' Henry's law constant considering both volume and surface partitioning was only <4% higher than the experimental effective Henry's law constant. Therefore, we think the adsorption and oligomerization effects may contribute to but cannot explain the observed aqueous supersaturation phenomenon here. We have revised the text by adding more discussion, as follows,

'Oligomerization on droplets surface layer induced by chemical production and adsorption *has been suggested to be able to enhance the supersaturation of less-soluble carbonyls in the aqueous phase (van Pinxteren et al., 2005;Li et al., 2008). Djikaev and Tabazadeh (2003) had proposed an uptake model to account for the gas adsorption at the droplet surface, in which some adsorption parameters and adsorption isotherm need to be known. The lack of these parameters and measurement of droplet surface area or surface-to-volume in the present work did not allow us to quantify the effects of the adsorption and oligomerization. According to the simulation with some organic species (e.g., acetic acid, methanol and butanol) by Djikaev and Tabazadeh (2003), the 'overall' Henry's law constant considering both volume and surface partitioning was only <4% higher than the experimental effective Henry's law constant. Thus the adsorption and oligomerization effects may contribute to but cannot explain the observed aqueous supersaturation phenomenon here.*'

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 SO2/VOC ratios at Mt Tai to those found by Sorooshian et al. (2007)?

Response: As the reviewer pointed out that the relative increase of oxalate vs sulfate should depend on their precursors, it is not feasible to compare the absolute oxalate/sulfate ratio among different locations because the absolute SO_2 and VOC concentration and even SO_2/VOC ratios can be quite different. We shall make it clear that the use of oxalate/sulfate ratio change here is to compare the oxalate formation relative to sulfate at different stages of one cloud event or in aerosols with and without cloud processing, rather than to compare the absolute oxalate/sulfate ratios in aerosols or cloud water at different locations. Besides, the oxalate/sulfate ratios studied are for cloud water at Mt. TMS, but were for aerosols in Sorooshian et al. (2007), and we won't compare the ratio directly. Moreover, the oxalate production does not exhibit the same degree of sensitivity to its precursor concentrations as does sulfate to SO_2, since the multistep formation of oxalate may not be in direct proportion to its precursor VOC (Sorooshian et al., 2006). The average concentrations of SO_2, toluene, ethane and isoprene were 0.8, 2.3, 1.8 and 0.16 ppbv in this study, respectively, in comparison to those of 0.5, 0.06, 0.05 and 0.04 ppb in a flight measurement over northeast America (Sorooshian et al., 2006). No clear conclusions on oxalate/sulfate ratio can be simply drawn from the comparison.

In the revised manuscript, we revised the text with more discussions, as follows:

‘The oxalate/sulfate ratio can be indicative of the in-cloud oxalate formation relative to sulfate. For example, aircraft observations (Sorooshian et al., 2007; Wonaschuetz et al., 2012) have shown an increasing aerosol oxalate/sulfate ratio throughout the mixed cloud layer from 0.01 for below-cloud aerosols to 0.09 for above-cloud aerosols, suggesting more aqueous production of aerosol oxalate relative to sulfate by cloud processing. Similarly, the observed oxalate/sulfate and DOM/sulfate ratios in cloud water for case E.2 increased from 0.04 to 0.09 and from 2.7 to 3.3 after sunrise, respectively, also demonstrating the increased cloudwater organics formation as contributed by cloud processing’.

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?

Response: In the theoretical calculation, only the processes represented in effective Henry’s law partitioning was considered. As stated by the reviewer, the chemical reactions may convert the respective species, resulting less aqueous concentration than the equilibrium concentration corresponding to the gas phase. Some fast chemical reactions producing less-soluble organics or consuming carbonyls that may contribute to the supersaturation or undersaturation, respectively, were not considered in the theoretical calculation and could be a partial reason for the deviation of the measurement from the theoretical fraction. We clarify the relevant part in the revised text,

‘The complicated partitioning behaviors could be affected by both physical (e.g., interface adsorption effect) and chemical processes (e.g., *fast aqueous reactions producing less-soluble organics and/or consuming dicarbonyls that result in a disequilibrium between gas and aqueous phases*) (van Pinxteren et al., 2005, and references therein). It is currently impossible to account for the results in detail. Further laboratory and theoretical studies are critically warranted.’

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

Response: Thanks for the correction. The text was revised as follows:

‘Using the effective Henry’s law constants considering hydration for glyoxal (4.2×10^5 M atm^{-1}) (Ip et al., 2009) and methylglyoxal (3.2×10^4 M atm^{-1}) (Zhou and Mopper, 1990), the calculated equilibrium partitioning of these dicarbonyls in the aqueous phase is comparable to the measured fraction. In contrast, the less-soluble mono-carbonyls are still supersaturated’

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 SO2 concentrations.

Response: Thanks for the helpful suggestion. We estimated the potential of hydroxymethanesulfonate (HMS) formation from the literature data and found that it only has a minor contribution to HCHO deficit. More discussions are added in the revised text, as follows,

‘Formaldehyde was deficient in the cloud water, with a F_{me}/F_{theo} value of 0.12. *It is similar to the lower measured formaldehyde in aqueous phase than that expected at equilibrium reported by Li et al. (2008), who suggested that it was probably associated with aqueous oxidation of formaldehyde. The reaction* *of formaldehyde with S(IV) can readily form hydroxymethanesulfonate (HMS) (Rao and Collett, 1995; Shen et al., 2012). Based on the average SO_2 concentration (~1 ppb) and cloud water pH (3.63) at Mt. TMS, the upper limit of in-cloud HMS formation was estimated to be 0.07 μM, which only accounts for 4.2% of total formaldehyde and thus is insufficient to explain the formaldehyde deficit.'*

Minor comments

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

Response: At the first appearance of 'carbonyl compounds' in Abstract and main text, we specified it as aldehydes and acetone, i.e. 'carbonyl compounds (*refer to aldehydes and acetones*)'.

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.

Response: Accept. As the partitioning behaviors of carbonyls were not well accounted for at present, we deleted this vague conclusion.

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

Response: It refers to ambient particles sampled during the periods without cloud events. We reworded it to be 'ambient (cloud-free) particles', the original expression used in the reference (Zhang et al., 2017).

Zhang, G., Lin, Q., Peng, L., Yang, Y., Fu, Y., Bi, X., Li, M., Chen, D., Chen, J., Cai, Z., Wang, X., Peng, P., amp, apos, an, Sheng, G., and Zhou, Z.: Insight into the in-cloud formation of oxalate based on in situ measurement by single particle mass spectrometry, Atmospheric Chemistry and Physics, 17, 13891-13901, 10.5194/acp-17-13891-2017, 2017.

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).

Response: We agree that many other factors such as the dissolution of volatile organics might add to the O/C differences. However, in this sentence, we discussed the differences in organic molecular compositions between cloud water and ambient particles under similar O/C ratio condition as investigated by Boone et al., (2015). This sentence was clarified and revised as

'*Even with similar O/C ratios, the molecular compositions of organics in aerosols and cloud water could be quite different, for example, the organosulfate hydrolysis and nitrogen-containing compounds formation were observed in cloud water compared to atmospheric particles, suggesting the significant role of cloud processing in changing the chemical properties of aerosols* (Boone et al., 2015).'

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.

Response: Yes. The sulfate formation in clouds and its contribution to droplet-mode aerosols have been intensively studied since the 1980s. We have mentioned some of these studies in the first part of the introduction section. Given the emphasis of cloud processing effects on aqSOA in the context, we added a classic study of in-cloud sulfate formation by Lelieveld and Heintzenberg (1992) and more recent study by Harris et al. (2013) in the beginning and here, and modified text reads,

'In-cloud sulfate production, which causes acid rain, has been extensively characterized *(Lelieveld and Heintzenberg, 1992*; Harris et al., 2013; Guo et al., 2012).'

'In addition to the in-cloud sulfate formation (Meng and Seinfeld, 1994), the in-cloud organics formation is also likely to add substantial mass to droplet-mode particles (Ervens et al., 2011).'

Lelieveld, J.; Heintzenberg, J., Sulfate Cooling Effect on Climate through in-Cloud Oxidation of Anthropogenic SO2. Science 1992, 258 (5079), 117-120.

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

Response: AIM was an abbreviation of ambient ion monitor, instead of the thermodynamic Aerosol Inorganics Model. To avoid misunderstanding, the abbreviation AIM now is removed and full names are used in the text.

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

Response: The numbers were rounded to their significant digits as suggested.

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

Response: It refers to our analysis results. This sentence was revised as,

'Transition metals of Fe, Cu and Mn, which play important roles in the heterogeneous catalytical formation of sulfate (Harris et al., 2013), were also found to be abundant in this study with mean concentrations of 50.6, 10.0 and 5.9 μg L^{-1}*, respectively.'*

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.

Response: All discussion of the F/A ratios was moved to page 10, as mentioned in the above response to comment #4a.

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

Response: The inverse-power fits are empirical, which describe the effects of LWC and pH on solute concentrations in cloud water. It has been clarified in the revised text.

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

Response: Added.

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

Response: As discussed by Lim et al. (2010) and references therein, aqueous-phase glyoxal can be oxidized by both radical and non-radical reactions. The latter includes hemiacetal formation, aldol condensation, oligomers formation, etc. Here we also cited the laboratory work by Gomez et al. (2015) which revealed the heterogeneous reaction mechanism of glyoxal involving hydration followed by oligomer formation. We removed the reference (Sui et al., 2017) and adjusted the positions of references as follows,

'Many laboratory experiments have demonstrated that radical (mainly ·OH) *(Lee et al., 2011; Schaefer et al., 2015)* and non-radical aqueous oxidation of glyoxal *(Lim et al., 2010; Gomez et al., 2015)* can produce abundant small carboxylic acids (e.g., oxalic and formic acids), oligomers and highly oxidized organics, which subsequently lead to mass increase in SOA upon droplet evaporation (Galloway et al., 2014).'

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

Response: Replaced.

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

Response: Thanks for the suggestion. The text is revised as,

'*Although aqueous-phase oligomers can be formed at nighttime, the oligomer formation is most likely not important in clouds (Lim et al., 2010) and thus not relevant here.*'

p. 16, l. 1: During E.4, the sum of sulfate and DOM formation rates (0.52 + 0.45 ug /m3/h) almost equal the total growth rate (1.07 ug/m3/h). However, during E.5 the discrepancy is much greater (0.05+ 0.03 ug/m3/h vs 0.35 ug/m3/h). Can you comment on possible reasons?

Response: The rough calculation of net growth rates of DOM and sulfate in cloud water as well as ambient $PM_{2.5}$ was intended to show the trend of aerosol mass growth related to cloudwater sulfate and organics production qualitatively but not quantitatively. Many chemical and physical processes such as cloud scavenging, aqueous oxidation, wet deposition and external air mass intrusion can impact the net change of cloudwater compositions and aerosols. In addition, not all the produced cloudwater sulfate and organics remain in the particulate phase after cloud cycling and contribute to aerosol mass. So the sum of cloudwater sulfate and DOM formation rates is not necessarily equal to the $PM_{2.5}$ growth rate. We expect that the much lower sulfate and DOM formation rates than $PM_{2.5}$ could be ascribed to the intrusion of air masses with elevated SO_2 and aerosol particles at the end of cloud event, as well as the artificial calculation of the $PM_{2.5}$ growth rate due to its coarse time resolution of one hour.

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

Response: As shown in Figure 7, the nighttime decrease in cloud water DOM corresponds to the decreased glyoxal and carboxylic acids in case E.5, which is consistent with the less decrease in sulfate. However, the DOM/sulfate ratios only slightly decreased from 1.19 to 0.92. To represent the similarly lower DOM/sulfate ratios at lower pH for case E.4 and E.5, we stated the DOM/sulfate ratios to be nearly constant at ~1.0, which is not contradictory to the decrease in DOM as well as sulfate.

Technical comments

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

Response: Removed.

p. 2, l. 19: …was three times…

Response: Corrected.

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

Response: It was revised to be ‘*transferred into a volumetric flask using 2 ml high-pressure liquid chromatography (HPLC) grade acetonitrile*.’

p. 5, l. 12: average LWC

Response: The ‘averaged’ was corrected to be ‘average’ here and throughout the manuscript.

p. 5, l. 22: at many sites

Response: Corrected.

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

Response: Corrected.

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

Response: The red cross was replaced by a black one with a larger size.

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

Response: These sentences were revised as ‘*Unexpectedly, individual carbonyl compounds showed different relationships with LWC and pH. For instance, as LWC and pH increased, glyoxal concentrations decreased in a power function while methylglyoxal tended to increase linearly*.’

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

Response: Corrected.

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

Response: The presentation of ranges throughout the manuscript was revised as suggested.

p. 15, l. 2: ‘unsaturation’ should be ‘subsaturation’

Response: Corrected.

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Response to Referee #2

General Comments: This study reports on field measurements of trace gases, aerosols, and cloud water at a mountaintop site in Hong Kong. A valuable set of results are provided that are important for the research community interested in cloud processes, especially aqueous processing in clouds. The paper is written fairly well and the methods used seem sound. The conclusions are supported by the data. I did not find too much to comment on in terms of issues and it is my opinion that the paper was constructed well. I only have minor comments below that should be addressed prior to publication.

Response: We thank the reviewer for the helpful suggestions on our manuscript. We have made all of the suggested changes and clarifications. The reviewer's comments are in black and our responses are in blue, and the changes in the manuscript are in *italic*.

Specific Comments: Page 15, Line 23-26: This study showed how the oxalate:sulfate ratio grows in clouds and worth noting here for the discussion:

Wonaschuetz, A., et al. (2012). Aerosol and gas re-distribution by shallow cumulus clouds: an investigation using airborne measurements, J. Geophys. Res., 117, D17202, doi:10.1029/2012JD018089.

Response: Thanks for the suggestions. We have read this article carefully and cited it in the revision. In addition, the oxalic/sulfate ratio was checked and corrected, which increased from 0.04 to 0.09 as cloud processed and solar radiation intensified. The revised sentence is as follows.

'The oxalate/sulfate ratio can be indicative of the in-cloud oxalate formation relative to sulfate. For example, aircraft observations (Sorooshian et al., 2007; Wonaschuetz et al., 2012) have shown an increasing aerosol oxalate/sulfate ratio throughout the mixed cloud layer from 0.01 for below-cloud aerosols to 0.09 for above-cloud aerosols, suggesting more aqueous production of aerosol oxalate relative to sulfate by chemical cloud processing.'

Page 18, Line 19-21: This proposal is also supported by the following and can be added in the discussion to support the authors' speculation: Ervens, B., et al. (2018), Is there an aerosol signature of chemical cloud processing? Atmos. Chem. Phys., 18, 16099-16119, doi: 10.5194/acp-18-16099-2018.

Response: Thanks for the suggestions. We read through this paper and learned that the increased mass in larger (droplet-mode) particles could be a signature of chemical cloud processing due to in-cloud sulfate and aqSOA formation. So we cited this paper in the discussion and the texts as follows,

"Model simulations have revealed that the relative mass increase of droplet-mode aerosols after cloud processing could be up to ~100% for marine air masses with significantly accumulated sulfate and oxalate at 0.56 μm range (Ervens et al., 2018). Hence we can expect that sulfate (air equivalent concentration of 4.9 μg m^{-3}*) and the low-volatile fraction of DOM (15.0 μg* m^{-3}*) measured in cloud water are mostly retained in droplet-mode aerosols upon cloud evaporation, contributing to the droplet-mode mass fraction. Although the mass size distributions of particle compositions were not measured in this study, the abundant droplet-mode oxalate, organic carbon and sulfate aerosols reported in Hong Kong (Bian et al., 2014; Gao et al., 2016) seem to support our hypothesis."*

Technical Comments: Page 11: "organics" is spelled wrong

Response: The typo is corrected.

Chemical characteristics of cloud water and the impacts on aerosol properties at a subtropical mountain site in Hong Kong

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Abstract. To investigate the cloud water chemistry and the effects of cloud ~~processes~~ processing on aerosol properties, comprehensive field observations of cloud water, aerosols, and gas-phase species were conducted at a mountaintop site in Hong Kong in October and November 2016. The chemical composition of cloud water including water-soluble ions, dissolved organic matter (DOM), carbonyl compounds (refer to aldehydes and acetones), carboxylic acids, and trace metals was quantified. The measured cloud water was very acidic with a mean pH of 3.63, as the ammonium (174 μeq L^{-1}) was insufficient for neutralizing the dominant sulfate (231~~0~~ μeq L^{-1}) and nitrate (160 μeq L^{-1}). Substantial DOM was found in cloud water, with carbonyl compounds and carboxylic acids accounting for 18~~.2~~% and ~~5.~~6%, respectively. Different from previous observations, concentrations of methylglyoxal (19.1 μM) and glyoxal (6.72 μM) were higher than that of formaldehyde (1.59 μM). The partitioning of carbonyls between cloud water and the gas phase was also investigated. The measured aqueous fractions of dicarbonyls were comparable to the theoretical estimations, while significant aqueous-phase supersaturation was found for less soluble monocarbonyls~~, suggesting complicated effects of both physical and chemical processes~~. ~~Abundant glyoxal is suggested to be the most likely precursor of cloud water organics~~measured . In-cloud oxidation played an important role in producing both organics and sulfate, ~~increasing and sulfate in the cloud water.Abundant glyoxal is suggested to be the most likely precursor of cloud water organics. T~~and the aqueous formation of organics was more enhanced by photochemistry and under less-acidic conditions. Moreover, ~~As a result of the chemical cloud processes DOM organics mass fractions in the in-cloud aerosols were~~cloud processing was found to ~~be significantly elevated in in-cloud aerosols, which was~~ likely~~ to~~ contribute~~d~~ to the increase in droplet-mode mass fraction of ~~cloud~~ cloud-processed aerosols. This study demonstrates the significant role of clouds in altering the chemical composition and physical properties of aerosols via scavenging and aqueous chemical ~~processes~~processing~~, and~~ ~~provides~~ providing valuable information about gas–cloud–aerosol~~–cloud~~ interactions in subtropical and coastal regions.

1 Introduction

Ubiquitous clouds in the troposphere play a key role in atmospheric aqueous-phase chemistry by acting as efficient media for the in-cloud formation of sulfate and secondary organic aerosol (SOA) (Harris et al., 2013; Ervens, 2015). Numerous studies on cloud and fog chemistry have been conducted in Europe and North America since the 1990s (Collett et al., 2002; Ervens, 2015; van Pinxteren et al., 2016). During the past decade, studies of the compositions of cloud/fog water, cloud scavenging and aqueous-phase reactions have also been carried out in Asia, particularly in China and Japan (Aikawa et al., 2007; Guo et al., 2012). In-cloud sulfate production, which causes acid rain, has been extensively characterized (Lelieveld and Heintzenberg, 1992; Harris et al., 2013; Guo et al., 2012). Recently, more attention has been given to organic materials, which are present in comparable amounts as sulfate and nitrate in cloud and fog water (Collett et al., 2008; Herckes et al., 2013), because of the significant contribution of ~~in~~ chemical cloud ~~processes~~ processing to aqueous SOA (aqSOA) formation in high-humidity environments (Ervens et al., 2011; Huang et al., 2011; Tomaz et al., 2018).

Many field observations and laboratory studies have reported direct evidence for the in-cloud formation of low-volatile products and aqSOA. ~~(~~Kaul et al.~~,~~ (2011) observed enhanced SOA production and increased ratios of organic to elemental carbon (OC/EC) upon fog evaporation due to aqueous-phase chemistry. Comparison of the mass spectra of ambient aerosols and cloud organics suggests that functionalization of dissolved organics possibly dominates the formation of SOA through oxidative cloud ~~processes~~ processing (Lee et al., 2012). A chamber study showed faster SOA formation (by a factor of 2) from isoprene photo-oxidation under cloud conditions than dry conditions (Brégonzio-Rozier et al., 2016), highlighting the importance of aqueous-phase reactions. Aircraft measurements by ~~(~~Sorooshian et al.~~,~~ (2007) found ubiquitous layers of enhanced organic acids levels above clouds, implying that the in-cloud formation of organic acids contributes significantly to emerging organic aerosol layers after droplet evaporation. Oxalate, an aqueous-phase oxidation product, has been considered as a good tracer for aqSOA formation, given the common in-cloud formation pathway of oxalate and sulfate (Yu et al., 2005; Sorooshian et al., 2006). Single-particle mass spectrometry analysis confirmed that oxalate ~~contained~~ in cloud droplet residuals and cloud interstitial particles ~~were~~ was three times as abundant as that in ambient (cloud-free) particles (Zhang et al., 2017), demonstrating the in-cloud formation of oxalate. At present, soluble dicarbonyls are recognized as the primary precursors of carboxylic acids and oligomers in the aqueous phase (Lim et al., 2010; Ervens et al., 2011). The irreversible uptake and aqueous oxidation of glyoxal, the simplest dicarbonyl compound, is suggested to be the primary formation pathway of oxalic acid and aqSOA (Warneck, 2003; Carlton et al., 2007). In general, water-soluble organic compounds (e.g., carbonyls) can partition into cloud droplets and form low-volatility products such as carboxylic acids and oligomers, which stay in the particle phase after cloud evaporation and form aqSOA (Blando and Turpin, 2000; Lim et al., 2005; van Pinxteren et al., 2005; Carlton et al., 2007; Lim et al., 2010; Galloway et al., 2014; Brégonzio-Rozier et al., 2016).

Chemical c~~C~~loud ~~processes~~ processing not only contributes to aerosol mass production but also alter the chemical composition of aerosols. Highly oxidized aqSOA usually exhibits higher O/C ratios (1–2) compared to SOA formed in the gas phase (0.3–0.5) (Ervens et al., 2011), as indicated by model predictions that glyoxal SOA formed in cloud water and wet aerosols are predominantly oxalic acid and oligomers, respectively (Lim et al., 2010). Even ~~in the same~~with similar O/C ratio~~ ranges~~s, the ~~organic~~molecular compositions of organics in ~~atmospheric particles~~aerosols and cloud water ~~are~~ could be quite different ~~because of~~ , for example, the organosulfate hydrolysis ~~of organosulfate~~ and nitrogen-containing compounds formation were observed in cloud water compared to atmospheric particles, suggesting the significant role of cloud processing in changing the chemical properties of aerosols ~~of nitrogen-containing compounds by cloud processing~~ (Boone et al., 2015). In addition to the in-cloud sulfate formation (Meng and Seinfeld, 1994), the in-cloud formation of organics is also likely to add substantial mass to droplet-mode particles (Ervens et al., 2011).~~’~~. For example, maximum droplet-mode organics and a shift in particle mass size distribution were observed in~~ a~~ simulated cloud ~~process~~ events (Brégonzio-Rozier et al., 2016). However, our current knowledge of aqSOA formation mechanisms and how aerosol properties change during real cloud ~~processes~~ processing remains limited.

The Hong Kong and Pearl River Delta (PRD) region is one of the most industrialized areas in Asia, and experiences serious particulate and photochemical air pollution. High cloudiness and abundant water vapor lead to significant gas–cloud–aerosol interactions in this region, and half of all surface SOA are estimated to be contributed by the aqueous chemistry of dicarbonyls (Li et al., 2013). To better understand the role of chemical cloud ~~processes~~ processing in aerosol production and the associated changes in its physicochemical properties, we conducted a comprehensive field campaign with simultaneous measurements of trace gases, aerosols and cloud water at a mountaintop site in Hong Kong. In this paper, we first present an analysis of the chemical composition of cloud water and then discuss the partitioning of individual carbonyl compounds between gaseous and aqueous phases. Finally, the effects of cloud ~~processes~~ processing on cloud water organics formation, aerosol mass production, and aerosol properties are investigated.

2 Methodology

2.1 Observation site and sampling

The field campaign was carried out at the summit of Mt. Tai Mo Shan (Mt. TMS, 22°24'N, 114°16'E, 957 m a.s.l.), the highest point of Hong Kong in the southeastern PRD region (Wang et al., 2016), where the coastal and subtropical climate leads to frequent occurrence of cloud/fog events. The site is influenced by both urban/regional ~~pollution~~pollutions from the PRD region and cleaner marine air masses from the western Pacific Ocean. Cloud water, aerosols, and gas-phase carbonyl compounds were simultaneously sampled from 9 October to 22 November 2016.

Cloud water samples were collected in a 500 mL acid-cleaned HPDE bottle by using a single-stage Caltech Active Strand Cloudwater Collector (CASCC) with a flow rate of 24.5 m^3 min^{-1}. A detailed description of the collector can be found in our previous work (Guo et al., 2012). The sampling duration was set to 1–3 hours to obtain enough sample volume. Cloudwater pH and electrical conductivity were measured ~~on~~ on-site using a portable pH meter (model 6350M, JENCO). After filtration through 0.45 μm microfilters (ANPEL Laboratory Technologies (Shanghai) Inc.), aliquots of the cloud water samples for dissolved organic carbon (DOC, 30 ml), carbonyl compounds (20 ml), water-soluble ions (15 ml), organic acids (15 ml, add

5% (*v*/*v*) chloroform added) and trace metals (15 ml, 1% (*v*/*v*) hydrochloric acid added) were properly prepared and stored at 4 °C in the dark until laboratory analysis. Derivatization of carbonyl compounds (refer to aldehydes and acetones) with 2,4-dinitrophenylhydrazine (DNPH) was performed ~~on~~ on-site after adjusting the pH to 3.0 using a buffer solution of citric acid and sodium citrate. Interstitial gas-phase carbonyl compounds were sampled with acidified DNPH-coated silica cartridges (Waters Sep-Pak DNPH-silica) at a flow rate of 0.5 L min^{-1} for 2–4 hours using a semi-continuous cartridge sampler (ATEC Model 8000). A Teflon filter assembly and an ozone scrubber were installed before the cartridge to remove large droplets and particles and prevent the influence of ozone. All cartridges were refrigerated at -20 °C after sampling.

Daily ~~PM$_{2.5}$~~fine aerosol samples were collected on quartz filters (47 mm diameter, Pall Inc.) using a four-channel sampler (Thermo Anderson, RAAS-400, USA) with a size--selective inlet removing~~e~~ particles/droplets larger than 2.5 µm, ~~with~~ a flow rate of 16.7 L min^{-1} and sampling duration of 23 hours. The sample filters were then refrigerated at -20 °C before laboratory analysis. An ambient ion monitor (~~AIM;~~ URG 9000) with a 2.5 µm cut-size cyclone inlet was used to measure the hourly concentrations of water-soluble ions in PM$_{2.5}$. During the cloud event, the collected fine aerosols were most of the interstitial aerosols, together with some residual particles of smaller droplets < 3 µm. A NanoScan SMPS nanoparticle sizer (Model 3910, TSI Inc.) and an Optical Particle Sizer (OPS) spectrometer (Model 3330, TSI Inc.) were used to measure particle mass size distributions in the range of 0.01 to 9.05 µm with 29 size bins at 1-minute scan intervals. Because of instrument test and failure, the valid data for ~~AIM~~ ambient ions and particle size distribution were only available from 2 to 11 November and 3 to 21 November, respectively. Trace gases including SO$_2$, NO$_x$, and O$_3$ were measured with a pulsed UV fluorescence analyzer (Thermo, Model 43c), a chemiluminescence analyzer (Thermo, Model 42i) and a UV photometric analyzer (Thermo, Model 49i), respectively. Hourly PM$_{2.5}$ mass concentration data were provided by the Hong Kong Environmental Protection Department. Ambient temperature and relative humidity were measured using a MetPak Weather Station (Gill, UK), and the solar radiation was monitored using a spectral radiometer (Meteorologie Consult GmbH, Germany).

2.2 Laboratory chemical analysis

Water-soluble organic carbon (WSOC) in PM$_{2.5}$ sample filters was extracted with 20 ml Milli-Q water (18.25 MΩ cm, Millipore) via sonication for 30 min and then filtration. The DOC in cloud water and WSOC in PM$_{2.5}$ were quantified by nondispersive infrared detection of CO$_2$ after thermocatalytic oxidation at 650 °C using a TOC analyzer (Shimadzu TOC-L, Japan). Sucrose standards were used for calibration, with a method detection limit of 0.112 mg L^{-1}. In this study, t~~T~~he dissolved organic matter (DOM) in cloud water ~~(~~and water-soluble organic matter (WSOM) in~~or PM$_{2.5}$~~ fine aerosols~~)~~ ~~was~~ were estimated to be 1.8 times of DOC ~~(or~~and WSOC, respectively~~)~~ (van Pinxteren et al., 2016).

The DNPH-derivatives of carbonyl compounds in the cloud water samples were extracted into 20 ml dichloromethane for three times. The extract was then concentrated to dry yellow powder by reduced pressure distillation at 38 °C and transferred into a volumetric flask using 2 ml ~~a~~ high-pressure liquid chromatography (HPLC) grade acetonitrile. The sampled cartridge of gas-phase carbonyl compounds was similarly eluted with 2 ml HPLC grade acetonitrile to a volumetric flask. The cloud water and cartridge extracts were analyzed using HPLC system (PerkinElmer 200 Series) equipped with a UV detector. The method detection limits were determined to be 0.22 μM for formaldehyde, 0.02 μM for acetaldehyde, 0.13 μM for acetone, 0.13 μM for propanal, 0.05 μM for butanal, 0.09 μM for iso-pentantal, 0.06 μM for p-tolualdehyde, 0.07 μM for glyoxal and 0.15 μM for methylglyoxal. The recovery rate ranged from 81% to 98% for individual carbonyls.

Concentrations of water-soluble ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}) in the cloud water samples were measured using an ion chromatograph (Dionex, ICS 1000). Four carboxylic acids (acetic, formic, pyruvic and oxalic acids) were analyzed using an ion chromatograph (Dionex, ICS 2500), with an IonPac AS11-HC separator column under NaOH gradient elution. Trace metals including Al, V, Cr, Mn, Fe, Ni, Cu, As, Se, Cd, Ba and Pb were measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500a) based on the EPA 200.8 method. More details on the ions and trace metal analyses were described in our previous works (Guo et al., 2012; Li et al., 2015).

2.3 Aqueous~~-~~ phase ~~partitioning~~ fraction of carbonyl compounds

The measured ~~partitioning~~ fraction of carbonyl compounds partitioning in the aqueous phase (F_{me}) is calculated by Eq.1,

$$F_{me}=\frac{C_{cw}}{C_{cw}+C_{int}} \qquad (1)$$

where C_{cw} is the air equivalent concentration of carbonyl compounds in cloud water, μg m^{-3}; and C_{int} is the interstitial gas-phase carbonyl compounds concentration, μg m^{-3}.

Assuming equilibrium, the theoretical aqueous~~-~~ phase ~~partitioning~~ fraction (F_{theo}) can be calculated from the following equation (van Pinxteren et al., 2005),

$$F_{theo}=\frac{K_H \cdot R \cdot T \cdot \mathrm{LWC} \cdot 10^{-6}}{1+K_H \cdot R \cdot T \cdot \mathrm{LWC} \cdot 10^{-6}} \qquad (2)$$

where K_H is the Henry's law constant, M atm^{-1}; R is the gas constant of 0.08205 L atm mol^{-1} K^{-1}; T is the mean temperature in K; and LWC is the cloud liquid water content, g m^{-3}.

3 Results and discussion

3.1 Characterization of cloud water chemistry

Thirty-two cloud water samples in six cloud events were collected at Mt. TMS in Hong Kong during the campaign (Figure S1). The ~~averaged~~average LWC was 0.26 g m^{-3} with a range of 0.08–0.53 g m^{-3}. Cloud water pH ranged between 2.96 and 5.94 with a volume-weighted mean (VWM) value of 3.63, lower than the cloud and fog pH observed in most other areas (e.g., Mt. Tai: 3.86 (Guo et al., 2012); Baengnyeong Island: 3.94 (Boris et al., 2016); Lulin mountain, Taiwan: 3.91 (Simon, 2016); southeastern Pacific: 4.3 (Benedict et al., 2012); and Mt. Schmücke, Germany: 4.30 (van Pinxteren et al., 2016)), indicating the severe acidification of cloud water in this region.

3.1.1 Overview of chemical composition of cloud water

Table 1 summarizes the VWM concentrations of water-soluble ions, DOC, carboxylic acids, carbonyl compounds and trace metals in the cloud water samples. The concentrations of sulfate, nitrate and ammonium ions were 23~~0.8~~1, 160~~.1~~ and 17~~3.8~~4 μeq L^{-1}, respectively, accounting for 8~~0.8~~1% of the total measured ions. The sulfate and nitrate concentrations were much lower than those in clouds in northern China (Guo et al., 2012) and in fogs at Baengnyeong Island (Boris et al., 2016), but higher than those ~~in~~ at many sites in America, Europe and Taiwan (Straub et al., 2012; van Pinxteren et al., 2016; Simon, 2016). Meanwhile, there was insufficient ammonium to neutralize the acid ions, as indicated by the low slope (0.46) of charge balance between $[NH_4^+]$ and $[NO_3^- + SO_4^{2-}]$. The elevated Cl^- (10~~8.9~~9 μeq L^{-1}) and Na^+ (6~~8.7~~9 μeq L^{-1}) indicated the considerable influence of maritime air from the western Pacific Ocean. In contrast to the commonly observed chloride depletion in coastal cloud water (Benedict et al., 2012), the molar ratio of Cl^-/Na^+ (1.86) at Mt. TMS was obviously higher than the sea-salt ratio (1.16). The abundant Cl^- in cloud water can be ascribed to potential anthropogenic chloride sources (e.g., coal-fired power plants, biomass burning) in the PRD region (Wang et al., 2016). Non-sea-salt sulfate (nss-SO_4^{2-}) was determined to be 96~~.4~~ ± ~~2.6~~3% of total sulfate based on the SO_4^{2-}/Na^+ molar ratio in seawater (0.06), demonstrating that SO_4^{2-} was mainly derived from in-cloud oxidation of SO_2 (Harris et al., 2013; Guo et al., 2012) rather than marine source.

Table 1. Concentrations of inorganic and organic species in cloud water samples measured at Mt. TMS during November 2016.

	Unit	VWM	Average	Min	Max
pH	-	3.63	3.87	2.96	5.94
Na^+	μeq L^{-1}	6~~8.7~~9	93~~.0~~	~~3.8~~4	447~~.0~~
NH_4^+	μeq L^{-1}	17~~3.8~~4	23~~4.9~~5	~~0.9~~1	141~~2.7~~3
K^+	μeq L^{-1}	~~4.1~~4	~~7.5~~8	BDL	5~~3.6~~4
Mg^{2+}	μeq L^{-1}	15~~.3~~	2~~2.7~~3	BDL	10~~4.9~~5
Ca^{2+}	μeq L^{-1}	1~~3.9~~4	49~~.1~~	BDL	66~~0.8~~1
Cl^-	μeq L^{-1}	10~~8.9~~9	13~~8.5~~8	0.3	61~~6.9~~7
NO_3^-	μeq L^{-1}	160~~.1~~	23~~7.6~~8	~~3.9~~4	128~~4.9~~5
SO_4^{2-}	μeq L^{-1}	23~~0.8~~1	305~~.3~~	3~~.0~~	13~~39.5~~40
DOC	mgC L^{-1}	9.3	12.9	2.0	108.6
Formic	μM	10.8	17.1	0.2	201.8
Acetic	μM	7.2	10.2	0.6	88.2
Pyruvic	μM	1.5	2.7	0.2	22.7
Oxalic	μM	8.3	10.3	7.6	17.5
Formaldehyde	μM	1.59	2.10	BDL	6.35
Acetaldehyde	μM	0.03	0.04	BDL	0.11
Acetone	μM	0.76	0.77	BDL	2.42
Propanal	μM	0.26	0.34	BDL	1.42
Butanal	μM	0.08	0.09	BDL	0.19
iso-pentanal	μM	5.90	7.05	0.63	22.9
p-tolualdehyde	μM	0.36	0.39	BDL	1.16

Glyoxal	µM	6.72	9.00	0.73	47.9
Methylglyoxal	µM	19.1	26.7	BDL	45.0
Al	µg L^{-1}	131.9	180.2	23.2	737.8
V	µg L^{-1}	7.9	9.5	0.2	35.7
Cr	µg L^{-1}	0.7	1.2	BDL	5.0
Mn	µg L^{-1}	5.9	10.9	0.9	42.6
Fe	µg L^{-1}	50.6	106.5	BDL	316.8
Ni	µg L^{-1}	7.1	7.7	0.2	33.0
Cu	µg L^{-1}	10.0	17.3	BDL	85.9
As	µg L^{-1}	6.7	7.4	0.7	22.2
Se	µg L^{-1}	1.9	2.6	0.1	11.5
Cd	µg L^{-1}	0.5	0.8	BDL	2.9
Ba	µg L^{-1}	3.0	7.2	BDL	25.1
Pb	µg L^{-1}	18.7	23.2	0.2	117.9

BDL: below detection limit

DOC concentrations varied from 2.0 to 108.6 mgC L^{-1} with a VWM value of 9.3 mgC L^{-1}, lower than those in polluted urban fogs but much higher than most remote and marine clouds (Herckes et al., 2013; van Pinxteren et al., 2016; Ervens et al., 2013; Benedict et al., 2012). The VWM concentrations of formic, acetic, pyruvic and oxalic acids were measured to be 10.8, 7.2, 1.5 and 8.3 µM, respectively, accounting for ~~5.6~~6 ± ~~2.2~~2% (molar ratio of carbon) of the DOC in total. ~~The formic-to-acetic acid (F/A) ratio in the air has been used to estimate the sources of carboxylic acids in rainwater and cloud water, assuming that they reach gas-liquid equilibrium (Fornaro and Gutz, 2003; Servant et al., 1991; Wang et al., 2011b). Lower (<1) or higher (>1) F/A ratios indicate direct emissions or secondary formation of carboxylic acids, respectively (Wang et al., 2011b). In this study, a remarkable correlation between formic and acetic acid (r = 0.97, p <0.01) suggests their similar sources or formation pathways, while the mean F/A ratio of 1.18 (varying from 0.41 to 1.89 in different cloud events, Table S1) indicates the more importance of secondary formation for cloud water carboxylic acids.~~

Carbonyl compounds (Table 1) comprised 18~~.2~~ ± 10~~.4~~% of DOC in cloud water. Methylglyoxal (19.1 µM) was the predominated carbonyl species, followed by glyoxal (6.72 µM), iso-pentanal (5.90 µM) and glycolaldehyde (3.56 µM), while formaldehyde (1.59 µM) and acetaldehyde (0.03 µM) were much lower. The ~~greater~~ nearly triple abundance of ~~cloud water~~ methylglyoxal ~~compared to~~than glyoxal ~~and formaldehyde~~ at Mt. TMS differed from the previous ~~many other~~ observations at~~,~~ ~~for example, at Whistler, Canada (Ervens et al., 2013),~~ Puy de Dôme, France (Deguillaume et al., 2014)~~, and~~ Mt. Schmücke, Germany (van Pinxteren et al., 2005), and Davis, USA (Ervens et al., 2013),~~,~~ where glyoxal concentrations ~~was~~ were 2 to 10 times ~~more~~ higher ~~abundant~~ than methylglyoxal, but was similar to the results observed at Whistler, Canada (Ervens et al., 2013) where the methylglyoxal/glyoxal ratio was much higher~~but much less than formaldehyde~~. These~~se~~ ~~differences~~different patterns could partially be attributed to the large differences in precursors at various locations (Table S1) and also the availability of oxidants. Generally, the overall yields of these aldehydes from isoprene are much lower than those from the oxidation of aromatics (Ervens et al., 2013) and the latter also contributes to higher yields of methylglyoxal than glyoxal (Ervens et al., 2011).~~ could, at least partially, be attributable to~~ ~~as different precursors could lead to different yields~~ For example, the glyoxal and methylglyoxal yields from toluene are approximately equal (0.14 and 0.12, respectively, at high NO$_x$ conditions), and methylglyoxal yields from xylene exceed the ones of glyoxal by a factor of 5 (0.08 and 0.47, respectively) (Nishino et al., 2010; Ervens et al., 2011). The higher aromatics concentrations (toluene of 2.3 ppb, xylene of 0.9 ppb) than the biogenic isoprene (0.16 ppb) measured at Mt. TMS are expected to be the important precursors of these aldehydes and lead to the different ratio observed in the cloud water. The less cloud water formaldehyde is likely associated with the deficient partitioning of formaldehyde in the aqueous phase as discussed in Section 3.2.~~of glyoxal and methylglyoxal (Ervens et al., 2011).the higher level of toluene (2208 ppt) than xylene (319 ppt) and isoprene (41 ppt) measured at Mt. TMS (Lam et al., 2013), as different precursors could lead to different yields of glyoxal and methylglyoxal (Ervens et al., 2011).~~

Aluminium (131.9 μg L^{-1}) dominated the cloud water trace metals, of which the concentration was comparable to that measured at other mountain sites in China (99.7 to 157.3 μg L^{-1}) (Li et al., 2017). ~~Abundant t~~Transition metals Fe, Cu and Mn, which play important roles in the heterogeneous catalytical formation of sulfate (Harris et al., 2013), were also found to be abundant in ~~this study~~the cloud water, with mean concentrations of ~~ Fe (~~50.6~~ μg L^{-1})~~, ~~Cu (~~10.0 ~~μg L^{-1})~~and ~~and Mn (~~5.9 μg L^{-1}~~), which played important roles in the heterogeneous catalytical formation of sulfate (Harris et al., 2013)~~, respectively~~ were also found~~. The toxic Pb concentration in cloud water (18.7 μg L^{-1}) was tens of times higher than that ~~in ~~observed at sites in Europe (1.4 μg L^{-1}) (Fomba et al., 2015) and America (0.6 μg L^{-1}) (Straub et al., 2012), probably due to traffic emissions from the surrounding city-cluster. Relatively high concentrations of V (7.9 μg L^{-1}) and Ni (7.1 μg L^{-1}) implied notable impacts of residual oil combustion from shipping emissions (Viana et al., 2009; Wang et al., 2014). Clearly, the cloud water at Mt. TMS was significantly influenced by anthropogenic emissions.

3.1.2 Comparisons among different air masses

Three-day~~s~~ back~~ward~~ trajectories were reconstructed using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model to investigate the origins of air masses arriving at Mt. TMS, which were influenced by both continental and marine air masses. Three types of air mass plumes for the six cloud events (E.1–6) are identified and displayed in Figure 1: continental (E.1–2), mixed (E.3–4) and marine (E.5–6). Detailed descriptions are given in Table ~~S1~~S2.

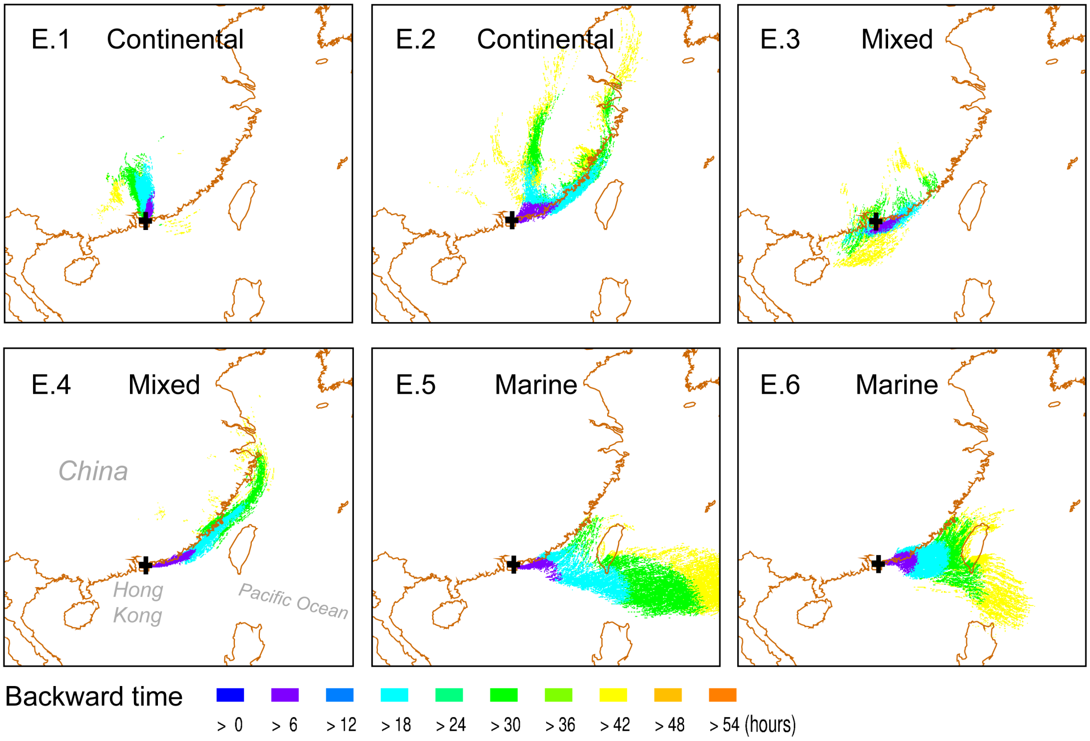


Figure 1. Air mass plumes arriving at Mt. TMS (~~red plus sign~~black cross) in Hong Kong for six cloud events (E.1–6) simulated using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model.

The concentration and distributions of major components ~~of~~ in cloud water during six cloud events are compared in Figure 2a and Figure S2. In general, continental air masses brought more abundant major components including DOM, SO_4^{2-}, NO_3^- and Ca^{2+} compared with marine ones, which had lower total concentrations but higher proportions of Cl^- and Na^+. For example, ~~polluted~~ continental E.1, which was heavily polluted by anthropogenic emissions within the passage of a cold front (Table S2 and Figure S2), exhibited the largest amount of major components (393.9 mg L^{-1}) whereas marine E.6 had the least (15.7 mg L^{-1}). For each event, DOM dominated the major components (29–53%), followed by SO_4^{2-} (17–28%) and NO_3^- (17–30%). Nss-SO_4^{2-}/NO_3^- ratios in E.1 (1.03) and E.3 (0.91) were lower than in other events (1.38–1.69), indicating the strong influence of regional air masses from the PRD region. The elevated NO_x from traffic emissions in the HK-PRD region (Zheng et al., 2009) is likely to be responsible for the higher nitrate proportions and lower nss-SO_4^{2-}/NO_3^- ratios in these two events. Ca^{2+} mainly existed in continental cloud water and ~~the~~ 3% of Ca^{2+} in E.1 likely contributed to the higher pH (5.50). Influenced by marine air masses, the concentration (and proportions) of Cl^- and Na^+ ~~in continental cloud water (E.2)~~ notably increased from 0.2 mg L^{-1} (0.4%~~ (absolute concentration of 0.2 mg L^{-1}~~) and 1.0 mg L^{-1} ~~2%~~ (2%~~1.0 mg L^{-1}~~) in continental cloud water (E.2) to ~~5%~~ (2.5 mg L^{-1}~~)~~ (5%) and ~~11%~~ (5.9 mg L^{-1}~~)~~ (11%) in the marine one (E.5), respectively. Meanwhile, the equivalent molar ratios of Cl^-/Na^+ and Ca^{2+}/Na^+ decreased from 3.11 and 5.06 to 1.50 and 0.04, respectively, close to their ratios in seawater (Table ~~S1~~S2). Figure 2a shows elevated proportions of V were observed in marine-influenced E.4–6, which is consistent with plumes passing over the busy international shipping routes (Figure ~~S2~~S3), suggesting the contribution of residual oil combustion by shipping to coastal cloud water chemistry (Gao et al., 2016).

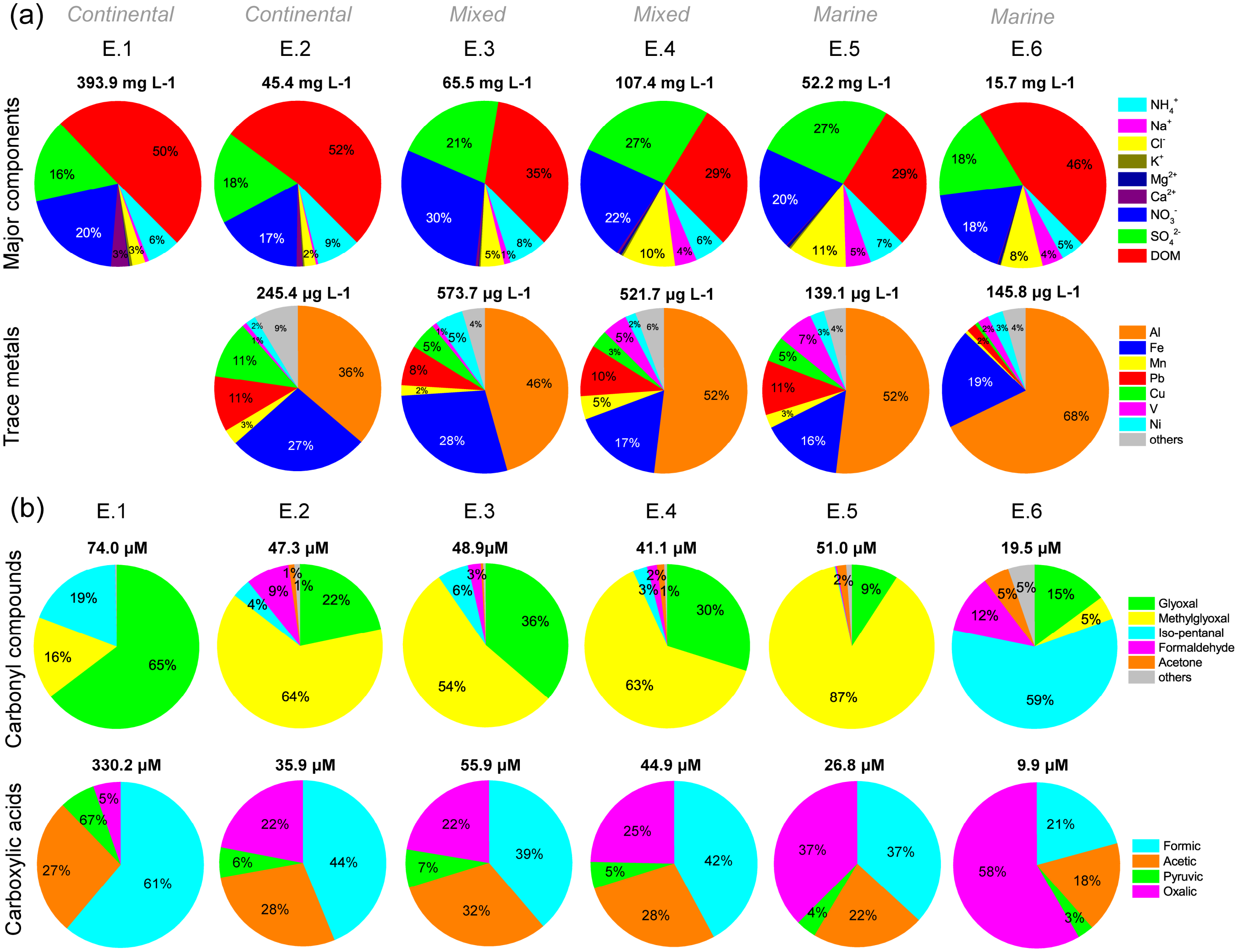


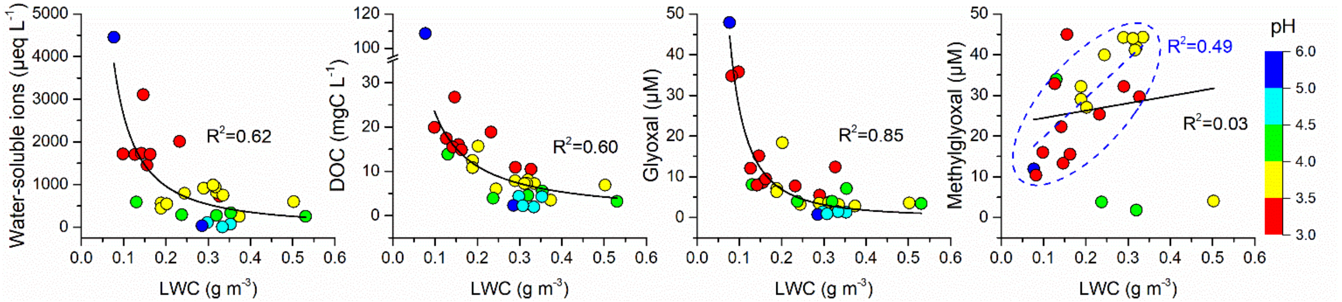
Figure 2. Concentration distributions of (a) major components and trace metals, and (b) carbonyl compounds and carboxylic acids in cloud water for each cloud event (E.1–6). The volume-weighted mean concentrations of individual species are used. Percentages of carbonyl compounds and carboxylic acids in DOC are determined by carbon molar concentration. Trace metals are absent from E.1 due to limited sample volume.

Similar trends for the carbonyl compounds and carboxylic acids with major components can also be seen in Figure 2b, but the distribution patterns are obviously distinct. Methylglyoxal dominated the carbonyl compounds in E.2–5, accounting for 54–87% of total carbonyls. In contrast, glyoxal (65%) became the major species in E.1, followed by iso-pentanal (19%) and methylglyoxal (16%); meanwhile, iso-pentanal (59%) was dominant in E.6, which had more glyoxal (15%) than methylglyoxal (5%). The concentration ratios of formaldehyde/acetaldehyde (C1/C2) and acetaldehyde/propanal (C2/C3) in the gas phase during E.3–6 were calculated (Table ~~S2~~S3), to diagnose the possible sources of carbonyls in cloud events. The C1/C2 ratios in the range of 2.8~~3~~–4.5~~3~~ suggest the combined contributions of both anthropogenic emissions and biogenic sources to the measured carbonyls, because C1/C2 ratios are normally 1 to 2 for urban areas but close to 10 for the rural forests, due to more photochemical production of formaldehyde than acetaldehyde from natural hydrocarbons (Servant et al., 1991; Possanzini et al., 1996; Ho et al., 2002). As propanal is believed to be associated only with anthropogenic emissions, the C2/C3 ratio, which is high in the rural atmosphere and low in polluted urban air, can be used as an indicator of anthropogenic origin of carbonyl compounds (Possanzini et al., 1996). The average C2/C3 ratios recorded for Mt. TMS were 4.7 ~~1~~± 2.~~6~~7, similar to those measured in roadside and urban environments in Hong Kong (5.0 ± 0.8) (Cheng et al., 2014), indicating the ~~significant~~ considerable anthropogenic sources (e.g., vehicle emissions) of carbonyls at Mt. TMS. The higher concentrations and proportion of iso-pentanal in E.1 (14.02 μM, 19%) and E.6 (11.37 μM, 59%) than in other events were also noted, possibly resulting from unconfirmed direct sources.

The formic-to-acetic acid (F/A) ratio has been suggested to be a useful indicator of sources of carboxylic acids from direct emissions (e.g., anthropogenic sources, biomass burning) or secondary photochemical formation~~,~~ in the gas phase (Talbot et al., 1988), rainwater (Fornaro and Gutz, 2003) and cloud water (Wang et al., 2011b). Direct anthropogenic emission of acetic acid from vehicle-related sources is higher than of formic acid, resulting in F/A ratios much less than 1.0, whereas photochemical oxidation of natural hydrocarbons leads to higher concentrations of formic acid than acetic acid, and therefore the increase in F/A ratios (> 1.0) (Talbot et al., 1988; Fornaro and Gutz, 2003). The F/A ratio in the liquid phase (rainwater or cloud water) is expected to be higher than in the gas phase at equilibrium conditions, which is dictated by Henry's law constants, dissociation constants of formic and acetic acids and pH. So the corresponding gas-phase F/A ratio can be calculated from the aqueous concentrations to evaluate the dominant sources.~~in the air has been used to estimate the sources of carboxylic acids in rainwater and cloud water, assuming that they reach gas-liquid equilibrium (Fornaro and Gutz, 2003;Servant et al., 1991;Wang et al., 2011b). Lower (< 1) or higher (> 1) F/A ratios indicate direct emissions or secondary formation of carboxylic acids, respectively (Wang et al., 2011b).~~ In this study, a remarkable correlation between formic and acetic acid (r = 0.97, p < 0.01) suggests their similar sources or formation pathways~~, while~~. The high F/A ratios (1.2–1.9) than 1.0 for E.2–5 ~~The mean F/A ratio of 1.18~~ (~~varying from 0.41 to 1.89 in different cloud events,~~ Table S~~1~~2) indicate~~s~~ the more importan~~ce of~~t secondary formation for ~~cloud water~~ carboxylic acids in cloud water. In contrast, the F/A ratios ~~for~~in E.1 and E.6 were ~~calculated to be~~ 0.4 and 0.5, respectively, suggesting the ~~dominant~~significant contributions ~~by~~from direct emissions during these two events. In addition, despite the decrease~~d~~ of total concentrations, t~~T~~he proportion~~s~~ of oxalic acid notably increased from 5~~.3~~% to 58~~.4~~% ~~under~~ underas more ~~the~~ influenced more of ~~of~~ by marine air masses~~, although the total concentrations decreased~~. ~~High F/A ratios in E.2–5 (1.18–1.89) demonstrated the more importance of secondary formation of carboxylic acids (i.e., aqueous oxidation). However, F/A ratios in E.1 and E.6 were calculated to be 0.41 and 0.50, respectively, indicating the dominant influence of primary emissions in these two events.~~ ~~The concentration and proportion of iso-pentanal in E.1 (14.02 μM, 19%) and E.6 (11.37 μM, 59%) were notably higher than that in other events, possibly resulting from direct sources, although this is unconfirmed.~~

3.1.3 Relationships of cloud water composition with LWC and pH

LWC and pH are important factors influencing the phase partitioning, chemical reactions and solute concentrations in cloud water (Tilgner et al., 2005; Li et al., 2017). Figure 3 and Figure ~~S3~~ S4 show the relationships of individual chemical species with LWC and pH. The non- and semi-volatile species in cloud water at Mt. TMS including water-soluble ions, DOC, carboxylic acids and trace metals were inversely related to LWC in ~~the~~empirical power functions due to dilution effects, which have been widely observed in previous studies (Herckes et al., 2013; Li et al., 2017). Similar inverse-power relationships of water-soluble ions, DOC and carboxylic acids with pH were also found (Figure 3 and Figure S~~xx~~4). Increased air pollution and secondary acid ions formation likely made the cloud water more acidic, in turn promoting the dissolution of trace metals (Li et al., 2017). Unexpectedly~~However~~, individual carbonyl compounds ~~behaved unexpectedly nonmonotonic~~showed ~~various~~ different relationships with LWC and pH. For ~~example~~instance, as LWC and pH increased, glyoxal ~~drastically~~ concentrations decreased in a power function ~~as LWC and pH increased, whereas~~while methylglyoxal tended to increase ~~exhibited a~~ linearly ~~increasing tendency~~. The increase ~~and~~ or decrease in other carbonyls concentrations with increased LWC and pH are shown in Figure ~~S3~~S4. In addition to aqueous-phase reactions, the aqueous/gas phase partitioning of each carbonyl compound~~s~~ influenced by LWC and pH is another possible reason for the observed relationships (Lim et al., 2010; Ervens et al., 2013; Ervens et al., 2011).



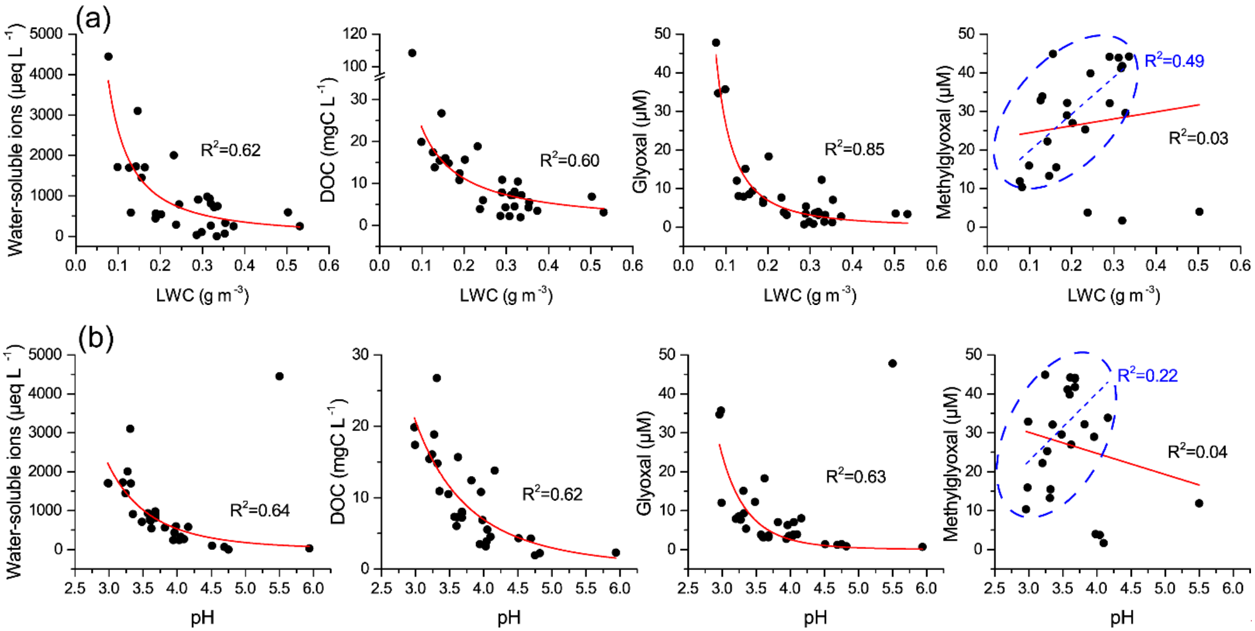


Figure 3. Relationships of water-soluble ions, dissolved organic carbon (DOC), glyoxal and methylglyoxal with~~ (a)~~ liquid water content (LWC)~~ and (b) pH~~. Color scale represents the pH range. Solid lines are empirical inverse-power or linear fits to the data. Methylglyoxal has better linear fitting curves for samples within blue ~~dotted~~ dashed circles.

3.2 Gas/a~~A~~queous ~~-~~phases ~~partitioning~~ partitioning of carbonyl compounds

The simultaneous measurement of carbonyl compounds in both gas and aqueous phases enables the investigation of their partitioning between different phases (Figure 4~~ (a)~~ and Table ~~S3~~S4). Acetone, formaldehyde, and acetaldehyde were the dominant carbonyl species (9~~2.6~~2%) measured in the gas phase during cloud events, while methylglyoxal (~~3.6~~4%) and glyoxal (1~~.0~~%) were the minors. Due to high K_H (and solubility) (Table ~~S3~~S4), the dicarbonyls were found much more abundant in cloud water, with methylglyoxal and glyoxal accounting for 6~~2.8~~3% and 2~~8.~~9% of total carbonyl species, respectively, despite their low gas-phase mixing ratios. However, diverse discrepancies were observed between the measured (F_{me}) and theoretical (F_{theo}) aqueous ~~-~~phase ~~partitioning~~ fraction~~s~~ of the individual carbonyl compounds. The F_{me}/F_{theo} ratios for each carbonyl are plotted as a function of K_H in Figure 4b. The F_{me} values for carbonyls with small K_H were about 1–3 orders of magnitude higher than F_{theo}, while for highly soluble dicarbonyls the F_{me}/F_{theo} ratios approached unity, similar to the result found at Schmücke mountain in the FEBUKO study (van Pinxteren et al., 2005). ~~Oligomerization on droplets surface layer induced by chemical production and adsorption may lead to the supersaturation of less-soluble carbonyls in cloud water, but it cannot sufficiently explain the supersaturation alone (van Pinxteren et al., 2005;Li et al., 2008).~~

~~The "salting" effect is of particular importance in the effective uptake of carbonyl compounds such as glyoxal and methylglyoxal by concentrated solutions (e.g., sulfate, nitrate) (Waxman et al., 2015).~~

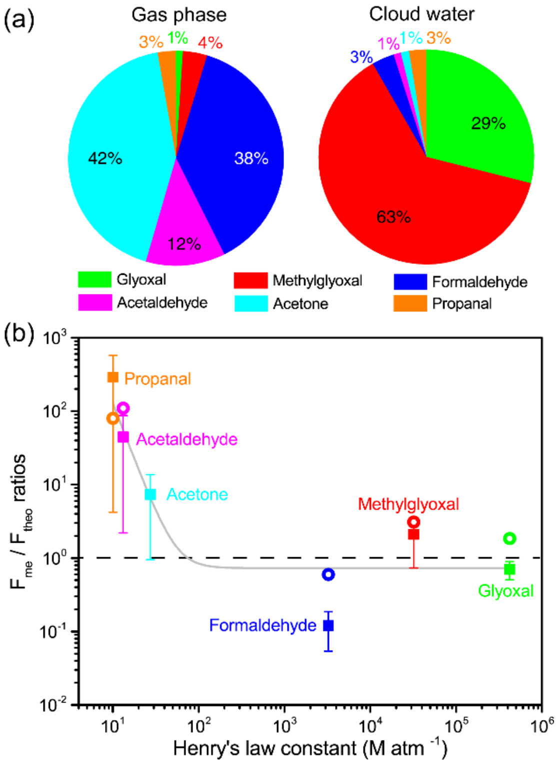


Figure 4. (a) Mass concentration fractions of measured carbonyl compounds in gas phase and cloud water, and (b) F_{me}/F_{theo} ratios as a function of Henry's law constant (K_H). Colored squares represent the mean F_{me}/F_{theo} ratios and whiskers indicate standard deviation. For comparison, F_{me}/F_{theo} ratios measured at Schmücke mountain (van Pinxteren et al., 2005) are indicated by open circles. The gray fitted line shows the decreasing trend of F_{me}/F_{theo} ratios with increasing Henry's law constant for all species. The dashed line indicates the F_{me}/F_{theo} ratio of 1.

The cloudwater sulfate molality (~0.1 mol kg^{-1} LWC on average) at Mt. TMS should be far from high enough to cause significant salting-in/out effect (i.e. an increased/decreased solubility of organics by higher salt concentrations) to remarkably alter the solubility of carbonyls in the dilute cloud water, although the salting-in/out effect is of particular importance in the effective uptake of carbonyl compounds by concentrated solutions (Waxman et al., 2015) and ambient particles (Shen et al., 2018). ~~Considering the hydration reactions,~~ Oligomerization on droplets surface layer induced by chemical production and adsorption has been suggested to be able to enhance the supersaturation of less-soluble carbonyls in the aqueous phase (van Pinxteren et al., 2005; Li et al., 2008). ~~(~~Djikaev and Tabazadeh~~,~~ (2003) had proposed an uptake model to account for the gas adsorption at the droplet surface, in which some adsorption parameters and adsorption isotherm need to be known. The lack of these parameters and measurement of droplet surface area or surface-to-volume in the present work did not allow us to quantify the effects of the adsorption and oligomerization. According to the simulation with some organic species (e.g., acetic acid, methanol and butanol) by ~~(~~Djikaev and Tabazadeh~~,~~ (2003), the ‘overall’ Henry’s law constant considering both volume and surface partitioning was only <4% higher than the experimental effective Henry’s law constant. Thus the adsorption and oligomerization effects may contribute to but cannot explain the observed aqueous supersaturation phenomenon here.

Using the effective Henry’s law constants considering hydration for glyoxal (4.2×10^5 M atm^{-1}) (Ip et al., 2009) and methylglyoxal (3.2×10^4 M atm^{-1}) (Zhou and Mopper, 1990), the calculated equilibrium partitioning of these dicarbonyls in the aqueous phase ~~are~~is comparable to the measured fraction. In contrast, the less-soluble monocarbonyls are still supersaturated~~.~~. ~~Recently, (Shen et al., 2018) found that partitioning of six carbonyls to particles was enhanced by more than two orders of magnitude compared to the Henry’s law prediction, which was partially explained by the observed “salting-in” effect (i.e., an increased solubility of oragnics with salt concentration), a result inconsistent with the laboratory “salting-out” effect (Waxman et al., 2015), due to the more complex composition of ambient atmosphere and particles. However, the cloud water sulfate molality (~ 0.1 mol kg^{-1} LWC on average) is far from high enough to cause significant “salting” effect, and the effective Henry’s law partitioning of carbonyls in the dilute cloud water at Mt. TMS would only be affected very slightly. It is noteworthy that the K_H employed for less soluble carbonyls refers to pure water as solvent, which may be underestimated in ambient cloud water as influenced by various factors (e.g., hydration and heterogeneous reactions). Considering the hydration reactions, the effective Henry’s law constants for glyoxal (4.2×10^5 M atm^{-1}) (Ip et al., 2009) and methylglyoxal (3.2×10^4 M atm^{-1}) (Zhou and Mopper, 1990) were used to calculate their equilibrium partitioning fractions in the aqueous phase, which consequently agreed with F_{theo}.~~ Formaldehyde was deficient in the cloud water, with a F_{me}/F_{theo} value of 0.12~~,~~. It is similar to the lower measured formaldehyde in aqueous phase than that expected at equilibrium reported by ~~(~~Li et al.~~,~~ (2008), who suggested that it was probably associated with aqueous oxidation of formaldehyde. The reaction of formaldehyde with S(IV) can readily form hydroxymethanesulfonate (HMS) (Rao and Collett, 1995; Shen et al., 2012). Based on the average SO_2 concentration (~1 ppb) and cloud water pH (3.63) at Mt. TMS, the upper limit of in-cloud HMS formation was estimated to be 0.07 μM, which only accounts for 4.2% of total formaldehyde and thus is insufficient to explain the formaldehyde deficit. ~~similar to the less measured aqueous phase formaldehyde than that expected at equilibrium as result reported by (Li et al., 2008). This deficiency was probably associated with aqueous oxidation of formaldehyde (Li et al., 2008) and hydroxymethanesulfonate formation with S(IV) (Rao and Collett, 1995;Shen et al., 2012), although the detailed mechanism is uncertain here.~~

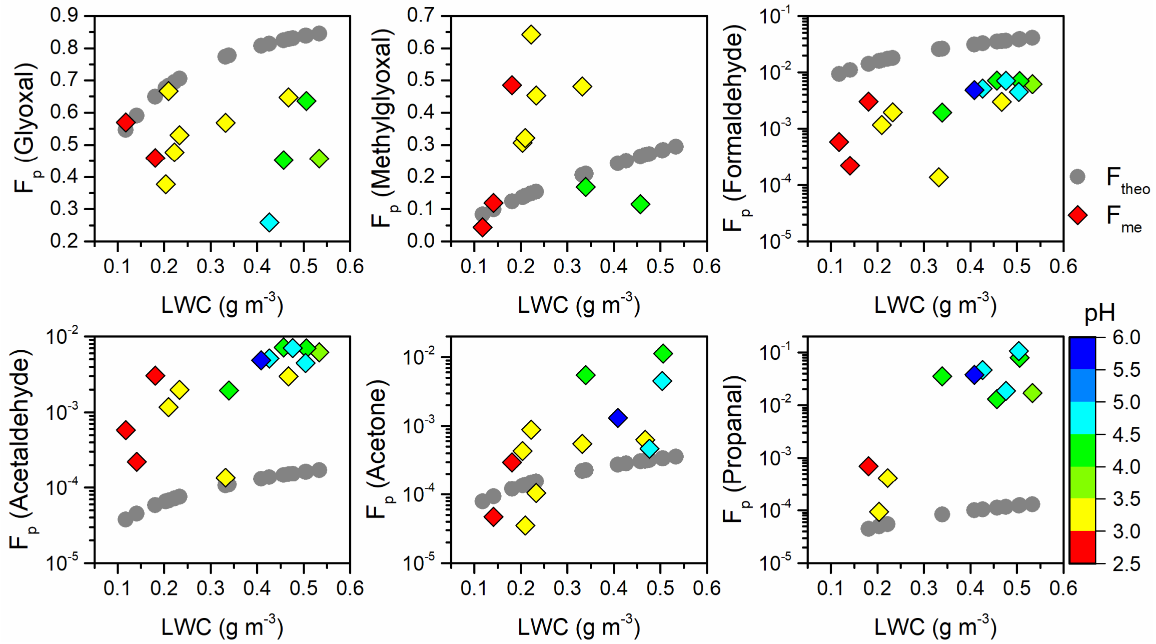
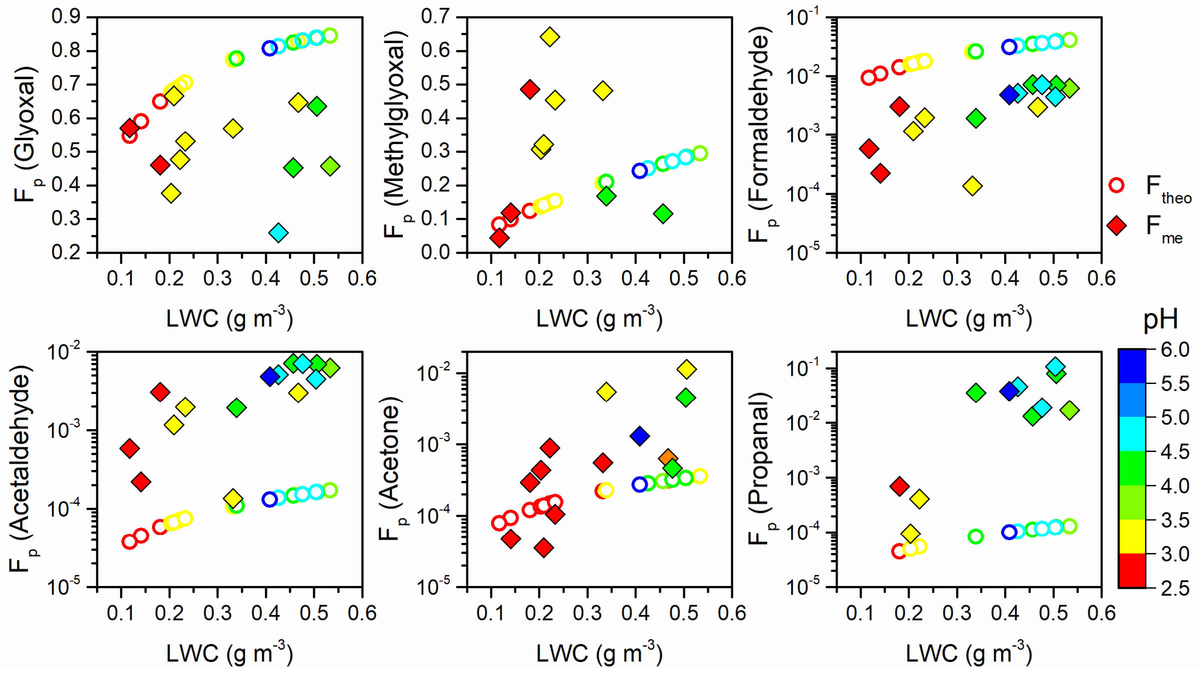


Figure 5. Theoretical (F_{theo}, gray circle) and measured (F_{me}, colored diamond) aqueous phase fraction (F_p) of carbonyl compounds as a function of LWC and pH.

Figure 5 depicts the dependence of F_{me}/F_{theo} ratios of carbonyl compounds on LWC and pH. In general, the F_{theo} of measured carbonyls increased to different degrees with enhanced LWC, because larger water content has a greater capacity to retain organic species. The F_{me} also increased remarkably as the LWC increased, but deviated to different degrees from F_{theo}. For example, the F_{me} values for methylglyoxal and acetone surpassed their F_{theo} values when LWC exceeded ~0.2 g m^{-3}, whereas the F_{me} values of formaldehyde and acetaldehyde were approximately parallel to their F_{theo} throughout the LWC range, being one order of magnitude lower and higher, respectively. ~~Cloud water acidity may contribute to the deviation between F_{me} and F_{theo} for individual carbonyl compounds.~~ It should be noted that pH value was positively related to LWC but not involved in the F_{theo} calculation, so the elevated F_{theo} and increase in pH were not necessarily correlated. In contrast, the F_{me} seemed to be more close to F_{theo} at lower pH, but increased more rapidly than F_{theo} at higher pH for the monocarbonyls except for formaldehyde. For dicarbonyls, the F_{me} of glyoxal slightly decreased at higher pH and showed a larger departure from F_{theo}, while the F_{me} of methylglyoxal far exceeded the theoretical values around pH of 3.0–3.5. Previous studies have found that the solution acidity can largely affect the reactive uptake of dicarbonyls (Gomez et al., 2015; Zhao et al., 2006). ~~It seems that t~~The cloud water acidity may also~~has somewhat~~ influences ~~on~~ the ~~actual~~ partitioning of carbonyls, and to some extent contribute to ~~leading to~~ the different gaps between F_{me} and F_{theo}~~.~~ in the present study. ~~For example, solution acidity is found to largely affect the reactive uptake of dicarbonyls (Gomez et al., 2015;Zhao et al., 2006).~~ The ~~above~~ complicated partitioning behavio~~u~~rs could be affected by both physical (e.g., interface adsorption effect) and chemical processes (e.g., fast aqueous reactions producing less-soluble organics and/or consuming dicarbonyls that result in a disequilibrium between gas and aqueous phases) (van

Pinxteren et al., 2005, and references therein). It is ~~not~~ currently impossible to account for the results in detail. Further laboratory and theoretical studies are critically warranted.



~~Figure 5. Theoretical (F_{theo}, open circle) and measured (F_{me}, solid diamond) aqueous-phase fraction (F_p) of carbonyl compounds as a function of liquid water content (LWC) and pH.~~

3.3 Correlations between carbonyls and carboxylic acids

To investigate the potential precursors of carboxylic acids and DOM in cloud water, the correlations among all detected organic compounds and water-soluble ions were examined. Significant correlations were found for secondary water-soluble ions (SO_4^{2-}, NO_3^- and NH_4^+) with glyoxal (~~r=~~0.76 < ~~–~~r < 0.88, p < 0.01) and carboxylic acids (~~r=~~0.72 < r < ~~–~~0.94, p < 0.01). As sulfate is primarily produced by in-cloud S(IV) oxidation (Harris et al., 2013), a strong correlation (r = 0.75, p < 0.01) between oxalic acid and sulfate suggests the significant in-cloud formation of oxalic acid. Likewise, the chemical cloud processing might have contributed to the secondary formation of other organic matters in the aqueous phase, such as DOM with a significant correlation with sulfate (r = 0.83, p < 0.01) (Ervens et al., 2011; Yu et al., 2005).

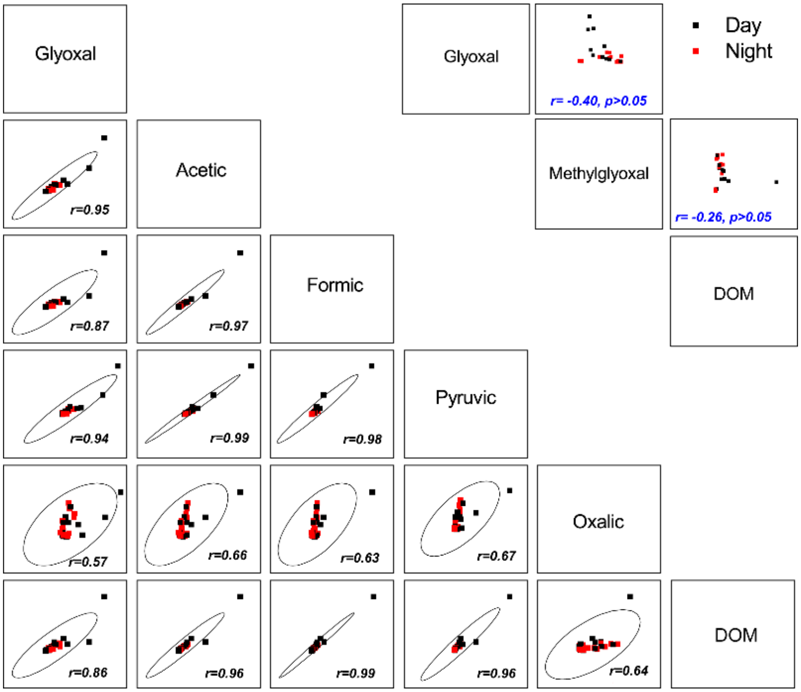


Figure 6. Pairwise scatter plot of selected organic species in cloud water. The ellipses indicate confidence coefficient of 99%.

Figure 6 shows the pairwise correlations ($p < 0.01$) among the selected organic species. Aqueous-phase glyoxal was positively correlated with all carboxylic acids (~~r =~~ 0.57 < r < ~~–~~ 0.95) and DOM (r = 0.86) in both daytime and nighttime. Moreover, the gas-phase glyoxal performed positive relationships with aqueous-phase glyoxal and carboxylic acids, particularly oxalic acid (Figure ~~S4~~S5). Many laboratory experiments ~~(Lim et al., 2010;Lee et al., 2011;Schaefer et al., 2015;Gomez et al., 2015)~~ have demonstrated that radical (mainly ·OH) (Lee et al., 2011; Schaefer et al., 2015)~~;~~ and non-radical -aqueous oxidation of glyoxal (Lim et al., 2010; Gomez et al., 2015) can produce abundant small carboxylic acids (e.g., oxalic and formic acids), oligomers and highly oxidized organics, which subsequently lead to mass increase in SOA upon droplet evaporation (Galloway et al., 2014). In this study, the abundant methylglyoxal showed no significant correlations with glyoxal, carboxylic acids or DOM in both daytime and nighttime. ~~Therefore, g~~Given the high solubility of glyoxal and its potential yield of carboxylic acids (Carlton et al., 2007; Lim et al., 2005; Lim et al., 2010; Blando and Turpin, 2000), glyoxal ~~is likely to~~should be ~~the most important precursor of~~of great importance in the secondary organic matters formation in cloud water at Mt. TMS. Thus~~,~~ the consumption of glyoxal in the oxidation reactions may partially contribute to its slight sub~~un~~saturation in the aqueous phase (Figure 5). In addition, as oxalic acid is predominantly formed in clouds (Myriokefalitakis et al., 2011; Ervens et al., 2011), the good interrelationships among carboxylic acids and DOM (Figure 6) indicates that carboxylic acids can ~~directly~~ contribute to DOM formation directly and/or~~ contribute~~ indirectly ~~by~~ via oxidizing to oligomers (Carlton et al., 2006; Tan et al., 2012).

3.4 Aqueous organics formation and cloud effects on aerosol properties

3.4.1 Variation of cloud water organics and aerosol particles

Cloud ~~processes~~ processing can efficiently remove aerosol particles from the air by nucleation scavenging and impaction scavenging (Ervens, 2015), especially at the initial stage of cloud events (Wang et al., 2011a; Li et al., 2017). At the same time, chemical cloud ~~processes~~ processing greatly favors the in-cloud formation of sulfate (Harris et al., 2013) and SOA (Brégonzio-Rozier et al., 2016). To investigate the scavenging and changes of aerosols during cloud events, temporal variations of glyoxal, carboxylic acids, DOM and sulfate in cloud water, and ambient $PM_{2.5}$ during three cloud events (E.2, E.4, and E.5) were examined (Figure 7). Based on hourly $PM_{2.5}$ and water-soluble ions data (not shown here), the ~~averaged~~average scavenging ratios were determined to be 0.72 for $PM_{2.5}$, 0.85 for aerosol sulfate, 0.69 for nitrate and 0.68 for ammonium within the first 1–2 h of cloud ~~processes~~processing, which were ascribed to the high cloud density, long cloud duration and little external aerosol invasion.

Figure 7 illustrates the variations of cloud water organics, sulfate and ambient $PM_{2.5}$ along with cloud evolution. Positive change rates were found during the daytime with enhanced solar radiation, while negative change rates appeared with reduced solar radiation at sunset and nighttime. This result agreed with the simulation by ~~(~~Huang et al.~~,~~ (2011), in which increasing solar radiation enhanced organic acids and SOA production through ~~photolysis~~ photochemical reactions. During the clean continental case E.2, the total carboxylic acids in cloud water increased by a factor of ~~2–5~~1.9 ~~times~~ and DOM was elevated from 3.7 to 5.7 μg m^{-3} as solar radiation intensified to ~300 W m^{-2}, corresponding to the dramatic growth in aqueous glyoxal from 69 to 216 ng m^{-3}; while the increment of sulfate was relatively small, with only 0.15 μg m^{-3} (i.e.~~,~~ 10%).

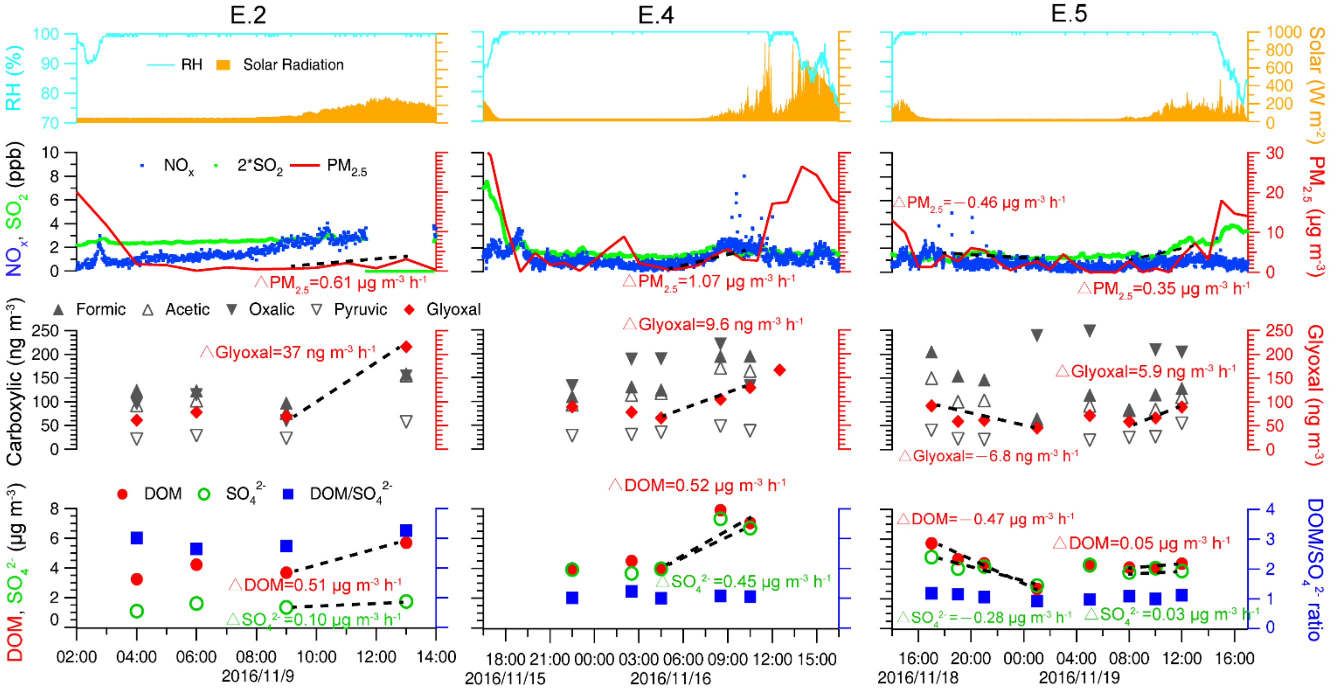


Figure 7. Temporal variation of air equivalent concentrations of glyoxal, carboxylic acids, dissolved organic matter (DOM), SO_4^{2-} and DOM/SO_4^{2-} ratio in cloud water, and ambient $PM_{2.5}$ during three cloud events (E.2, E.4 and E.5). Meteorological parameters (relative humidity and solar radiation) and trace gases (NO_x and SO_2) are also displayed. Mass change rates of cloud water components and ambient $PM_{2.5}$ are indicated by dashed lines and slopes.

The oxalate/sulfate ratio can be indicative of the in-cloud oxalate formation relative to sulfate. For example, ~~The ratios of oxalic/sulfate and DOM/sulfate increased from 0.6×10^{-3} to 2.6×10^{-3} and from 2.7 to 3.3, respectively, similar to the~~ aircraft observations (Sorooshian et al., 2007; Wonaschuetz et al., 2012) ~~of~~ have shown an increasing~~ed~~ aerosol oxalate/sulfate ratio throughout the mixed cloud layer ~~in~~ from ~~aerosols~~ 0.01 for below-cloud aerosols to 0.09 for above-~~-~~cloud~~s~~ aerosols~~(Sorooshian et al., 2007;Wonaschuetz et al., 2012)~~, ~~which indicated~~suggesting ~~much more efficient~~more~~-in-cloud~~ aqueous ~~formation~~ production of aerosol oxalate ~~and DOM relative to~~relative to sulfate by chemical cloud processing. Similarly, the observed oxalate/sulfate and DOM/sulfate ratios in cloud water for case E.2 increased from 0.04 to 0.09 and from 2.7 to 3.3 after sunrise, respectively, also demonstrating the increased cloudwater organics formation as contributed by cloud processing. A chamber study demonstrated that the faster photochemical uptake of glyoxal under irradiation than that in dark conditions remarkably enhanced the aqSOA formation rate by several orders of magnitude (Volkamer et al., 2009), and the radical-initiated photo-production of aqSOA mass in the daytime was predicted to be an order of magnitude higher than at nighttime (Ervens and Volkamer, 2010). Therefore, photochemical reactions are expected to enhance the production of cloudwater organics (0.51 μg m^{-3} h^{-1}) compared to sulfate (0.10 μg m^{-3} h^{-1}) in case E.2, which likely lead to the observed increase in daytime $PM_{2.5}$ (0.61 μg m^{-3} h^{-1})~~observed during E.2 could be attributed to the cloud water organic matters which have a much higher formation rate than sulfate~~. During the mixed E.4, the approximate growth rates of DOM (0.52 μg m^{-3} h^{-1}) and sulfate (0.45 μg m^{-3} h^{-1}) were comparably fast to induce a high $PM_{2.5}$ growth rate (1.07 μg m^{-3} h^{-1}). In comparison, the slow growth of DOM (0.05 μg m^{-3} h^{-1})~~, and~~ sulfate (0.03 μg m^{-3} h^{-1}) and $PM_{2.5}$ (0.35 μg m^{-3} h^{-1}) was observed during the marine E.5~~ induced only 0.35 μg m^{-3} h^{-1} of $PM_{2.5}$~~. ~~This~~ It suggests that the in-cloud formation of both DOM and sulfate influences the fine aerosol production. It was also noted that aqueous glyoxal gradually increased after sunrise, which likely produced carboxylic acids such as oxalic acid rapidly via photo-oxidation of glyoxal and contributed to formation of aqueous organics (Carlton et al., 2007; Warneck, 2003). Although aqueous-phase oligomers can be formed at nighttime, the ~~In contrast,~~ oligomer formation is most likely not important in clouds (Lim et al., 2010). ~~Although aqueous-phase oligomers can be formed at nighttime, their contributions to aqSOA formation are too small to compensate for the organic losses compared to aqueous photo-oxidation reactions during the daytime (Ervens et al., 2011)~~. In case E.5, the reduction of DOM (-0.47 μg m^{-3} h^{-1}) corresponding to the decrease in nighttime glyoxal (-6.8 ng m^{-3} h^{-1}), together with decreased sulfate (-0.28 μg m^{-3} h^{-1}), ~~was accompanied by the reduction of carboxylic acids and loss of DOM (-0.47 μg m^{-3} h^{-1}), which~~ could be responsible for the net decrease in $PM_{2.5}$ mass (-0.46 μg m^{-3} h^{-1}).

Figure 7 also shows that DOM/SO_4^{2-} ratios during E.4 and E.5 remained nearly constant at ~~around~~ ~1.0 with stronger cloud water acidity (pH of~~=~~ 2.96–3.68), whereas the ratios during other cloud events varied from 1.6 to 6.5 under higher pH conditions (3.62–5.94). Figure 8 shows the DOM/SO_4^{2-} ratios as a function of pH values and the significantly positive relationship between DOM and sulfate, which indicates their common source of in-cloud aqueous production. The increased sulfate leads to ~~as a function of pH values and the significantly positive relationship between DOM and sulfate. The DOM/SO_4^{2-} ratios reduced under~~ more acidic conditions (i.e. lower pH~~ values due to increased sulfate~~), except the most polluted case E.1. Although the DOM also showed higher concentration in lower pH condition, the DOM/SO_4^{2-} ratios clearly decreased at lower pH range. It is well known that in-cloud oxidation of S(IV) by H_2O_2 is ~~. The DOM/SO_4^{2-} ratios~~~~As~~ the predominant pathway ~~of~~ for sulfate formation at pH < 5~~in-cloud~~ ~~,sulfate~~ within which the oxidation rate is ~~oxidation by H_2O_2 in the pH range of 3–6 is~~ independent of pH (Seinfeld and Pandis, 2006; Shen et al., 2012). The reduced DOM/SO_4^{2-} ratios with pH suggest that DOM production was reduced compared to the sulfate in the more acidic condition. It is consistent with a previous study which found ~~(Sorooshian et al., 2007) found~~ that ~~the production of~~ oxalic acid production was more efficient relative to sulfate in the larger size and less acidic droplets (Sorooshian et al., 2007). ~~with lowered pH suggest that DOM production slowed, probably due to adverse effects of cloud water acidity. Competition for H_2O_2 between carbonyl compounds and S(IV) is unlikely because substantial H_2O_2 is usually found in cloud water (Shen et al., 2012). (Sorooshian et al., 2007) found that the production of oxalic acid was more efficient relative to sulfate in larger size and less acidic droplets.~~ Laboratory studies~~ (Gomez et al., 2015;Zhao et al., 2006)~~ also found that the uptake of both glyoxal and methylglyoxal by acidic solutions increased with decreasing acid concentration, contributing to the formation of organic aerosols more efficiently (Gomez et al., 2015; Zhao et al., 2006). Additionally, the possibility of competition for H_2O_2 between carbonyl compounds and S(IV) can be excluded because substantial H_2O_2 is usually found in cloud water (Shen et al., 2012). Although the influence mechanism of cloud water acidity on organics production remained unclear, ~~The observed increase in DOM/SO_4^{2-} ratio at higher pH~~the observed DOM/SO_4^{2-} dependent trend on pH ~~suggests~~ suggests that the in-cloud formation of DOM ~~was much~~is likely more efficient ~~than sulfate~~ under less acidic conditions.

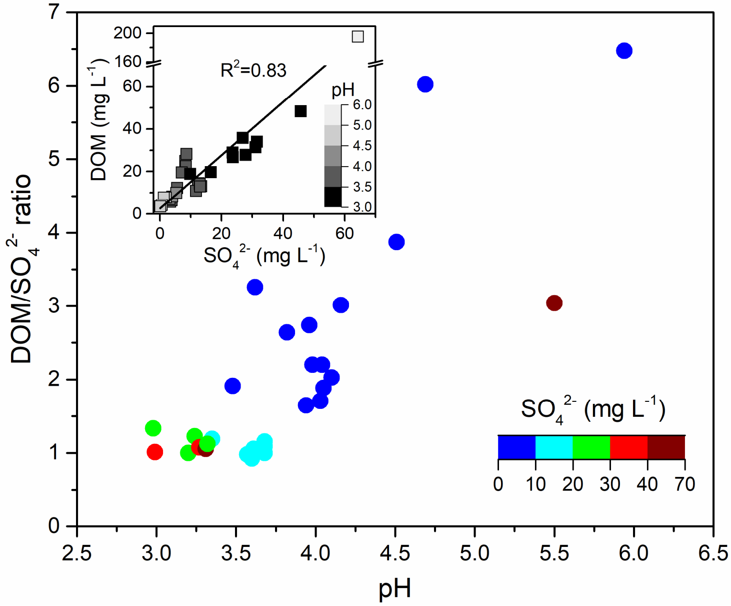


Figure 8. DOM/SO_4^{2-} ratio as a function of ~~cloudwater~~cloud water pH~~ value~~. ~~Color scale represents SO_4^{2-} concentrations in cloud water.~~ The embedded graph shows the relationship between DOM and SO_4^{2-}. SO_4^{2-} concentrations and pH values are both indicated by ~~C~~color scales~~ represents SO_4^{2-} concentrations in cloud water.~~

3.4.2 Impacts of cloud ~~processes~~ processing on aerosols ~~particles~~ composition and size distribution

To evaluate the impacts of cloud ~~processes~~ processing on aerosol chemistry, the major water-soluble components in pre-cloud aerosols and in-cloud interstitial aerosol~~s particless~~ (~~$PM_{2.5}$~~size < 2.5 μm) are compared in Figure 9 and Figure S6. Except for the highly polluted E.1 case, in which major components were increased in the ~~in-cloud~~interstitial aerosols (15.8 μg m^{-3}) compared with the pre-cloud aerosols (10.7 μg m^{-3}), the other cloud events showed significant decreases in major components concentrations because of cloud scavenging. The chemical compositions of ~~in-cloud~~interstitial aerosols obviously differed from the pre-cloud aerosols. In the polluted case E.1, sulfate was the most abundant species in pre-cloud aerosols, accounting for 60% of mass concentration, but decreased to 31% in the in-cloud interstitial aerosols. Meanwhile, the mass fraction of ~~DOM~~ WSOM in aerosols was elevated from 20% (~~in~~ pre-cloud~~ aerosols~~) to 30% (~~in~~ in-cloud interstitial~~ aerosols~~), and nitrate increased from 4% to 19%, probably due to the large increase in NO_2 (over 4-fold). For the mixed case E.4, ~~DOM~~ WSOM mass fraction in the ~~in-cloud~~interstitial aerosols was twice of that ~~of~~ in pre-cloud aerosols, consistent with the increasing trend of DOM in cloud water shown in Figure 7. It has been suggested that highly oxidized cloud water organics readily remain in evaporating cloud droplets and contribute to aqSOA mass production, whereas ~~semi-~~volatile products are prone to escape into the gas phase (Schurman et al., 2018). ~~HoweverIn this study, the DWSOMOM/SO_4^{2-} ratios for in-cloud interstitial aerosols during both cloud events were about 3 times greater than that for pre-cloud aerosols, although the ratios did not change much in corresponding cloud water, implying that the substantial contributions of oxidized and low-volatility cloud water organics~~

~~are predominantly retained into cloud-processed aerosols. Overall, the evidently increased DOM mass fraction and DOM/SO$_4^{2-}$ ratios in the in-cloudinterstitial aerosols indicated the significance of cloud processes in the aqSOA formation.~~

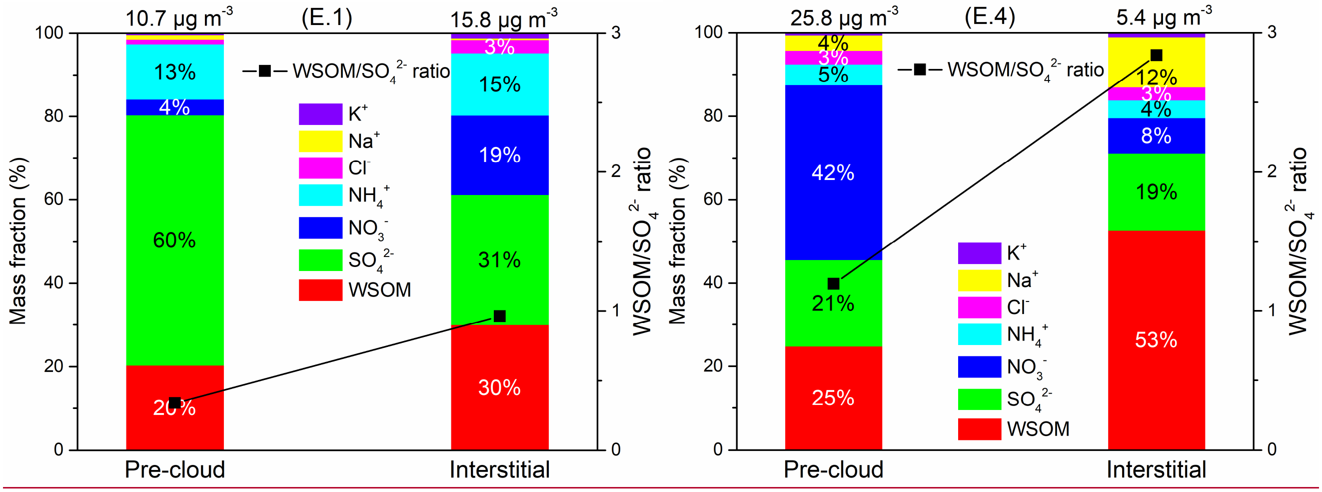


Figure 9. Mass concentration distributions of major water-soluble components and ~~DOM~~WSOM/SO$_4^{2-}$ ratios in the pre-cloud aerosols and in-cloud ~~PM$_{2.5}$~~interstitial aerosols ~~during~~ for cloud events E.1 (left) and E.4 (right).

In Figure 10, the ~~averaged~~average mass size distributions of aerosols during different cloud periods are compared. Multimodal distribution is apparent, with the dominant accumulation mode peaking at ~0.4 µm and a second coarse mode at ~2.0 µm. Accumulation-mode aerosols (0.1–1.0 µm) usually consist of two subgroups, the condensation and droplet modes peaking typically at 0.2–0.3 and 0.5–0.8 µm, respectively (Hinds, 2012). In this study, the overlapping of the two subgroups likely made the accumulation mode peak and a small peak near 1.0 µm. During the polluted E.1, the accumulation-mode aerosols exhibited higher concentrations than the pre-cloud aerosols, whereas the coarse aerosols were largely scavenged. As the cloud dissipated, accumulation-mode aerosols decreased, while the concentrations of aerosols with a diameter of over 0.6 µm remained the same as the in-cloud interstitial ones. The droplet-mode (0.5–1.0 µm) mass fraction increased significantly after the cloud processing, growing from the pre-cloud 9~~.3~~% to ~~14.1% (in-cloud) and~~ 18~~.0~~% (dissipation periods). For the mixed event E.4, the cloud-processed ~~particles~~aerosols also showed an elevated droplet-mode mass fraction (19~~.2~~%) compared to the pre-cloud ~~particles~~aerosols (15~~.2~~%), even though ~~particles~~aerosols were scavenged in all modes. As droplet-mode ~~particles~~aerosols are mainly produced from aqueous reactions, the increase in droplet-mode mass fraction after cloud dissipation may be associated with the in-cloud formation of sulfate and aqSOA (Blando and Turpin, 2000; Ervens et al., 2011). Model simulations reveal that the relative mass increase of droplet-mode aerosols after cloud processing can be up to ~100% for marine air masses with significantly accumulated sulfate and oxalate at 0.56 µm range (Ervens et al., 2018). Hence w~~W~~e ~~propose~~ can expect that sulfate (air equivalent concentration of 4.9 µg m^{-3}) and the low-volatile fraction of ~~substantial~~ DOM (~~air equivalent concentration of~~ 15.0 µg m^{-3}) ~~and sulfate (4.9 µg m^{-3})~~ measured in cloud water are mostly retained in droplet-mode ~~particles~~aerosols upon cloud evaporation, contributing to the droplet-mode mass fraction. ~~(Ervens et al., 2018)~~

Although the mass size distributions of particle compositions were not measured in this study, ~~This proposition is supported by~~ the abundant droplet-mode oxalate, organic carbon and sulfate aerosols reported in Hong Kong (Bian et al., 2014~~_ENREF_3~~; Gao et al., 2016) seem to support our hypothesis~~, although the mass size distributions of particle compositions were not measured in this study~~. ~~In addition~~Moreover, given the elevated ~~DOM~~ WSOM fractions and ~~DOM~~WSOM/SO_4^{2-} mass ratios in the in-cloud aerosols (Figure 9), aqSOA formation seemed to play a more important role ~~than~~ compared to sulfate in producing droplet-mode ~~particles~~aerosols.

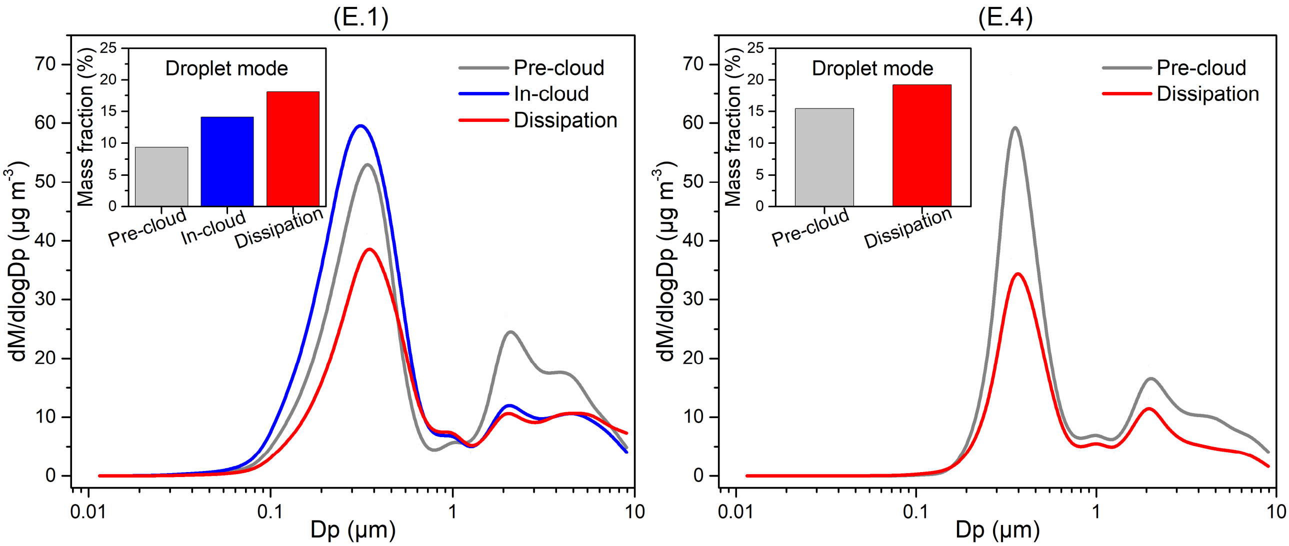


Figure 10. ~~Averaged~~Average mass size distributions of aerosols during the pre-cloud, in-cloud and dissipation periods for cloud events E.1 and E.4. Embedded graphs show the droplet-mode ~~particles~~ fraction of the total mass.

4 Conclusions

Gas–cloud–aerosol interactions can ~~change~~ determine the fate of trace gases and the physicochemical properties of aerosols, but the multiphase processes in the subtropical PRD-HK region are still poorly understood. This study presents the results from a field campaign with concurrent measurements of gases, particles and cloud waters conducted at a mountain site in Hong Kong for the first time. The chemical compositions of the acidic cloud water (pH ranges of ~~=~~2.96–5.94) during different cloud events were dominated by DOM and secondary inorganic ions, which were heavily influenced by anthropogenic emissions from continental air masses. Continental air masses generally contributed more pollutants to cloud water than the marine air masses did. The distinct relationships of carbonyl compounds with LWC and pH were likely controlled by their partitioning between cloud water and the gas phase. Simultaneous measurements in the two phases enabled the investigation of their partitioning behaviors. The F_{me} values of dicarbonyls considering hydration reactions agreed well with their theoretical values, whereas large discrepancies were found between F_{me} and F_{theo} of monocarbonyls. The complicated partitioning behaviors of carbonyls possibly result from the combined effects of physical adsorption and chemical production/loss, which require further study.

The good correlation between DOM and sulfate indicated the in-cloud formation of aqueous organics, for which abundant glyoxal ~~was identified as the most likely~~likely played an important role given its significant correlations with carboxylic acids and DOM~~ precursor~~. Apart from cloud scavenging of aerosol particles, cloud ~~processes~~ processing played crucial roles in changing the chemical composition and mass size distribution of particles. During cloud ~~processes~~processing, increases in daytime $PM_{2.5}$ (0.35–1.07 μg m^{-3} h^{-1}) were observed as solar radiation increased, with simultaneously increased glyoxal (5.9–37 ng m^{-3} h^{-1}) and net-production of cloud water DOM (0.05–0.52 μg m^{-3} h^{-1}) and sulfate (0.03–0.45 μg m^{-3} h^{-1}). The cloud water DOM production, which is more efficient under less acidic conditions, is likely to have contributed to aerosol mass growth more significantly than sulfate, as the ~~DOM~~ WSOM mass fractions in the cloud-processed aerosols were remarkably increased. Moreover, sulfate and DOM produced in cloud water are expected to remain in the particle phase and ~~cause~~ lead to a mass increase in droplet-mode particles after cloud dissipation. The observations provide direct evidence for the ~~aqueous formation~~modification of ~~secondary~~ aerosols in cloud ~~processes~~processing, ~~and~~ promoting~~e~~ our understanding of the gas–cloud–aerosol interactions and multiphase chemistry of polluted coastal environments.

Data availability

The original data can be provided upon request to the corresponding author (z.wang@ust.hk) and the first author (lt@sdu.edu.cn).

Author contribution

ZW, TW and YW designed the research; TL, YW, CW, YL performed the field measurement of cloud water and sample analysis; MX, CY, HY, WW conducted the measurement of trace gases and aerosols; TL, ZW and JG performed data analysis and wrote the manuscript. All authors contributed to discussion and commented on the paper.

Competing interests

The authors declare that they have no conflict of interest.

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