Response Letter

Dear Editor Dr. Alex Lee

Thank you very much for providing us this opportunity to revise our manuscript. We have carefully and thoughtfully addressed the reviewer's concerns. We deleted the discussions on the particle phase state, because the particle phase state calculation was based on the O/C elemental ratio of organic aerosols in submicro particles (PM_1), which is not applicable for $PM_{2.5}$ and dust coarse particles we studied in the work. By removing the inconsistent discussions on the particle phase state and revising the discussion on the effect of $PM_{2.5}$ loading on WSOC partitioning, which are the two major concerns raised by the reviewer, we believe the scientific quality of the current version of the manuscript is improved a lot. Please see our detailed response below.

Sincerely yours
Gehui Wang
July 25, 2025

Editor comments

One of the reviewers still has a few major comments that are strongly related to the scientific quality of this manuscript. These new comments are critical and need to be addressed carefully and thoughtfully for further consideration. Although the reviewer recommend rejecting this version, I would like to provide you another opportunity to address these major concerns before making the final decision.

Reply: Thank you very much for giving us the opportunity to address the reviewer's concerns and to improve our manuscript quality. We sincerely appreciate the time and effort the reviewer has dedicated to evaluating our work, and we acknowledge the importance of their critical comments in enhancing the scientific quality of the paper.

We have carefully reviewed all the concerns raised and have prepared a detailed point-by-point response, including necessary revisions to the manuscript. We believe these revisions have significantly strengthened the manuscript, and we sincerely hope the changes meet the reviewer's expectations. Thank you again for your consideration. We look forward to your feedback and hope the revised version is suitable for a publication in the journal.

Referee #1

Comments

Li et al. did a good job in addressing most of my comments and the concerns raised by the reviewers. The manuscript has been improved, but I still have some minor comments on the replies and revised manuscript.

For the response to comment 2 of reviewer 2: The author presented the results of the equivalent ratios of total measured ions in $PM_{2.5}$ *during the whole dust cases. This indicated the concentration of cations was excessive, especially in stagnant dust. Why this happened? How was the equilibrium of anion-cation in the normal ambient (clean day or haze)? Another question was that during the dust, how was this equilibrium? It showed the higher nitrate concentration in dust case compared to non-dust case was observed in Figure S9. How was the equilibrium of anion-cation in* $PM_{2.5}$ *and PMcoarse? May this different equilibrium affect the Fp?*

Reply: Thank for the comments. (1) In DS period, atmospheric particles were enriched with carbonate-containing particles, such as $CaCO_3$ and $Ca(HCO_3)_2$. As shown in Fig. R1a, the equivalent ratio of total anions (Cl^-, $NO_3^-$and SO_4^{2-}) to total cations (Na^+, NH_4^+, K^+, $Mg^{2+}$and Ca^{2+}) was less than unity in DS period (slope = 0.82), if we don't considered carbonate. In this study we have measured water-soluble inorganic carbon (WSIC) in the samples, which is HCO_3^- (Wang et al., 2010). When we add HCO_3^- to the total measured anions, the equivalent ratio slope of cations to anions in all the dust samples is equal to 1:1. Thus, the concentration of cations in DS period was actually not excessive. Such results again suggest abundant carbonate-containing particles occurring in the Shanghai atmosphere during the dust storm period. In the clean and haze periods, carbonate-containing particles are minor and WSIC concentrations are below the detection limit of the instrument. The ratios of total cations (Na^++NH_4^++K^++Mg^{2+}+Ca^{2+}) to total anions (Cl^-+NO_3^-+SO_4^{2-}) were 0.97~1.0 in CP and HE periods.

(2) Dust particles in East Asia are not only enriched in $CaCO_3$ but also enriched in hygroscopic mineral salts such as NaCl, gypsum ($CaSO_4$•$2H_2O$) and mirabilite (Na_2SO_4•$10H_2O$) (Wang et al., 2014; Wu et al., 2020). We found that during transport nitrate can be formed on coarse dust particles by reactions of gaseous HNO_3 with $CaCO_3$ and hydrolysis of N_2O_5 on those hygroscopic salts followed by neutralization with NH_3 (Wang et al., 2014; Wu et al., 2020). Thus, a higher nitrate concentration in dust case compared to non-dust case was observed in Figure S9. The aged dust particles with $Ca(NO_3)_2$ can absorb water vapor under very dry conditions (RH>8%), providing a medium for the uptake and oxidation of gaseous water-soluble organics. During DS period, the NO_3^- and Ca^{2+} concentrations (1.6 and 1.4 μg m^{-3}, respectively) in the coarse mode (>2.1μm) was higher than that in the fine mode (<2.1μm) (0.6 and 0.4 μg m^{-3}, respectively). In addition, the coarse particles were more alkaline than the fine particles, which facilitates the organic acids partitioning to the particle phase. Thus, as shown in Figure S7, the partitioning coefficient (Fp) of WSOC in the coarse mode (>2.1μm) was higher than that in the fine mode (<2.1μm) during the DS period.

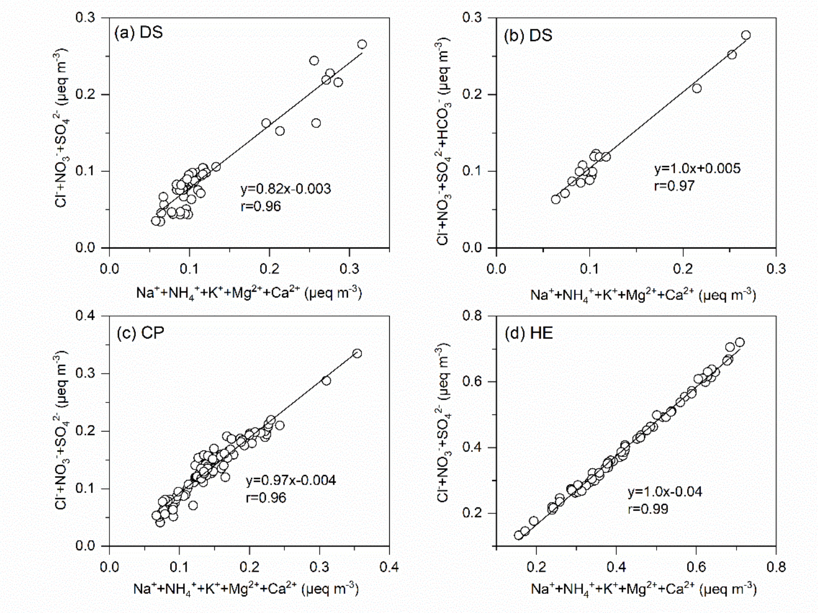

Figure R1. Correlations between cations and anions during DS, CP and HE periods. Carbonates were measured by TOC/TN analyzer with 3h time resolution.

Referee #2

Li et al. have addressed some of the concerns raised previously. However, the revised manuscript still does not meet the criteria for being considered for publication on ACP. Even though the authors provide additional details and information, I find the inconsistency and ambiguity between the claims about the phase state, gas-particle partitioning, and reactions during the measurement periods of the dust storm (DS). Therefore, I would suggest that the manuscript be rejected.

Reply: We are sorry that in the last revised manuscript there are some inconsistency of the discussions between the heterogeneous reactions and particle phase state. We deleted the phase state related discussions, because we think it is not applicable for our dust storm observations. Please see the detailed explanations in our replies #2 and #4 below.

Major Comment:

1. Lines 98 – 107: What was the cut-off size for the sampling inlet connected to the in-situ gas and aerosol compositions (IGAC) monitor? Whether the sampling was conducted with the $PM_{2.5}$ or PM_{10} inlet has different meanings for the claim you are making. For example, if sampling was done with the PM_{10} inlet, one might wonder why the aerosol liquid water content (ALWC) estimates based on the $PM_{2.5}$ speciation were applicable.

Reply: We are sorry for not explaining the IGAC sampling system clearly. The cut-off size of IGAC sampling system is 2.5 µm. In section 3.2, the aerosol composition analysis and ALWC, pH calculations were based on the $PM_{2.5}$. We have added more detailed information in the revised manuscript. Please see lines 98-100, page5.

"For the IGAC sampling system, the air was drawn into a $PM_{2.5}$ cyclone inlet and passed through either a wet rotating denuder (gases) or a steam jet aerosol collector (aerosols)."

2. Particle phase state: In lines 216-217, the authors argued that the RH during the DS periods was lower than the deliquescent point of SNA. In lines 270 -275, the authors claim that fine aerosols were mainly in solid or semi-solid states during the DS period. According to these claims, I wonder how authors can still use the ISORROPIA model to calculate the ALWC and pH. The ISORROPIA model is supposed to be based on the thermodynamic equilibrium assumption!

Reply: We are sorry for those inconsistent claims. As we described in lines 216-217, the SNA, i.e., sulfate, nitrate and ammonium, were the largest contributors to ALWC in haze period. However, there are some hygroscopic salts substances in atmosphere with low deliquescence RH (DRH). For example, during dust long-range transport $CaCO_3$ particles react with acids such as HNO_3 to form $Ca(NO_3)_2$. $Ca(NO_3)_2$ is a strongly hygroscopic species with DRH as low as 8% (Sullivan and Prather, 2007), which means that as soon as $Ca(NO_3)_2$ formed on a dust particle surface, it starts to absorb water vapor, forming a liquid film on the dust surface. In our research, we also found abundant nitrate and calcium (1.6 and 1.4 $\mu g\ m^{-3}$, respectively) at the coarse mode in DS period in Shanghai, suggesting that a liquid phase could be formed on the dust surface in the city during the dust storm event. Such results are consistent with those observed in Nanjing, an upwind city with a distance of 300 km west to Shanghai. Zhi et al recently found that Ca-rich dust particles in Nanjing city were coated with water during DS (Figure R2) (Zhi et al., 2025), indicating that formation of a liquid phase on dust particle surface is very common.

As shown in Table R1, DRH of ammonium nitrate and ammonium sulfate are 59.4% and 79.2% at 303 K, respectively. However, for the mixture of salts, their DRH can down to 52% (Wexler and Seinfeld, 1991). For other low DRH species, the mutual solubility point is lower than their corresponding original species, indicating that atmospheric particles can be in liquid-phase at very low RH conditions. For example, as RH decreases below the 80% DRH, $(NH_4)_2SO_4$ particle water evaporates but not completely. The particle remains liquid until a RH of approximately 35 % (Table R2), where crystallization finally occurs (Martin, 2000). For pure NH_4HSO_4, NH_4NO_3 and $NaNO_3$, their aqueous particles do not readily crystallize even at very dry conditions (Martin, 2000), suggesting that dust particles in Shanghai during the DS period could have a liquid film, and thus the ISORROPIA model was applicable.

O/C ratio is a key factor for calculating ambient organic aerosol phase state. During the campaign we simultaneously performed a HR-AMS measurement for submicro particles (PM_1). Due to the unavailability of the O/C ratio of organic aerosols in $PM_{2.5}$ and dust particles, we used the O/C ratio of organic aerosols in PM_1 to calculate the phase state of organic aerosols in $PM_{2.5}$ and dust particles. However, the WSOC partitioning we studied are related to $PM_{2.5}$ and dust coarse particle, of which chemical compositions are different from PM_1 especially in the DS period. As seen in Figure 3 and Figure S6, a large amount of WSOC, oxalic acid, pyruvic acid and methanesulfonic acid stayed in the size of 1.0-2.5 μm in the DS period, suggesting that we used the PM_1 O/C ratio to calculate the fine aerosol phase state in the dust storm period was not accurate. Therefore, we think the related discussions about particle phase state in the previous manuscript are not reasonable.

In the current version we deleted the discussions on phase states and revised the related discussions. Please see page 10, line 215-222.

"In contrast, ALWC in the DS period was almost one order of magnitude lower than that in the HE period (Table 1) and did not correlate with F_p (Figure 2a), because SNA concentrations in the DS period were much lower than those in the HE period (Table 1). Moreover, RH in the DS period was 44 ± 18% (Table1), which is higher than the efflorescence RH of SNA but lower than their deliquescence RH and thus not favorable for the formation of aerosol liquid water (Wang et al., 2016). Therefore, WSOC partitioning process during the DS was not regulated by ALWC."

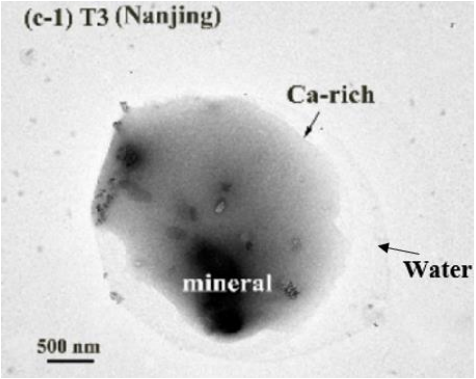

Figure R2. Microscopic observations of aged dust particles collected at Nanjing (300 KM away from Shanghai) during dust storm period (Zhi et al., 2025).

Table R1. Deliquescence RH (DRH*) at mutual solubility point at 303K (Wexler and Seinfeld, 1991)

Compound 1	Compound 2	DRH*	DRH1	DRH2
NH_4NO_3	NaCl	42.2	59.4	75.2
NH_4NO_3	$NaNO_3$	46.3	59.4	72.4
NH_4NO_3	NH_4Cl	51.4	59.4	77.2
$NaNO_3$	NH_4Cl	51.9	72.4	77.2
NH_4NO_3	$(NH_4)_2SO_4$	52.3	59.4	79.2
$NaNO_3$	NaCl	67.6	72.4	75.2
NaCl	NH_4Cl	68.8	75.2	77.2

Table R2. Efflorescence RH (ERH) at 298 K (Martin, 2000)

Salt	ERH (%)
$(NH_4)_2SO_4$	35 ± 2
NH_4HSO_4	Not observed
$NH_4H(SO_4)_2$	35
NH_4NO_3	Not observed
Na_2SO_4	56 ± 1
NaCl	43 ± 3
$NaNO_3$	Not observed
NH_4Cl	45

Comment:

3. Gas-particle partitioning: In lines 251 – 262, the authors claim that the main focus of R1 is the partitioning coefficient (Fp) of WSOC in $PM_{2.5}$ and thus used the concentration of aerosol organic mass (Morg) in the equation. According to Pankow (1994), it should be the mass concentration of total suspended particulate matter. Based on Table S2, WSOC only accounts for a small part of $PM_{2.5}$. In this case, if the IGAC indeed sampled behind the $PM_{2.5}$ inlet, the authors should use the $PM_{2.5}$ concentration for the gas-particle partitioning analysis.

Reply: Thanks for the comments. Indeed, using the $PM_{2.5}$ concentration was more appropriate than WSOC concentration in this study. We re-discussed the effect of $PM_{2.5}$ mass loading on the partitioning of WSOC during HE and DS periods in our revised manuscript. Please see lines 253-273, pages 11-12.

"Apart from the above factors that influence the F_p variations, aerosol mass loading may also affect the partitioning of organic species (Pankow, 1994; Lutz et al., 2019). According to the Raoult's law, the field gas-particle partitioning coefficient can be described as follows (Pankow, 1994):

$$K_i = \frac{i_{particle}}{i_{gas} TSP} \qquad (R1)$$

where K_i is the partitioning constant of i compound, $i_{particle/gas}$ are the particle and gas phase concentrations of compound i (formic and acetic acids in $PM_{2.5}$ are chosen here), and *TSP* is the concentration of total suspended particulate material ($PM_{2.5}$ are used here). Figure S5 presents the $i_{particle}/i_{gas}$ ratios versus $PM_{2.5}$ for formic and acetic acids during HE and DS periods. Particle/gas ratios of formic and acetic acids did not correlate with $PM_{2.5}$ in both HE and DS periods (Figure S5), indicating that the effect of aerosol mass loading on the uptake of organic acids during the campaign was not significant. As shown in Table 1, the $PM_{2.5}$ loadings in DS were comparable to those in HE, although PM_{10} loading was much higher in the dust storm period. Moreover, the pH (4.8 ± 1.5, Table 1) of $PM_{2.5}$ in DS was 1.4 units higher than that (3.4 ± 0.3) in HE, which means that H^+ concentration in DS was one order of magnitude lower than that in HE. According to the equations R2 and R3, the low H^+ concentration in DS was favorable for the organic acid equilibria shifting toward the aerosol aqueous phase. Thus, the impact of pH variation on F_p was much more significant than $PM_{2.5}$ mass loading in DS, taking a key role in WSOC partitioning process during the DS event."

$$\mathrm{RCOOH(g)} \longleftrightarrow \mathrm{RCOOH(aq)} \qquad (R2)$$

$$\mathrm{RCOOH(aq)} \longleftrightarrow \mathrm{RCOO^{-}(aq) + H^{+}(aq)} \qquad (R3)$$

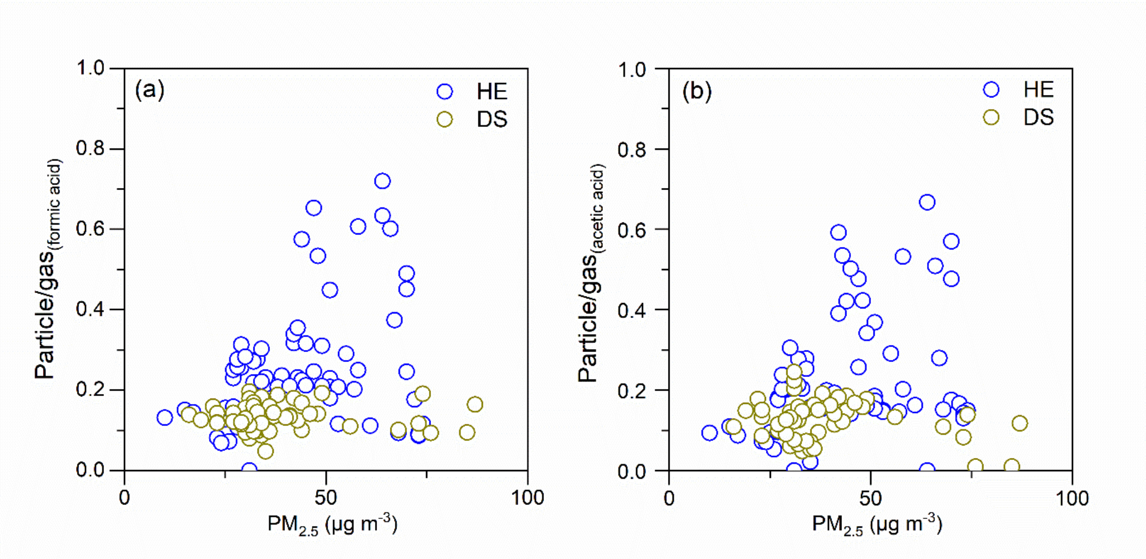

Figure S5. Partitioning coefficients of low molecular organic acids (formic and acetic acids) versus $PM_{2.5}$ during HE and DS periods.

Comment:

4. Aqueous phase reactions: The authors claim the possible presence of aqueous phase reactions in the DS periods in several places, as noted at lines 268, 321-322, and 385. If aerosol particles were indeed semi-solid or solid during the DS periods, how could aqueous-phase reactions take place?

Reply: We are sorry for the inconsistency. As we replied in Comment #2, we incorrectly used the PM_1 composition to calculate the phase state of $PM_{2.5}$ and dust coarse particles. Although submicro particles in the DS periods were possibly semi-solid or solid during the DS periods, as seen in Figure 3 and Figure S6, WSOC partitioning process in the DS period was dominated by aerosols larger than PM_1.What we discussed in the previous manuscript on the phase state based on PM_1

were incorrect, which is the reason resulting in the inconsistency. Thus, we deleted the phase state related discussions.

Minor Comments:

1. Lines 185 – 188: I do not think the comparison in Table S1 is valid. The upwind region measurements were made 20 years ago!

Reply: Thanks for the comment. We have updated the references data in the Table S1, which were measured in 2017 and 2021 in the upwind regions. We revised the related discussions with the new references. Please see page 8-9, line 188-190.

2. Figure 5: The reported compounds only contributed 0.05% to the light absorption. Could the authors clarify which other compounds contributed most to the light absorption?

Reply: There are numerous types of brown carbon molecules in the atmosphere. Common BrC chromophores in primary emission include polycyclic aromatic hydrocarbon (PAHs) and their derivatives such as oxygenated PAHs (O-PAHs) and phenols (Yuan et al., 2020). BrC can also be formed through gas-phase oxidation of volatile organic compounds such as nitro-aromatic compounds (NAC) and aqueous phase reaction of carbonyls with ammonium and amine (Wang et al., 2019; Gong et al., 2023). In this study, we have focused on the aqueous-phase formation of BrC on the dust particle surface during DS period. Imidazoles are the typica tracers of liquid-phase formed brown carbon in the atmosphere (Liu et al., 2023). Thus, we only compared the light absorption contribution of imidazoles on the coarse dust particles during NDS and DS periods. To date, in BrC research community the above PAHs, O-PAHs, NACs, and imidazoles are widely characterized for ambient aerosols, which account for typically less than 10% of total BrC, while the remaining are still unknown on a molecular level. Thus, at this moment we cannot clarify other compounds contributed most to the light absorption.

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