

Responds to the reviewer's comments:

We sincerely thank the reviewer for the valuable comments and suggestions concerning our manuscript entitled "Chemical composition and droplet size distribution of cloud at the summit of Mount Tai, China". These comments are all valuable and helpful for revising and improving our paper. The responses to reviewers are in blue. The changes are marked in red in the revised manuscript.

Reviewer 2

General comments

Comment 1:

1. In the discussion of the interaction of aerosols with clouds, it is mainly the number of CCN that affects cloud microphysical properties, not the PM_{2.5} mass concentration. Although the PM_{2.5} mass concentration and CCN number concentration may correlate during the cloud events studied here, it is not necessarily true in many cases because particles contributing mostly to CCN number and PM_{2.5} mass concentrations may differ in size ranges, depending on the particle size distribution. In this manuscript, PM_{2.5} mass concentration was used as a somewhat proxy for CCN. While the particle size distribution data are not available here, the authors need at minimum discuss the limit of using PM_{2.5} here.

Response: We sincerely thanks you for your pertinent comments and valuable suggestions. We added the reason for using PM_{2.5} mass concentration represent CCN in this study as in Page 7 Line 23- Line 27:

"But for both types of cloud events, the N_a significantly decreased and the PM_{2.5} levels evidently increased as cloud events began to dissipate. It may due to the evaporation of water contents that condensed on the particles, which freed the CCN and formed haze. This confirmed that PM_{2.5} was one of the important types of could condensation nuclei at Mt. Tai. So, PM_{2.5} mass concentration was used as a proxy for CCN number concentration in this study."

Comment 2:

2. Some of the discussion or statement are not quantitative enough and need further clarification or supporting data.

For example, in Pg 6 lines 2-11 on the relationship between PM_{2.5} level and LWC and cloud droplet size, instead of selecting a few cloud events with higher PM_{2.5} and qualitatively comparing the droplets sizes in these events, a quantitative way would be plot the droplet size versus PM_{2.5} level. Same principle applies for the effect of RH on droplet size explanation (low RH suppressing cloud droplets size). Since the effect of PM_{2.5} on droplet size is anyway discussed in Sect. 3.4, the authors could consider to merge this paragraph with the discussion of Sect. 3.4.

Response: We merged this paragraph with the discussion of Sect. 3.4.

Pg 6, lines 21-22, "...broadened the droplet size spectra...", it would be helpful to provide the

standard deviation or geometric standard deviation of the droplet size distribution, because such broadening is not clear from Fig. 1 (the green color becoming wider does not necessarily mean broadening, which could be only due to increasing concentrations in all sizes).

Response: Thanks for your suggestion. We added the standard deviation (SD) of cloud droplet size distribution in Fig. 1. As can be seen, both LWC and SD increased with the development of the cloud events. It represented that high LWC values could broaden the droplet size spectra. We updated Fig. 1 and added the corresponding discussion as in Page 7 Line 10- Line 12:

“With the development of the cloud event, the standard deviation of CDS D represented a positive correlation with LWC values. It represented that high LWC could broaden the droplet size spectra and increase the range of cloud droplets.”

Pg 7, lines 16-19, about the origins of air mass, it would be helpful to add the information on this, such as back trajectory. And the wind directions in Fig. 1 did not show consistent directions except for panel D, in which winds are mainly from eastern sector.

Response: We used the backward trajectory analysis, but no big difference existed in the origins of the air masses of event A, event B and event C as shown in Figure R1. By re-examining the data, we considered the ambient concentrations of $PM_{2.5}$ at the beginning stage of cloud events was probably the main reason to explain the difference between type I and type II. Because the original concentrations of $PM_{2.5}$ in event A and event B were higher than those in event C and event D. We revised the discussion as in Page 7 Line 22- Line 27:

“In type II cloud processes, the levels of $PM_{2.5}$ were relatively low at the initial stage. But for both types of cloud events, the N_d significantly decreased and the $PM_{2.5}$ levels evidently increased as cloud events began to dissipate. It may due to the evaporation of water contents that condensed on the particles, which freed the CCN and formed haze. This confirmed that $PM_{2.5}$ was one of the important types of could condensation nuclei at Mt. Tai. In this study, $PM_{2.5}$ mass concentration was used as a proxy for CCN number concentration.”

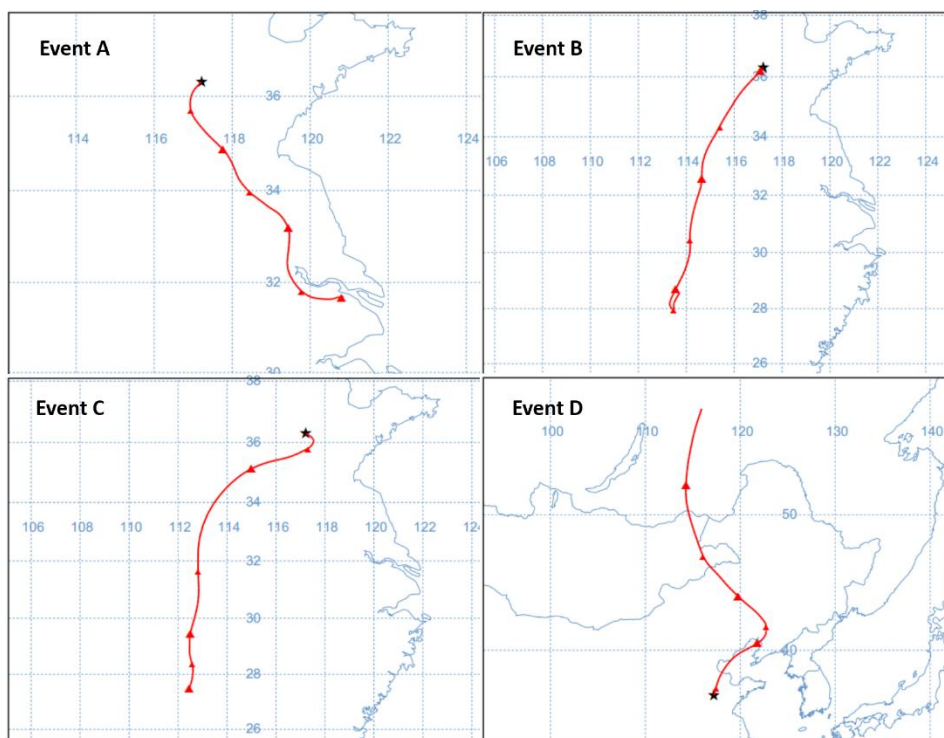


Figure R1. Backward trajectories of air masses for four cloud events at Mt. Tai

Pg 7, lines 22, “the TDIC was strongly correlated with the levels of PM_{2.5} and cloud acidity”, it looks like to me that the correlation of TDIC with acidity is not that strong if TDIC were plotted against pH. Unlike TDIC, pH should not only depend on the PM_{2.5} concentration but also chemical compositions of PM_{2.5}, for example, whether there are more acidic or basic compounds.

Response: Here, we want to emphasize the influence of PM_{2.5} on TDIC and pH values. Even though the pH of cloud samples was not only depend on the PM_{2.5} concentration, the lower pH values were likely to occur at higher concentrations of PM_{2.5} as can be seen in Fig. 1. We modified the description of this paragraph as in Page 7 Line 29- Page 8 Line 5:

“As illustrated in Fig. 2, the TDIC was strongly correlated with the levels of PM_{2.5}. High levels of PM_{2.5} normally lead to high TDIC, whereas low levels of PM_{2.5} usually lead to low TDIC. The pH values of cloud samples were somewhat affected by the concentrations of PM_{2.5}. The lower pH values were likely to occur at higher concentrations of PM_{2.5}. Generally, changes of the solute concentrations in cloud water can be caused by a combination of factors such as the microphysical conditions, the CCN properties, the chemical reactions in the cloud droplets and the gas-liquid phase equilibrium (Van Pinxteren et al., 2015). Our data emphasized the crucial effect of PM_{2.5} on the changes of ion concentrations. PM_{2.5} are likely to be the main source of ions in cloud water.”

Pg 8, lines 16-19, “the increase in the concentration of NH₄⁺ from CE-Aug23#2 to CE-Aug23#3 was much higher than those of SO₄²⁻ and NO₃⁻,” it would be helpful to provide the number of increase of NH₄⁺, NO₃⁻, and SO₄²⁻. (Do you mean the molar concentrations here?)

Response: Thanks for your comments. The increase factors of SO₄²⁻, NO₃⁻ and NH₄⁺ from CE-

Aug23#2 to CE-Aug23#3 had been described in Page 8 Line 14- Line 16. In the manuscript, we used the mass concentrations ($\mu\text{g mL}^{-1}$) to calculate the increase factors of ions. We revised the discussion as in Page 8 Line 26-29:

“It should be noted that, compared with SO_4^{2-} and NO_3^- , the concentration of NH_4^+ in aerosol phase did not directly increase at the dissipation stage of the cloud event. This was primarily due to the high solubility of NH_3 , which dissolved in the cloud water and gave rise to the increase in the concentration of NH_4^+ in cloud sample.”

Comment 3:

3. In some discussion, not enough background information is available to understand the discussion. For example, in Pg 6, line 2 “High $\text{PM}_{2.5}$ levels can lead to low LWC values, which can diminish the size of the cloud droplets”, at this point, I had difficulty to understand this statement here without further explanation, for exempling, using the findings from literature.

Response: This statement was summarized from our data in Table 3. Ackerman and colleagues (Ackerman et al., 2004) also found $\text{PM}_{2.5}$ levels could affected the LWC values and the sizes of cloud droplets. But considering the comment 2 in general comments, we merged this paragraph with the discussion of Sect. 3.4.

Also lines 9-10, “If the RH remains constant, each CCN shares less water vapor, which leads to lower LWC values and hinders the growth of cloud droplets.”, I also had difficult time understanding why it is so.

Response: High levels of $\text{PM}_{2.5}$ can lead to a large source of CCN and intensify the competition for the ambient water vapor. The low RH could not provide sufficient water vapor, which would reduce the hygroscopic growth of aerosols and hinder the activation of droplets (Gonser et al., 2012; Liu et al., 2011). The combination of the two factors determined the low LWC and ED values of the cloud droplets. But considering the comment 2 in general comments, we merged this paragraph with the discussion of Sect. 3.4.

Specific comments

Comment 1:

Pg 2, line 10 “...more than 30% of the total annual sulfur deposition was deposited as a result of cloud events (Shimadera et al., 2011).”, for me, that does not seem to be relevant to the arguments before on the role of non-precipitation vs. precipitation clouds.

Response: We revised the statement and updated the reference as in Page 2 Line 12-14:

“For example, Sun and colleagues (Sun et al., 2010) found that the concentrations of ammonium, sulfate and nitrate in cloud water were at least 5.17 times higher than those in rainwater.”

Comment 2:

Pg 4, line 3, what is effective diameter exactly defined?

Response: As described in the instruction manual of Fog Monitor, the definition of ED (Effective Diameter) is the ratio of liquid water content to the optical cross sectional area of

droplets. Effective diameter in μm is calculated according to the following definition:

$$ED = \frac{3LWC}{4G\rho_w} \times 2$$

where: LWC = Liquid Water Content in g m^{-3}

G = The geometric cross-sectional area of water drops (μm^2) per unit volume (μm^3)

ρ_w = The density of water (equal to 10^6 g m^{-3})

We added the reference in the revised manuscript as in Page 4 Line 13.

Comment 3:

Pg 5, line 24, "...may be attributable to the increasing consumption of agricultural fertilization and soil acidification...", I suppose this only refers to NH_4^+ not Ca^{2+} . If so, please clarify.

Response: Thanks for your comments. We have clarified as in Page 5 Line 31- Page 6 Line 2:

"Especially NH_4^+ , the VWM concentrations of NH_4^+ increased from 2007–2008 by factors of 1.56 (Guo et al., 2012). This may be attributable to the increasing consumption of agricultural fertilization and soil acidification (Cai et al., 2015; Xu et al., 2015)."

Comment 4:

Pg 5, line 32, "This diversity was a result of the characteristic formation...", the meaning of "characteristic formation" is vague.

Response: We have detailedly described the "characteristic formation" as in Page 6 Line 22- Line 24:

"Orographic cloud is a highly heterogeneous system consisting of randomly distributed air volumes with different characteristics (Gonser et al., 2012). This feature of orographic cloud generally determines the large differences in CDS, LWC and aerosol composition of different cloud events."

Comment 5:

Pg 6, lines 29-30, "It should be emphasized that although the levels of $\text{PM}_{2.5}$ decreased from event A to event D, there were no significant changes in the CDS properties." What does "CDS properties" mean? I suppose the droplet size (ED) is also a CDS property. If so, it is affected by $\text{PM}_{2.5}$ level as discussed in Sect. 3.4 and Fig. 4 and would contradict the statement here.

Response: The "CDS properties" here just means the size distribution obtained in Figure 1. This had been described in the first paragraph in Sect. 3.2.2 that the monitored cloud droplets were all smaller than $26 \mu\text{m}$, mainly distributed in $6.0\text{--}9.0 \mu\text{m}$ and concentrated in $7.0 \mu\text{m}$. In order to avoid misunderstanding, we deleted this sentence in the revised manuscript.

Comment 6:

Pg 7, Sect 3.2.3, why do the two types of cloud behave differently? Because of the origin of air mass?

Response: We applied the backward trajectory analysis, but no big difference existed in the origins of the air masses of event A, event B and event C. We considered the ambient

concentrations of $PM_{2.5}$ at the beginning stage of cloud events was probably the main reason to explain the difference between type I and type II.

Comment 7:

Pg 7, line 27, “CCN, especially particulate matters, are likely to be the main source of ions and acid-causing components in cloud water.” I suggest to omit “especially particulate matters” because it seems to indicate that some CCNs are not particulate matters.

Response: Thanks for your comments. We deleted “especially particulate matters”.

Comment 8:

Pg 7, line 28, “... the transmission and variation...”

Response: We changed the “transmission” as “exchange” in the paper.

Comment 9:

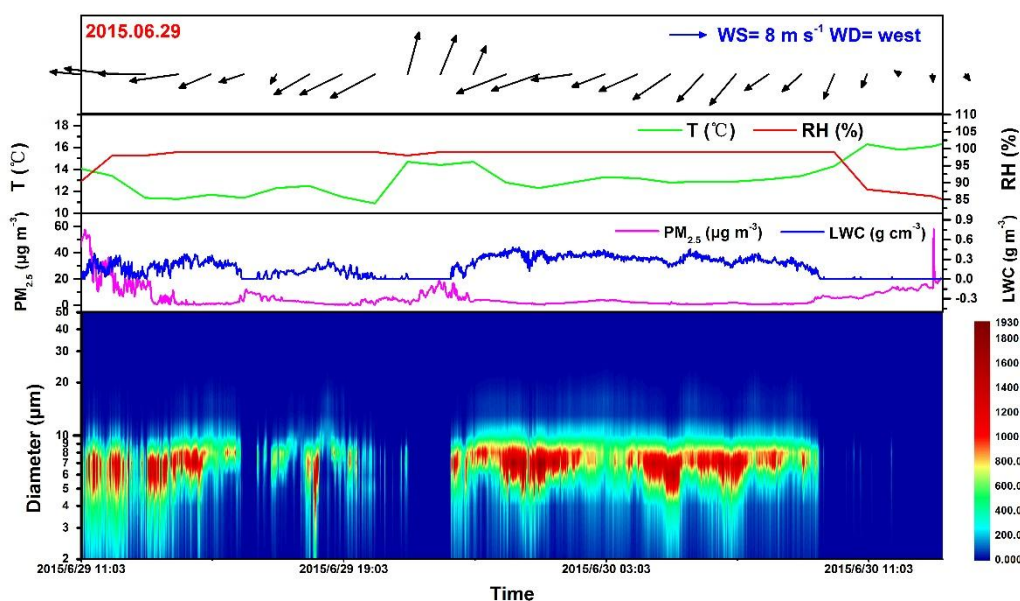
I suggest authors to further polish the languages.

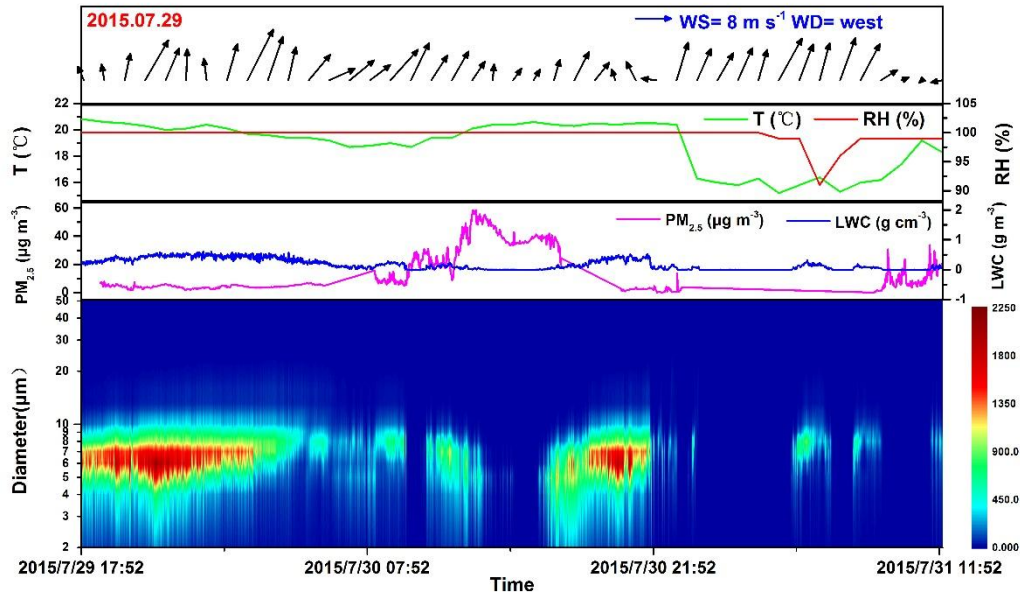
Response: We have polished the language, and improved the grammar and expressions.

Comment 10:

Fig.1d, the RH is flat. Is it constantly at 100%?

Response: Yes. Our data was constantly at 100% during this period. In 2015, we also carried out the cloud observation experiment at Mt.Tai. And we found the same phenomenon such as on June 29th and on July 29th. The RH remained at 100% for a long time.





Comment 11:

Fig. 5, how are the values of size D_p ($D_p=6.0$ for high $PM_{2.5}$ level and $D_p=13.0$ for low $PM_{2.5}$ level and so on) and ion content obtained? Please clarify.

Response: The cloud samples were divided into “high $PM_{2.5}$ level” and “low $PM_{2.5}$ level”. The data used for obtaining the values in Fig. 5 was shown in Table R1. The values of D_p and the concentrations of ion contents in Fig. 5 were obtained by calculating the average values of cloud samples in “high $PM_{2.5}$ level” and “low $PM_{2.5}$ level”. In the previous version, we chose $40 \mu\text{g m}^{-3}$ of $PM_{2.5}$ as the standard to distinguish the “high $PM_{2.5}$ level” and the “low $PM_{2.5}$ level”. Through comparing the air quality standard in China and in America, we considered that using $35 \mu\text{g m}^{-3}$ of $PM_{2.5}$ as the standard to divide the cloud samples as the “high $PM_{2.5}$ level” and the “low $PM_{2.5}$ level” was better. It should be emphasized that the change of the standard didn’t alter the mechanism of cloud droplet formation found in this paper. The clarification was added in the revised manuscript as in Page 10 Line 1- Line 3:

“According to the concentrations of $PM_{2.5}$, cloud events were divided into two categories. One was the $PM_{2.5}$ concentrations greater than $35 \mu\text{g m}^{-3}$. The other was the $PM_{2.5}$ concentrations less than or equal to $35 \mu\text{g m}^{-3}$.”

Table R1. Data of 17 cloud samples for calculating D_p and ion contents in Fig. 5

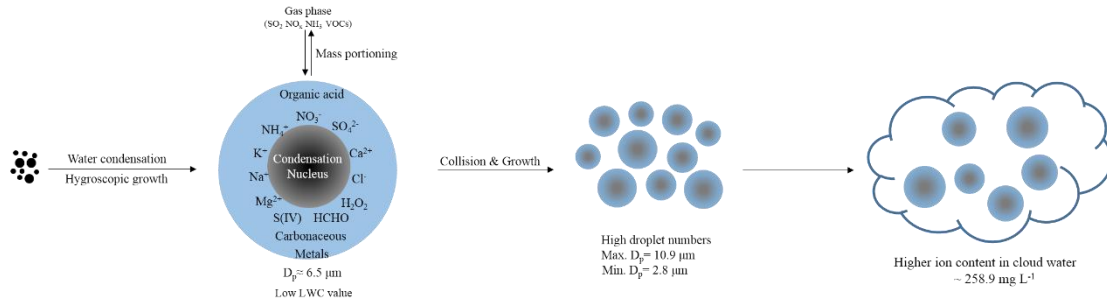
	Average	Average	No.	Cloud Sample	PM _{2.5}	Ion Contents	ED
	ED*	Ion Contents*					
	μm	mg L ⁻¹					
low PM _{2.5} level (PM _{2.5} ≤ 35 μg m ⁻³)	13.5	136.9	1	CE-Jul25#1	6.51	53.72	25.47
			2	CE-Aug1#1	13.63	72.72	11.60
			3	CE-Jul25#2	14.04	150.01	25.47
			4	CE-Aug1#2	14.59	66.17	14.57
			5	CE-Jul31#2	19.44	112.99	9.70
			6	CE-Aug23#2	22.28	132.04	10.35
			7	CE-Aug23#3	25.20	191.05	9.07
			8	CE-Aug23#1	26.22	317.56	9.73
			9	CE-Aug13#1	34.11	145.54	10.54
			10	CE-Aug13#2	34.22	127.07	8.60
high PM _{2.5} level (PM _{2.5} > 35 μg m ⁻³)	6.5	258.9	1	CE-Jul31#1	35.91	118.69	9.09
			2	CE-Aug14#3	40.23	109.94	3.47
			3	CE-Aug14#1	42.74	127.47	2.75
			4	CE-Aug17#2	47.98	328.07	8.39
			5	CE-Aug14#2	48.98	73.76	3.01
			6	CE-Aug17#1	60.38	476.38	10.89
			7	CE-Jul28#1	81.59	578.15	7.71

* Average ED represented “ D_p ” in Fig. 5

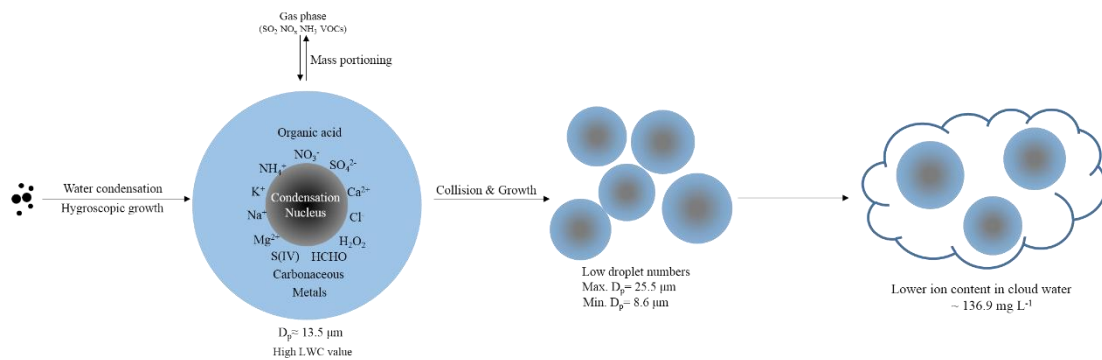
* Average Ion Contents represented “ion content” in Fig. 5

We have revised the Fig. 5 as following:

a. High PM_{2.5} level (PM_{2.5} > 35 μg m⁻³)



b. Low PM_{2.5} level (PM_{2.5} ≤ 35 μg m⁻³)



Technical comments

Comment 1:

Pg 2 line 6 "...taking place multiphase chemical reactions", maybe "...multiphase chemical reactions taking place" is better.

Response: Thanks for your comments. We revised "...taking place multiphase chemical reactions" as "...multiphase chemical reactions taking place" in the revised manuscript.

Comment 2:

Pg 3, line 17, add comma after "conductivity" and "formaldehyde" (and omit the "and" after).

Response: We rewrote the sentence as in Page 3 Line 22-23:

"The pH, the electrical conductivity, the concentrations of sulfur(IV), formaldehyde, hydrogen peroxide were measured immediately after sampling."

Comment 3:

Pg 7, line 27, "...acid-causing components..." does not sound the right wording. Please rephrase.

Response: Thanks for your comments. Maybe "acidic compounds" was more appropriate.

Comment 4:

Pg 7, line 28, "... the transmission and variation...", "transmission" does sound right, maybe "partitioning" or "exchange".

Response: We changed the "transmission" as "exchange" in the revised manuscript.

Comment 5:

Pg 8, line 7, "The above results demonstrate that cloud water is a dominant sink", by "dominant" I guess that authors meant important since they did not compare with other sinks.

Response: We modified "dominant" as "important" in the revised manuscript.

Comment 6:

Pg 8, lines 11-14, the author emphasize the importance of dilution effect of cloud water. However, based on strong correlation of PM_{2.5} and TDIC regardless of the LWC level, does the correlation suggest that the dilution effect throughout all these cloud events are similar and therefore not crucial?

Response: The dilution effect of LWC on ion concentrations could not be ignored. Previous studies also found the inverse relationship between total ionic content and LWC in cloud samples (Aleksic and Dukett, 2010; Elbert et al., 2000). Through this study, we could only confirmed that both PM_{2.5} and LWC would affect the estimation of TDIC in the cloud samples. This statement may become clearer if re-written as in Page 8 Line 23-Line 25:

"The similar variation trends of SO₄²⁻, NO₃⁻ and NH₄⁺ in both aerosol phase and cloud phase confirmed that LWC was an important factor affecting the ion concentrations in the cloud water at Mt. Tai (Aleksic and Dukett, 2010; Elbert et al., 2000)."

Comment 7:

Pg 8 line 21, "...were the main hygroscopic compounds.", add "hygroscopic compounds' of what? PM_{2.5}?

Response: Thanks for your comments. We added "...of particulate matters" as in Page 8 Line 31- Page 9 Line 2:

"Secondary inorganic aerosols especially ammonium sulfate and ammonium nitrate were the main hygroscopic compounds of particulate matters."

Comment 8:

Pg 8 line 31, "... N_d varied with the same PM_{2.5} level", change "with" to "at".

Response: Thanks for your comments. We have changed "with" to "at" as in the revised manuscript.

References

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