Dear ACP Editor:

As requested by the editor Prof. Dara Salcedo, here we corrected our manuscript for a possible publication in ACP. We greatly appreciate the time and effort that editor and reviewers spent in reviewing our manuscript. Their comments are really thoughtful and very helpful for us to improve the quality of our paper. After reading the comments from the reviewers, we have carefully revised our manuscript. All the changes in the manuscript and the supporting information are marked in blue color. Our responses to the comments are itemized below.

Anything for our paper, please feel free to contact me via ghwang@geo.ecnu.edu.cn.

All the best

Gehui Wang

Sept.28, 2024

Reviewer(s)' Comments to Author:

Reviewer: 1

Comments:

This manuscript describes a series of environmental chamber experiments designed to probe the effects of seed aerosol and ammonium on secondary organic aerosol formation from acetone. By starting with different seed aerosols, the authors are able to investigate the impacts of particle acidity on SOA formations -- although this is hard to separate from chemical composition, i.e., the availability of ammonium for heterogeneous reactions. To separate these effects, the authors then add ammonia to the chamber after turning off the lights, and find that ammonium availability enables formation of C-N bonds and light-absorbing compounds in the aerosol. Finally, the authors extrapolate the SOA yields observed in the chamber -- despite the fact that the oxidation and seed particle conditions in the chamber are vastly different from those in the atmosphere -- to calculate a rough global SOA formation from acetone and contribution of acetone to the SOA budget.

The manuscript flows well logically, with straightforward descriptions of the experiments, and the figures are clear and easy to understand. The authors' comprehensive modeling of wall losses -- not just of particles but of ammonia and organic vapors -- is a big plus. However, I believe some shortcomings with the manuscript require major attention before this paper can be publication-worthy -- most notably, some analysis of the effects of photolysis in the chamber, discussion and consideration of the RO_2 radical fate in the chamber, comparisons to other methylglyoxal chamber/modeling studies, and a clarification of assumptions (or, better yet, a more nuanced approach) behind the calculation of acetone's contribution to the global budget. More detail on all of these are included in the line-by-line comments below.

Response: We thank the comments and carefully revised our manuscript. Our responses to the comments are itemized as follows.

Comments:

1. L 63: It's not clear what's meant by "OAs" here (the acronym hasn't yet been defined, but seems reasonable to assume it's organic aerosol -- but even then I'm not sure what "all the OAs" in this case means).

Response: The "OAs" means organic acids. We deleted this acronym and used the full name throughout the manuscript. Please see the revised manuscript page 3, line 65.

Comments:

2. L 68: also not sure what "the uptake ... is of salting-in/salting-out effects" is supposed to mean. That uptake is *affected by* salting in and out?

Response: Thank the reviewer for pointing out the mistakes, and we have revised this sentence as "Moreover, a few studies reported that the uptake of VOC oxidation products by inorganic aerosols can be affected by a salting-in/salting-out effect (Waxman et al., 2015; Wang et al., 2016a)." Please see the revised manuscript page 3, lines 68-70.

Comments:

3. L 70: It's not entirely clear what's meant by "highly volatile" VOCs -- i.e., what's the volatility cutoff that counts as "highly" volatile? Many species that are widely considered

2

volatile are indeed included as SOA sources in models, such as glyoxal and methylglyoxal (see, e.g., Fu et al., 2008, DOI: 10.1029/2007JD009505 for GEOS-Chem) and even formaldehyde (see, e.g., Moch et al., 2020, DOI: 10.1029/2020JD032706 and Dovrou et al., 2022, DOI: 10.1073/pnas.2113265119). In fact, this likely overlaps with the proposed acetone SOA source estimated here, since acetone predominantly makes SOA via methylglyoxal. It would be worth comparing your results here to previous model estimates of methylglyoxal SOA.
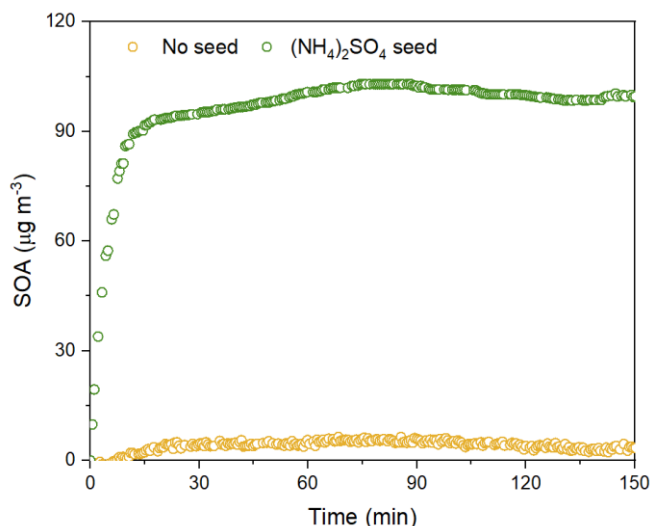
Response: Suggestion taken.

(1) We agree that the "highly volatile" in the manuscript was not clearly described. As shown in Table R1 below, compared to glyoxal, methylglyoxal and formaldehyde, acetone is much more volatile, which is of a Henry's law constant (K_H) being 2–4 orders of magnitude lower than the three species and abundantly exists in the atmosphere from the ground surface to the upper troposphere. Therefore, the multiphase reaction of acetone in aqueous phase of particles was generally ignored by previous model work. While the multiphase reaction of VOCs with a relatively higher K_H such as glyoxal and methylglyoxal are considered in models for calculating SOA.

However, our study observed a significantly enhanced SOA formation from acetone photochemical reactions in the presence of inorganic seeds compared to that in the absence of seeds (Figure R1), indicating an importance of SOA formation from acetone multiphase reactions on inorganic seeds, which has been ignored in the previous model researches.

Table R1. The Henry's law constants (K_H) of VOCs (Seinfeld and Pandis, 2006)

Compounds	K_H (M atm^{-1})
acetone	30
glyoxal	3.6×10^5
methylglyoxal	3.7×10^3
formaldehyde	6.3×10^3

Figure R1. Concentrations of acetone-derived SOA in the chamber during the Phase I as a function of reaction time in the absence and presence of $(NH_4)_2SO_4$ seeds, respectively.

(2) In this work, we found that besides methylglyoxal (MGly), many low volatility VOCs formed from the acetone photochemical reactions in the gas phase also were important SOA precursors. Moreover, many alcohol, organic acids and organic hydroperoxides compounds with high Henry's law constant (K_H) produced from acetone photochemical reactions in gas phase can dissolved into aqueous phase and undergo esterification reactions to form SOA. Therefore, we believe that only considering the irreversible uptake of methylglyoxal will probably underestimate the SOA formation from acetone. Thus, it is necessary to investigate the SOA formation from acetone and compare it with MGly-SOA.

To make the related statements clear enough, we have rephrased the sentences, see page 3-4, lines 70-82.

Comments:

4. L 77-83: it's disingenuous to suggest that SOA formation from acetone hasn't been studied before -- in fact it's been the subject of a lot of study, but those studies usually started with methylglyoxal instead of acetone. SOA formation from methylglyoxal, and the impacts on that process of heterogeneous reactions and aerosol properties, has been extensively characterized in the past -- see, e.g., De Haan 2018 (DOI 10.1021/bk-2018-1299.ch008), Tan et al. 2010 (DOI: 10.1016/j.atmosenv.2010.08.045), and Schwier et al.

2010 (DOI: 10.1021/es101225q) among many others. Starting with methylglyoxal is a reasonable tactic considering that acetone photooxidation in the atmosphere produces methylglyoxal in high yields and it's widely acknowledged (e.g. in your own Figure 6) that methylglyoxal is the dominant intermediate in SOA formation from acetone. Previous work on SOA formation from methylglyoxal should be acknowledged and summarized here in the intro, and compared to your results later in the manuscript.

Response: We agree with your comments totally and have taken your suggestion. Indeed, methylglyoxal is an important product of acetone photochemical reactions with 14% molar yield, which can partition into aqueous phase followed by oligomerization, oxidation by OH or/and reaction with NH_3 or organic amine to form SOA (De Haan et al., 2019; Aiona et al., 2017; Li et al., 2021b; Yasmeen et al., 2010; Zhang et al., 2022). Currently, estimation of acetone-derived SOA by chemical transport models only consider its product methylglyoxal as the SOA precursor (Fu et al., 2008). However, Ge et al. found that other products derived from acetone photo-oxidation such as alcohols and organic acids also can dissolve into the aqueous phase and transform into SOA by esterification (Ge et al., 2017), indicating that only considering the uptake of methylglyoxal will probably underestimate the contribution of acetone to the global SOA production. Thus, it is necessary to investigate the SOA formation from acetone and compare it with methylglyoxal-SOA.
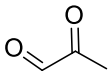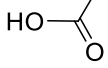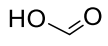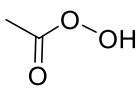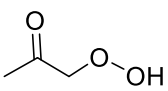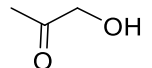
The above information could be further confirmed by the results of this study. Several alcohols, organic acids and organic hydroperoxides with high Henry's law constant (K_H) produced from acetone photochemical reactions in the gas phase were observed in this work. Their concentrations were calculated using OBM-MCM (the results shown in Table R2), in which $C_2H_4O_3$ and $C_3H_6O_3$ are intermediate volatility organic compounds (IVOCs) and can undergo gas-particle partitioning readily to form SOA. These IVOC concentrations were estimated by OBM-MCM (Table R2) that were the same order of magnitude with methylglyoxal, indicating that they cannot to be neglected. Therefore, only considering the irreversible uptake of methylglyoxal will inevitably underestimate the SOA formation from acetone.

Moreover, there are abundant gas-phase intermediate products containing hydrophilic

functional groups such as alcohol, ketone and organic acids formed from acetone photochemical reactions, which can dissolve into aqueous phase and undergo further oxidation reaction, esterification reaction and radical-radical reaction to form SOA on particles (Poulain et al., 2010; Ge et al., 2017). For example, the acetone alcohol can react with acetic acid to form esters $C_5H_8O_3$ in aqueous phase. The organic hydroperoxide $C_3H_6O_3$ produced from acetone-RO_2+HO_2 pathway also can react with acetic acid and pyruvic acid to form $C_5H_8O_4$ and $C_6H_8O_5$ in particle phase, respectively. These esterification reactions can also contribute to SOA formation effectively. Thus, only considering the role of methylglyoxal will not only underestimate the contribution of acetone photooxidation to SOA in the atmosphere but also cannot give a comprehensive understanding on the heterogeneous reactions of acetone in the atmosphere.

The above discussions were added into the revised manuscript and the supporting information. Please see the revised manuscript page 4-5 lines 90-101, page 14 lines 359-372, and Figure 6; Table S2-S3 and Figure S10 in the supporting information, respectively.

Table R2. Concentrations and saturation mass concentration ($C*$) of VOCs products from acetone photooxidation

Gaseous products	Molecular structure	Concentration (ppb)	$C*$ ($\mu g\ m^{-3}$)	Volatility	K_H ($M\ atm^{-1}$)
$C_3H_4O_2$		1.82	2.3×10^7	VOC	3.7×10^3
$C_2H_4O_2$		22.95	3.2×10^7	VOC	1.8×10^3
CH_2O_2		7.84	2.7×10^7	VOC	1.3×10^3
$C_2H_4O_3$		4.16	**1.4×10^6**	**IVOC**	7.2×10^2
CH_4O_2		7.95	2.7×10^7	VOC	1.5×10^2
CH_4O		0.35	6.7×10^8	VOC	2.3×10^2
$C_3H_6O_3$		1.65	**1.5×10^6**	**IVOC**	3.1×10^4
$C_3H_6O_2$		0.12	2.3×10^7	VOC	1.3×10^2

Comments:

5. L 113: Does acetone photolyze sufficiently quickly with the 254nm lights for this to be an appreciable loss process during the photooxidation stage? This should be modeled, ideally with a box model of the chamber that also accounts for the self-limiting effect of H_2O_2 as a source of OH radicals (high concentrations of H_2O_2 needed for OH production also serve as a strong OH sink through the OH + H_2O_2 reaction, limiting the concentration of OH that can be sustained). If acetone photolysis is indeed a factor in its loss in the chamber, what effect would this have on your conclusions?

Response: (1) Yes, acetone can photolyze sufficiently quickly with the 254nm lights. The OH radical concentrations calculated by the loss rate of acetone in experiments were underestimated. Thus, in the revised manuscript, an observation-based model (OBM) incorporating the latest version 3.3.1 of MCM (MCM v3.3.1; available at http://mcm.leeds.ac.uk/MCM/) was utilized to simulate the acetone photochemical reactions in the chamber, and the photolysis of acetone and the strong OH sink through the OH+H_2O_2 reaction were taken into account. The OH concentrations in this work are about 5.89×10^6 molecules cm^{-3}, which is two orders of magnitude lower than the values calculated by the loss rate of acetone. We have corrected the OH concentration in Table S1 and deleted the OH calculation method from the supporting information. The description about OBM-MCM calculation method was added into the manuscript, page 7, lines 175-181.

(2) In all experiments, the oxidation by OH and photolysis of acetone occurred simultaneously. The products of photolysis of acetone also can be oxidized by OH radicals, and OH radicals can be formed in photolysis of acetone. Thus, we corrected the photooxidation to photochemical reactions throughout the manuscript and the supporting information.

Comments:

6. L 120: The values in Table S1 suggest that these experiments had sustained OH and starting acetone concentrations much higher than would be representative of the atmosphere. First of all, how much H_2O_2 was used to achieve this? Second, what does this

mean for the fate (i.e. reactive pathways) of the peroxy radicals formed by acetone + OH (+ O_2)? I would imagine this high VOC and OH mixture would create very high peroxy radical (RO_2) concentrations, which would then react predominantly via $RO_2 + RO_2$ chemistry, although that's only a minor pathway in the troposphere. This could mean you're producing a lot of SOA from dimers that wouldn't have formed if the acetone-RO_2 were reacting with HO_2 or NO -- the dominant atmospheric pathways. Can a box model or other method be used to estimate the relative contributions of these pathways?
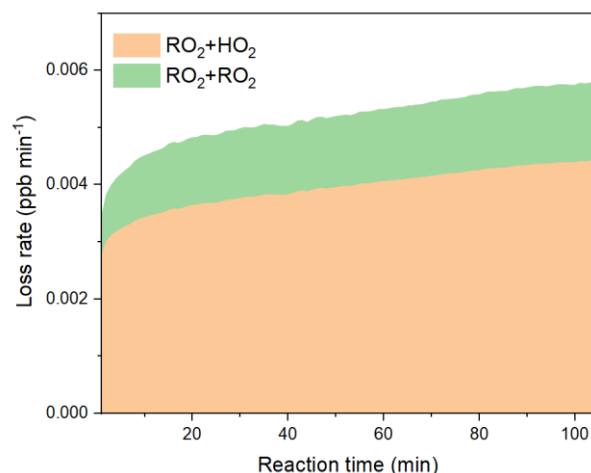
Response: Suggestion taken. The OBM-MCM was used to calculate the OH concentrations and RO_2 fate in this work. The concentrations of OH radicals in all experiments were about 5.89×10^6 molecules cm^{-3} that were consistent with the real atmosphere (Yang et al., 2021).

(1) The H_2O_2 concentrations injected into the chamber were 2.95×10^{13} molecules cm^{-3}. The information was added into the manuscript, see page 6, lines 131-132.

(2) In this work, the RO_2 fate include $RO_2 + HO_2$ and $RO_2 + RO_2$. The loss rates of two RO_2 pathways were shown in Figure R2. Obviously, $RO_2 + HO_2$ was the main pathway in RO_2 chemistry, the loss rate of which was 3.19 times that of $RO_2 + RO_2$ pathway. In addition, as shown in Table R2, abundant organic hydroperoxide compounds were formed from $RO_2 + HO_2$ pathway, indicating the importance of $RO_2 + HO_2$ in acetone photochemical reactions of this work.

The related information was added into the manuscript and supporting information. Please see page 13-14 lines 354-359 in revised manuscript, Figure S10 and Table S3 in supporting information.

Figure R2. Loss rates of RO_2+HO_2 and RO_2+RO_2 pathways in acetone photochemical reactions during the experiment

Comments:

7. L 141: were gamma(H^+) and m(H^+) also calculated by E-AIM?

Response: Yes, the gamma(H^+) and m(H^+) also calculated by E-AIM. We have corrected the sentence to "Where γ_{H+} and m_{H+} were the activity coefficient and molality of H^+ calculated by E-AIM model" in the manuscript, see the revised version, page 7, lines 159-160.

Comments:

8. L 162: need to spell out methylglyoxal before abbreviating it (MGly)

Response: Suggestion taken. The full name methylglyoxal first appearances at page 4 line 73 in the revised manuscript.

Comments:

9. L 173-176: how was the N/C ratio calculated -- it looks like only N in organic fragments was considered, since otherwise the ratio would've started out extremely high considering all the ammonium in the particles? Is it possible that N-containing organic fragments are made in the AMS (i.e. a reaction during the heating and discharging) rather than being representative of the aerosols in the chamber?

Response: (1) Yes, only N in organic fragments was considered here, and the N/C ratio was given by the HR-ToF-AMS. The N-containing organic fragments indicate the formation of C-N bonds that are associated with brown carbon (BrC) such as imine and

imidazole formed from the reaction of NH_3 and carbonyls (Liu et al., 2015). Thus, the N/C ratio and N-containing organic fragments were used to analyze the BrC formation on various inorganic seeds in this work.

(2) The N-containing organic fragments are representative of the aerosols in the chamber not made by the AMS during the heating and discharging for the following reasons:

① The HR-ToF-AMS used in this work consist of five individual, differentially pumped chambers: the aerosol sampling chamber, the particle-sizing chamber, the particle evaporation and ionization chamber and the ToF-AMS chamber (Drewnick et al., 2005). The particles with size of range 50-600 nm are sampled into the aerosol-sampling chamber, and the air is removed from the aerosol-sampling chamber by a 280 l/s turbo molecular pump. Therefore, most of NH_3 cannot arrive at the particle evaporation and ionization chamber through the aerosol-sampling chamber and react with the aerosols or gaseous reactants to form N-containing organic fragments during the heating and discharging process.

② Morris et al. investigated the mass spectrum of oleic acid oxidized by ozone using AMS of aerodyne, who found that the observed mass peaks were consistent with the results measured by a high performance liquid chromatography (Morris et al., 2002). Middlebrook et al. reported that the volatilization/ionization of AMS had fewer matrix effects than other instruments with the single steps laser desorption/ionization. In addition, the results of AMS are the difference between the signals of aerosols+air (chopper open state) and air (chopper close state) into the evaporation and ionization chamber, indicating that the signals caused by air molecules are deducted. In this work, no significant change on N/C ratio was observed during the Na_2SO_4 seed experiments, suggesting that our explanation on the increasing of N-containing fragments and N/C ratio on acidic seeds is reliable.

③ A number of researches have demonstrated the availability of the HR-TOF- AMS on measuring the N-containing fragments produced from the reaction of NH_3/NH_4+ and carbonyls. For example, De haan et al. and Hawkins et al. analyzed the N/C ratio of the
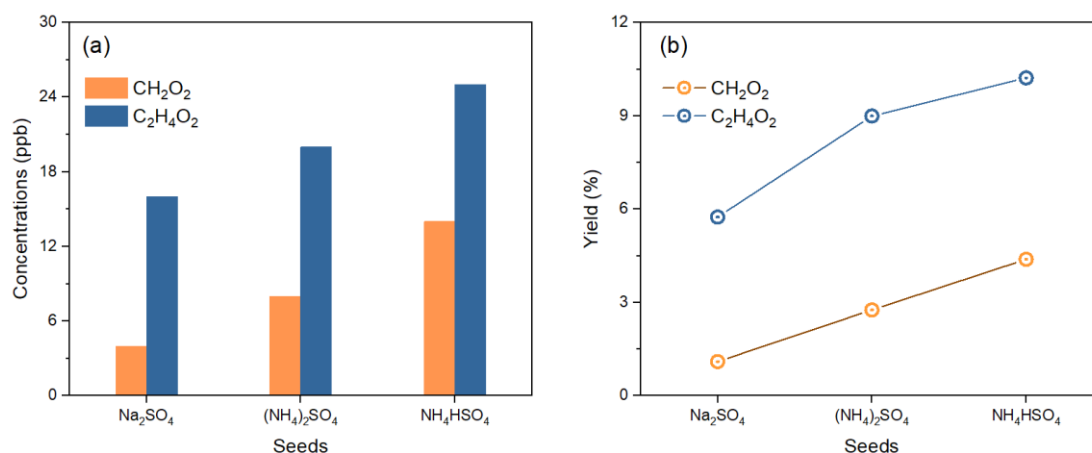
products of aqueous aldehyde amine reaction by AMS (De Haan et al., 2010; Hawkins et al., 2016). Kasthuriarachchi et al. investigate BrC formation from reactions of two aqueous-phase precursors, glyoxal and methylglyoxal, with ammonium sulfate or glycine in aqueous droplets after drying at a range of RH (30−90%), and found that the variations of the N:C ratios from AMS and mass absorption efficiency of aerosol products were generally consistent with each other (Kasthuriarachchi et al., 2020).

Therefore, it is reasonable that we used the N/C ratio from AMS to discuss the BrC formation from the aqueous reactions of carbonyls with ammonia in this work.

Comments:

10. L 240: this difference in acid partitioning between the different pH seed aerosols does seem a highly likely effect; can it be estimated from the differences in measured gas-phase concentrations of formic and acetic acids between the various experiments?

Response: The concentrations and yield of formic and acetic acids in gas phase at the end of Phase I on various seeds were calculated and shown in Figure R3(a) and (b) respectively. Significantly, the gas-phase concentrations of formic and acetic acids increased with the enhancement of the seed acidity due to the inhibition of acid aqueous phase to uptake of formic and acetic acids on seeds. The results were consistent with AMS that higher OSc and larger fraction of $C_xH_yO_z$ signals of SOA on Na_2SO_4 seeds (Figure 3a and Figure S5). We have added this information into the manuscript and supporting information, page 10 lines 267-269 in manuscript, Figure S6 in supporting information.

Figure R3. Concentrations (a) and yields (b) of gas-phase formic and acetic acids at the reaction end of Phase I during the different seed experiments.

11. L 256-260: couldn't it just be that the higher-order oligomers fail to form in the neutral aerosols, since the condensation reactions that produce them are acid-catalyzed and will preferentially occur on the acidic seeds? It doesn't seem like there is a need to invoke hydroperoxide decomposition here.

Response: Thank you very much for your important comments. Acid-catalyzed may be one of the reasons leading to more high-order oligomers on the acidic seeds than neutral seeds. We added this into the manuscript, page 11 lines 282-285.

On the other hand, the oligomers oxidized to low molecular weight (LMW) compounds by OH radicals may be another reason lead to smaller molecules SOA formed on neutral seeds than on acidic seeds. Because more oligomers of pyruvic acids were observed on the neutral seeds than on the acidic seeds; pyruvic acids are produced from the oxidization of the dissolved methylglyoxal by OH radicals in aqueous phase (Altieri et al., 2008). These results suggest that the reactivity of OH radicals on neutral seeds is stronger than on acidic seeds, which can be supported by the higher OSc of SOA formed on the neutral aerosols. The formation of OH radicals results from the photolysis and thermolysis of hydroperoxide compounds in aqueous phase (Hunt et al., 2018; Gerritz et al., 2024; Wei et al., 2022). Therefore, smaller molecules SOA formed on neutral seeds than acidic seeds are also related to the hydroperoxide decomposition.

Comments:

12. L 351-366: this method of calculating acetone's SOA formation and contribution to global SOA production effectively assumes that all acetone in the atmosphere (a) follows gas-phase photooxidation reactive pathways similar to those experienced in these chamber experiments, which seems unlikely given the high RO_2 and OH concentrations in the chamber, and (b) is exposed to the same high inorganic seed particle loadings that exist in this chamber, which is not the case. In the same way you normalized the SOA formation to surface area in Figure S4, estimates of ambient SOA formation should be scaled by the ambient aerosol surface area that acetone (or more accurately its photooxidation products) actually sees in the atmosphere, which would likely result in a far smaller contribution to

the global SOA budget. Without these adjustments the rough yields and budgets estimated here should not be reported as headline numbers in the abstract, since they are likely to strongly overestimate the contribution of acetone. In fact, once these assumptions are reconsidered, the estimates might be more in line with the "irreversible uptake" of methylglyoxal used in models.

Response: (1) The OH concentrations have been recalculated using a MCM model after considering the photolysis of acetone and strong sink of OH by H_2O_2, which were about 5.89×10^6 molecules cm^{-3}. The OBM-MCM results show that RO_2+HO_2 was the dominant RO_2 chemistry not RO_2+RO_2. These results are consistent with the real atmosphere.

(2) Suggestion taken. Higher concentrations of aerosol surface area may be an important reason resulting in more SOA formation from acetone photochemical reactions in this work. However, as reported by Martin et al. (2003), the global mean total aerosol surface area concentrations were in the range of $(0.5-25) \times 10^{-4}$ cm^2cm^{-3}. The wide-range brings a big uncertainty to estimate the contribution of acetone to global SOA. Moreover, there is considerable uncertainty in uptake coefficients (γ) of MGly used in current model work. The γ of MGly used by Fu et al. (2008) is 2.9×10^{-3} without taking into account the influence of salting effects. Curry et al. (2018) revised the γ to 10^{-10}-10^{-6} after considering salting effects, aerosol thermodynamics, mass transfer, and irreversible reactions of organic species with OH in aqueous phase. In addition, previous laboratory studies showed a large difference among the uptake coefficients of MGly, ranging from 4.0×10^{-7} to 2.4×10^{-2} (Li et al., 2023; Li et al., 2021b). Salting effects and other VOCs such as formaldehyde and acetaldehyde also can influence the SOA formation from aqueous reaction of MGly (Rodriguez et al., 2017; Waxman et al., 2015). These documented values suggest a big uncertainty for SOA model work on MGly. Therefore, the contribution of acetone to global SOA cannot be estimated accurately in this work. We have deleted the relevant content in the revised manuscript and modified the abstract. We have added these discussions into the revised manuscript, page 2 lines 35-39 in abstract, page 14-15 lines 386-396 in the revised manuscript.

Reviewer: 2

<u>*Comments:*</u>

Secondary organic aerosols are the major component of fine particles in the atmosphere and its evolution cannot be predicted by current numeric models due to some missing heterogeneous formation mechanisms. Zhang and co-authors investigated the heterogeneous reaction dynamics of SOA formation from the photochemical oxidation of acetone via chamber experiments and analyzed the effects of seeds and NH_3 on the formation of SOA and BrC, finding that no BrC formed on neutral particles although in the presence of NH_3 and only considering the role of MGly will inevitably underestimate the contribution of acetone to SOA production in the atmosphere. The research is interesting and would be helpful for improving our understanding on SOA and BrC formation mechanism. And the wall loss corrected of particles and volatile compound (NH_3 and VOCs) is detailed and systematic. This paper is well organized and the figures are clear. I can recommend its publication if the following issues can be addressed.

<u>**Response**</u>: We thank the above comments and have carefully revised our manuscript. Following is our response to the comments.
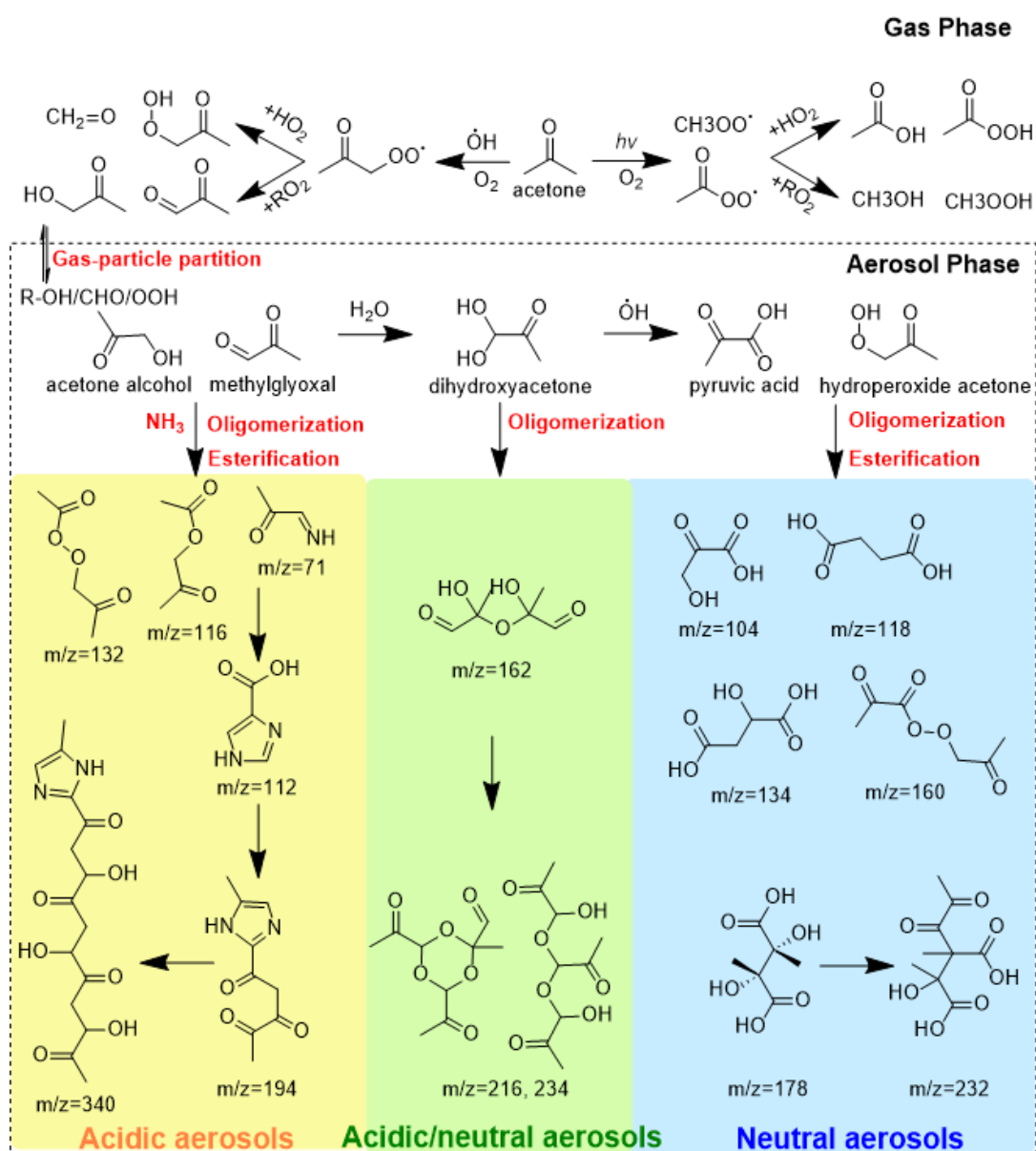
<u>*Comments:*</u>

1. In experiments, the photodissociation of acetone also can take place under 254 nm UV irradiating conditions at Phase I. Therefore, the influence of the photodissociation of acetone on the SOA formation should be considered.

<u>**Response**</u>: Thank the reviewer for the suggestion. We have estimated the OH concentrations using an observation-based model (OBM) incorporating the latest version 3.3.1 after considered the photodissociation of acetone. The photodissociation of acetone has been considered in the formation mechanism of SOA from acetone photochemical reactions (as shown in Figure R4). The photochemical reactions of acetone in this work include photolysis and oxidation by OH radicals, which produce various peroxy radical (RO_2) and undergo two RO_2 fates, RO_2+HO_2 and RO_2+RO_2 reactions. The loss rates of two RO_2 pathways are shown in Figure S10. Obviously, RO_2+HO_2 was the main pathway in

RO_2 chemistry, the loss rate of which was 3.19 times that of RO_2+RO_2 pathway. Concentrations of main gaseous products from RO_2 chemistry are shown in Table S3. $C_2H_4O_3$ and $C_3H_6O_3$ are intermediate volatility organic compounds (IVOCs) and can undergo gas-particle partitioning readily to form SOA. Moreover, there are abundant gas-phase intermediate products containing hydrophilic functional groups such as alcohol, ketone and organic acids formed from acetone photochemical reactions, which can dissolve into aqueous phase and undergo further oxidation reaction, esterification reaction and radical-radical reaction to form SOA on particles (Poulain et al., 2010; Ge et al., 2017). For example, the dissolved MGly can be hydrolyzed and then oxidized into organic acids such as pyruvic and oxalic acids or proceeds to a series of oligomerizations to produce many oligomers, giving rise to SOA formation. The acetone alcohol can react with acetic acid to form esters $C_5H_8O_3$ in aqueous phase. The organic hydroperoxide $C_3H_6O_3$ produced from acetone-RO_2+HO_2 pathway also can react with acetic acid and pyruvic acid to form $C_5H_8O_4$ and $C_6H_8O_5$ in particle phase, respectively. These esterification reactions can also contribute to SOA formation effectively.

And we corrected the SOA formation mechanism in Section 3.3 (page 13-14, lines 354-372) and Figure 6 in the revised manuscript. The description about OBM-MCM calculation method was added into the manuscript, page 7, lines 175-181.

Figure R4. A diagram for the formation pathway of SOA derived from acetone oxidation in the atmosphere.

Comments:

2. In different experiments with various inorganic seeds, can the reactions in gas phase be affected by the physicochemical properties of seeds? The authors should discuss the difference of the reactions in gas phase in the presence of different inorganic aerosols, including the differences in gaseous products concentrations.

Response: Suggestion taken. (1) In different experiments with various inorganic seeds, the concentrations of acetone and H_2O_2 injected into the chamber and the temperatures and relative humidity in the chamber were similar. The pseudo first-order rate constants for the acetone during photochemical reactions were estimated from exponential fitting of the measured decay of acetone concentration (eq.1) (Li et al., 2021a).

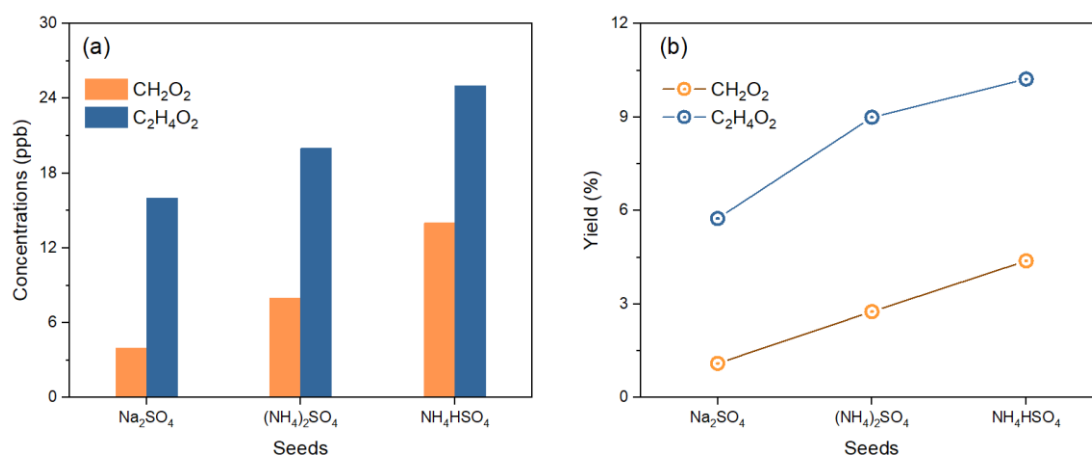$$[Acetone] = [Acetone]_0 e^{-kt} \tag{1}$$

where $[Acetone]_0$ is the initial concentration of acetone and k is the fitted pseudo first-order rate constant for the acetone photochemical reaction. The k values for the acetone of different inorganic seeds experiments were shown in Table R3. The k values of different seeds experiments were consistent with those in the absence of seeds, indicating that the reaction of acetone in gas phase including photodissociation and oxidation by OH was not affected by the physicochemical properties of seeds.

Table R3. The fitted pseudo first-order rate constant (k) for the acetone of different inorganic seeds experiments

Seeds	k (s^{-1})
Na_2SO_4	9.5×10^{-5}
$(NH_4)_2SO_4$	9.6×10^{-5}
$(NH_4)HSO_4$	9.6×10^{-5}
Without seeds	9.8×10^{-5}

(2) The gas-particle partitioning of organic products especially organic acids from acetone photochemical reaction could be influenced by inorganic seeds. In this study, the concentrations of formic and acetic acids in gas phase were measured by a PTR-MS. The concentrations and yield of formic and acetic acids in the gas phase at the reaction end of Phase I were calculated and shown in Figure R3(a) and (b), respectively. Significantly, the gas-phase concentrations of formic and acetic acids increased with the enhancement of the acidity of seeds due to the inhibition of acid aqueous phase to uptake of formic and acetic acids on seeds, which are consistent with the AMS result, i.e., higher OSc and larger fraction of $C_xH_yO_z$ signals of SOA on Na_2SO_4 seeds (Figure 3a and Figure S5). We have

added these discussions into the manuscript. See page 10, lines 267-269 in the revised manuscript, and Figure S6 in the supporting information.

Figure R3. Concentrations (a) and yields (b) of gas-phase formic and acetic acids at the reaction end of Phase I during the different seed experiments.

Comments:

3. Line 213, authors proposed that methylglyoxal is the key species in SOA formation from acetone. However, other gaseous products (e.g. acetone alcohol and organic acids) can also contribute to the SOA formation in aqueous phase. Their contribution on SOA formation and corresponding reaction pathways should be considered.

Response: Suggestion taken. Because methylglyoxal is one of the first -generation oxidation products of acetone photochemical reaction, and has been confirmed to be an important SOA precursor (Tan et al., 2009; Tan et al., 2010; Yasmeen et al., 2010). Therefore, we selected methylglyoxal as the proxy to explore the mechanism of SOA formation. However, on the basis of the results of OBM-MCM, some intermediate volatility organic compounds (IVOCs) such as $C_2H_4O_3$ and $C_3H_6O_3$ can be formed in gas phase, which can condense on particles readily and promote the formation of SOA. Moreover, there are abundant gas-phase intermediate products containing hydrophilic functional groups such as alcohol, ketone and organic acids formed in acetone photochemical reaction, which can dissolve into aqueous phase and undergo further reactions such as oxidation, esterification and radical-radical reaction to form SOA on particles (Ge et al., 2017). These SOA products were detected in the chamber by the

ultrahigh-resolution orbitrap mass spectrometer. For example, the acetone alcohol can react with acetic acid to form esters $C_5H_8O_3$ in aqueous phase. The organic hydroperoxide $C_3H_6O_3$ produced from acetone-RO_2+HO_2 pathway also can react with acetic acid and pyruvic acid to form $C_5H_8O_4$ and $C_6H_8O_5$ in particle phase, respectively. These esterification reactions can also contribute to SOA formation effectively.

We have added the above discussions into the manuscript. Please see page 14 lines 360-372; and the supporting information Tables S2-S3.

Comments:

4. In section 3.2, RO_2 fate can influence the SOA formation processes obviously, therefore, can the particle acidity and NH_3 change the RO_2 chemistry and further affect the SOA formation?
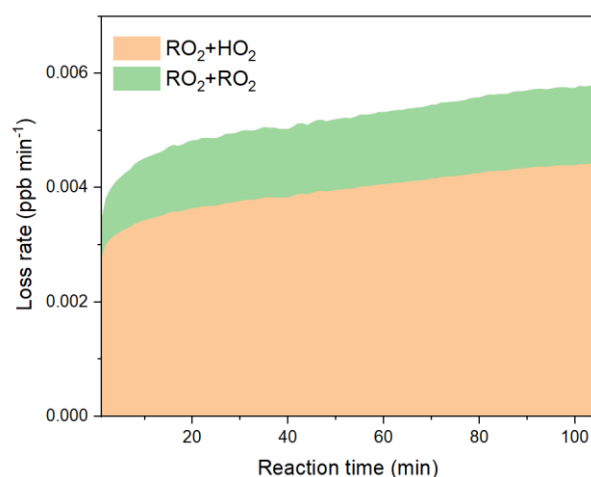
Response: (1) First, the concentrations of acetone and H_2O_2 injected into the chamber and the temperatures and relative humidity in the chamber were similar for all the experiments in this study. As shown in Table R3, the pseudo first-order rate constants for the acetone experiments with different seeds are almost equal to that in the absence of seeds, indicating that the gas-phase reactions of acetone including photodissociation and oxidation by OH were not significantly affected by the physicochemical properties of seeds.

Table R3. The fitted pseudo first-order rate constant (k) for the acetone reaction in the different seed experiments

Seeds	k (s^{-1})
Na_2SO_4	9.5×10^{-5}
$(NH_4)_2SO_4$	9.6×10^{-5}
$(NH_4)HSO_4$	9.6×10^{-5}
Without seeds	9.8×10^{-5}

(2) Second, in this study, the photochemical reactions of acetone in this work include photolysis and oxidation by OH radicals, which produce various peroxy radical (RO_2) and undergo two RO_2 fates, RO_2+HO_2 and RO_2+RO_2 reactions. The loss rates of two RO_2 pathways are shown in Figure R2. RO_2+HO_2 and RO_2+RO_2 can produce abundant gas-

phase intermediate products containing hydrophilic functional groups such as alcohol, ketone, organic acids and organic hydroperoxides compounds with a large Henry's law constant (K_H). The gas-particle partitioning of these hydrophilic organic compounds especially organic acids can be influenced by the particle acidity and NH_3, which can further affect the SOA formation. In comparison with those observed during the $(NH_4)_2SO_4$ and NH_4HSO_4 seed experiments, the lower yields of gaseous formic and acetic acids (Figure R3), and the higher OSc and larger fraction of $C_xH_yO_z$ signals of SOA were observed during the Na_2SO_4 seed, indicating that the uptake of carboxylic acids could be enhanced on neutral seeds. Moreover, the acidity of aerosol aqueous phase also can affect the uptake of ketone. For instance, Zhao et al. (2006) found that the effective Henry's law constant of MGly decreased with an increase of aqueous acidity in their laboratory experiments.

Figure R2. Loss rates of RO_2+HO_2 and RO_2+RO_2 pathways in acetone photochemical reactions during the experiment

The related discussions were added into the revised manuscript, please see page 10, lines 267-269 and page 13, lines 354-357.
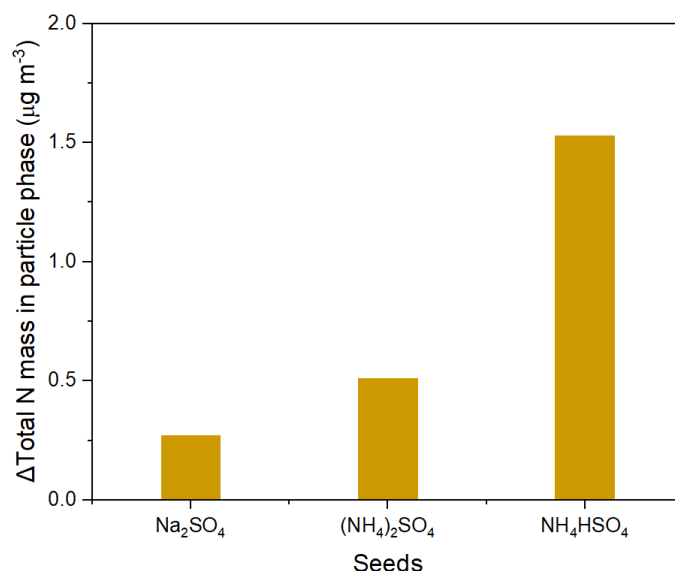
Comments:

5. Line 277, the partitioning coefficients of NH_3 on different seeds were estimated using the eq. S15 and S16 (Guo et al., 2017; Nah et al., 2018). The authors can compare the theoretical values with the actual values observed in experiments.

Response: Suggestion taken. In the revised manuscript, the gas-to-particle phase partition

coefficients of NH_3 ($\varepsilon(NH_4^+)$) on different seeds were calculated, which suggests that NH_3 was almost not absorbed by Na_2SO_4 seeds but efficiently absorbed by NH_4HSO_4 seeds. The enhancement of the total N mass in particle phase from the partitioning of gaseous NH_3 into particle phase and subsequent reaction with acid and ketone at the reaction end of Phase II was calculated and shown in Figure R5. Obviously, the results displayed more N mass partitioned onto acidic aerosols, which were consistent with the theoretical values. But it is difficult to obtain the actual $\varepsilon(NH_4^+)$ for the chamber experiments, because the concentration of NH_3 in the gas phase was not measured due to the unavailability of the instrument.

The related information was added into the manuscript and supporting information, page 12 lines 312-313 in the manuscript; Figure S7 in supporting information.

Figure R5. The enhancement of the total N mass in the particle phase at the reaction end of Phase II

Reference:

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