First, we want to thank the anonymous referee #1 for the comments and suggestions which have allowed us to improve the quality of the manuscript. Below, we copy the Referee’s comments in italics and our responses starting with “ Reply”.

This manuscript presents results from global modeling studies in order to explore the role of secondary organic aerosol formed in the aqueous phase of clouds and aerosol particles (aqSOA). Several approaches for the description of aqSOA formation are applied based on past laboratory and/or model studies. The results are compared to each other and to observations. SOA comprises a large fraction of total particulate matter in the atmosphere; however, current models cannot fully reproduce its total burden properties and spatial and temporal evolution. Several contemporary models include descriptions of varying complexities to predict formation of SOA by condensation of semivolatile gas phase species. However, the role of the formation of aqSOA has not been comprehensively evaluated yet on a global scale, even though many recent laboratory, field and model studies suggest its potential importance. The current study tries to fill this gap by using a global model. While I appreciate the effort in extending a global model by explicit and detailed chemistry, I think that many conclusions drawn from these calculations represent overstatements. Given the numerous uncertainties in our current understanding of aqSOA formation in both cloud and aerosol water, I do not think that a detailed comparison to observations is particularly meaningful and any agreement between observations and model could be easily a ’right answer for the wrong reasons’.

Reply: It is always true that a model can give the right answer for the wrong reasons. But it is still important to compare model results with observations, as we have done.

In addition, there seem to be numerous misunderstandings in interpreting reaction parameters as used in the applied aqSOA mechanisms; these affect the predicted aqSOA net formation rates and thus the interpretation of the results.

Reply: We have examined our reaction mechanism and in consultation with Barbara Turpin have corrected the mechanism for Case 1 and other cases (see our reply to major comment #5 below).

The value of a model study as performed here is to reveal the great inconsistencies that exist based on different aqSOA schemes.

Reply: We have done this, and thank the reviewer for this comment.

The results should not be used to claim ’realistic aqSOA predictions’ but rather to discuss parameters that most sensitively affect predicted aqSOA rates and thus should be focus of future lab and field studies. If the tone of the paper can be changed in this regard and if my comments below are addressed, this manuscript might have the potential to become a useful benchmark in the current SOA model literature.

Reply: We didn’t claim ‘realistic aqSOA predictions’ in any place in the paper. Instead, we just compared the model results in different cases to the available measurements and described their performance compared to these measurements. We agree that claiming "realistic aqSOA predictions" is going beyond what is known. Our study looks at the sensitivity of model results associated with the uncertainties resulting from different aqSOA schemes, different cloud fields, and with or without dissolved iron chemistry in cloud water. We found that the aqSOA formation rate is sensitive to the aqSOA scheme used in the model, cloud water content, and iron chemistry. Other sensitivity studies (e.g., based on altering cloud properties other than cloud water content, aerosol size distributions, and the parameters within the chemical mechanisms) are beyond the scope of this paper. Many of these sensitivity tests have been done in other studies and we will point to them in the revised manuscript (see our responses below). In addition, we have done an additional sensitivity test by increasing the effective Henry's law constants of glyoxal and methylglyoxal in aerosol water content due to the ion strength effect (for details, see our responses below). We also have examined the "tone" of our revised manuscript to aid in pointing out uncertainties in the modeling of aqSOA formation.

Major comments

1) One of the main conclusions of the study should be that an uptake coefficient ('gamma' for surface-limited process) leads to vastly different results than explicit chemistry. While this is hinted at, reasons for these discrepancies are not fully discussed.

Reply: We don't know the exact reasons for the inconsistency between these two methods, but as we stated in the Section 3.3., the reason for the discrepancy between measurement studies (i.e. Waxman et al. (2013) and Liggio et al. 2005) and the values derived here might be that the actual value of the uptake parameter in remote and rural regions is smaller than that derived in urban regions (i.e. Mexico city in the case of Waxman et al., 2013) or/and that the bulk phase reactions adopted from Ervens and Volkamer (2010) may not include the full set of reactions of glyoxal that are accounted for in the uptake parameter method. We will state this explicitly in the revised manuscript and discuss the possible reasons for the discrepancy more fully in the Section 3.3 as follows: "In particular, the smaller uptake parameter in rural regions than in urban regions might be due to the weaker acid particle acidity and lower dissolved organic compound concentration in rural regions. The glyoxal uptake rate is observed to be higher in more acidic particles (Liggio et al., 2005). The more concentrated organic compounds in aerosol water might lead to a higher oligomer formation rate (Tan et al., 2009). Also, the bulk phase reactions do not include any surface reactions of glyoxal that the uptake parameter method would include."

Does this mean that deriving gamma in lab studies is not useful? Is there any way to use a single parameter instead of an explicit chemistry scheme?

Reply: We don't mean that the deriving gamma in lab studies is not useful, but we believe that this scheme assumes that all of the gas incorporated into the aqueous phase stays in this phase and this must depend on the conditions within the lab experiment. We will state this in the revised manuscript. It would be useful if this approach worked well under all atmospheric conditions, since the simple uptake parameter is less demanding of computer time. While the explicit chemistry scheme is more demanding, it might capture the dynamic evolution of aqSOA formation. The purpose of comparison of these two different schemes here is to show whether they are consistent with each other in predicting the aqSOA mass. As we show, however, these two different schemes lead to quite different aqSOA mass.

Does the derived uptake parameter of _1e-5 (Section 3.3) indeed lead to the total and spatial aqSOA burden as predicted by the explicit scheme or merely to the same total SOA mass? If not, what does it tell us about the applicability of any gamma?

Reply: The derived uptake parameter of order 1×10^{-5} leads merely to the same total aqSOA mass. It is a globally averaged uptake parameter. Of course, the spatial aqSOA burden which would be predicted using this global average uptake parameter could be different than that using an explicit aqueous formation mechanism and this will be stated explicitly in the revised manuscript. The uptake parameter of order 1×10^{-5} derived from the explicit chemistry scheme only provides a simple and direct comparison with the uptake parameter measured from the lab studies or derived from other model studies.

2) The comparison of Case 1 and Case 4 (different cloud liquid water fields) reveals great differences in predicted aqSOA. Some more quantitative remarks on the uncertainties in predicting cloud properties vs predicting aqSOA should be given.

Reply: Liu et al. (2012) have studied the sensitivities of predicted aqSOA formed in cloud to the cloud lifetime, cloud droplet size and cloud fraction. They found that the predicted aqSOA was sensitive to the cloud lifetime and cloud fraction while the predicted aqSOA depended on the cloud droplet size weakly. One focus of our work is to look at the sensitivity of predicted aqSOA to the cloud liquid water content caused by different cloud fields, which was not studied in Liu et al. (2012). We will cite Liu et al. (2012) paper to discuss the uncertainties associated with the predicting cloud properties while our own results show uncertainties in predicting cloud water content. The change in cloud field causes the global aqSOA burden to decrease by 16%, while the use of different aqSOA formation mechanisms leads to a change in global aqSOA burden ranging from -50.9% to 185.7%. We will add this comparison to the discussion in Section 3.6.

3) Any observation-model comparison should be discussed more cautiously. As pointed out above, I do not think that comparing absolute numbers is useful, but rather relative trends should be discussed. Given the great uncertainties in terms of aqSOA mechanisms and cloud properties, I think that currently a 'good agreement' between observations and model prediction should be considered as being fortuitous instead of claiming a robust understanding of the underlying processes.

Reply: We agree that a good agreement between observations and model prediction does not imply that we have a robust understanding of the underlying processes. We will clarify this and will present a table (see below) to discuss the relative trends in model-measurement comparisons. A paragraph will be added on line 18, page 29654, as follows:

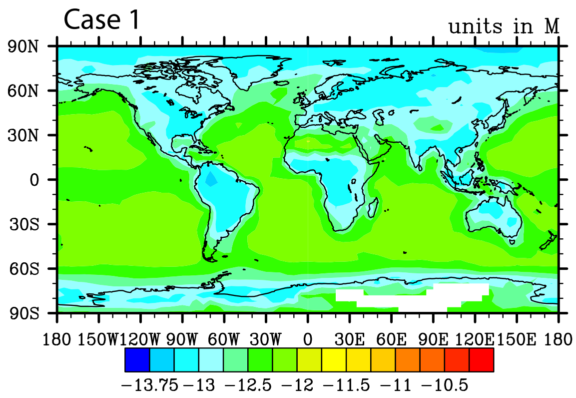
"It should be noted that that good agreement between observations and model predictions does not imply a robust understanding of underlying processes. However, the relative trends in how these comparisons change between different cases (Table 1) helps one to understand the benefits of different underlying processes and to determine the best current approach. For the Northern Hemisphere, the uptake method provides an approach that agrees better with the observations and the use of the GFDL cloud field also improves the model performance, while in the tropics using the multiphase reaction scheme helps to close the gap between the simulation and the observations, and including iron chemistry also decreases the model bias. On the other hand, including iron chemistry degrades the model's ability to predict the oxalate concentrations. Thus there is no single approach that is able to capture all the observations well. Further mechanism development and/or aerosol transport model and general circulation model development of cloud fields are needed to improve the agreement with observations."

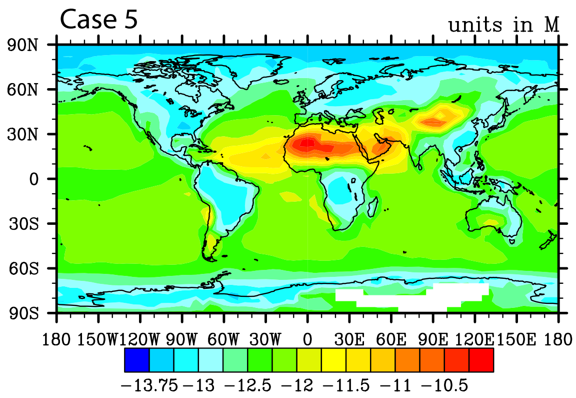
	AMS measurements at rural sites in Northern Hemisphere	AMS measurements in tropical regions	Oxalate measurements
Case 1	-32.4%	70.7%	-63.1%
Case 2	-42.5%	49.7%	-61.2%
Case 3	-42.9%	38.7%	-62.2%
Case 4	-13.8%	82.9%	-76.2%
Case 5	-33.1%	19.3%	-88.2%
Case 6	+20.0%	189.7%	N/A

Table 1. Comparison of the normalized mean bias (NMB) between observations and the model results for different cases.

4) Most of the aqSOA formation and loss rates, as used in the explicit scheme, depend directly on the concentration of the OH radical in the aqueous phase (OHaq). The difference between Case 1 and Case 5 is the inclusion of Fe chemistry that significantly increases the OHaq concentration. Even though a number of OHaq reactions is included in the model, they likely only comprise a very small number of OHaq sinks in 'real' atmospheric water since the total water-soluble organic carbon mass includes hundreds of different compounds (a small fraction of which can usually only be identified). In order to discuss these effects, predicted OHaq levels should be presented (e.g. as an additional panel in Figure 5) and compared to data derived based on measurements, e.g. by Arakaki et al.(2013).

Reply: We will add the predicted OHaq levels on a logarithmic scale (see below) as an additional panel in Figure 5.





We will also add a paragraph to describe the above figures and to compare the predicted OHaq levels to the estimated OHaq levels reported by Arakaki et al. (2013). This paragraph is as follows and will be added on line 27, page 29648. "Figure 5 also depicts the global distribution of annual mean aqueous OH radical concentrations near 971 hPa for Case 1 and Case 5. The largest increase of aqueous OH radicals due to the inclusion of iron chemistry occurs over regions where there are abundant dust aerosols. Arakaki et al. (2013) estimated the steady-state concentrations of OH in cloud sampled over North American remote continental regions. The estimated average OH concentration is 7.2×10^{-15} mol/L. The predicted average OH concentration in this region is 9.0×10^{-14} mol/L in Case 5 and 8.8×10^{-14} mol/L in Case 1. Thus the modeled OH concentrations in cloud for both cases are higher than those estimated by Arakaki et at. (2013). Arakaki et al. (2013) also estimated that the averaged total OH production rate in cloud is 1.9×10^{-9} mol/L/s and OH loss rate constant is 2.6×10^{5} s^{-1}. In the model, the averaged total OH production rate is 1.06×10^{-8} mol/L/s in Case 5 and 1.03×10^{-8} mol/L/s in Case 1. OH loss rate is 1.18×10^{5} s^{-1} in Case 5 and 1.17×10^{5} s^{-1} in Case 1. This suggests that the overestimation of OH source is the major reason for the higher OH concentration in the model. Arakaki et al. (2013) attributed the higher OH concentration in cloud water predicted in most of box models to their underestimation of OH loss rates. This is not the case in our model. About 1.2×10^{5} s^{-1} OH loss rate in our model is compared to the values ranging from 2.0×10^{4} s^{-1} to 7.7×10^{4} s^{-1} obtained in those box models (Table S2 in Arakaki et al. (2013)). "

5) The approach in Case 1 double-counts several processes. (i) The gamma values were derived from laboratory studies based on the loss rate of glyoxal (or related compounds). This loss rate is equal to the (absolute) net production rate of oligomers, and organic acids (and other products). Thus, including OH chemistry AND gamma values is not consistent since all uptake processes and chemical reactions (including organic acid formation and loss) are captured by the measured gamma values. (ii) In Table S3, the reaction of GLYX+OH (R1) is included, in addition to the lumped reaction (R25). This approach double-counts the loss of glyoxal in the aqueous phase. If both reactions are to be kept in the mechanism, a branching ratio should be estimated and the sum of both rate constants should amount to the measured, recommended value as cited for R1.

Reply: (i) We will explain the use of a gamma value for glyoxal together with OH chemistry in the revised manuscript as follows: " It might appear that the chemistry for Case 1 double counts the loss rate of glyoxal since it includes both a loss rate by reaction with OH as well as a loss rate due to a surface reaction characterized by an uptake parameter. However, the uptake parameter used in Case 1 was adopted from Waxman et al. (2013), who used a box model to test several chemical mechanisms, in order to fit the observed glyoxal concentrations in Mexico City. The best fit chemical mechanism that they found includes an uptake parameter (gamma) of 3.3×10^{-3} as well as the reaction of OH with glyoxal in dilute water. Therefore we also include the uptake parameter together with the OH chemistry in dilute water."

(ii) The reaction R25 is a complementary reaction to reaction R1. Carlton et al. (2007) demonstrated that reaction R1 alone could not reproduce the glyoxylic and oxalic acid concentration dynamics observed in experimental measurements. Extra reactions were thus proposed to explain the observations. However, these experiments were taken at glyoxal concentrations that were higher than those in real cloud water by 2~3 orders (B. J. Turpin, personal communication). Thus, in our revised manuscript, we removed the reaction R25 (the lumped reaction based on Carlton et al. (2007)) in all simulations. We have re-run all simulations and updated all results in the revised manuscript. The removal of the reaction of R25 decreases the oxalate formation rate and its burden, but our original conclusion on the uncertainties caused by different aqSOA formation mechanisms and cloud fields remains unchanged.

6) Several studies suggest that oxalate and related carboxylates are present as (moderately or poorly) soluble salts or stable complexes in aerosol particles, e.g. Furukawa and Takahashi (2011). This means that oxalate in aerosol water might not be readily oxidized by OHaq but present as insoluble fraction. While I admit that not sufficient information might be available to fully include such effects in a model, uncertainties in terms of oxalate sinks and reservoir should be at least discussed.

Reply: We will add a discussion in Section 3.6 as follows: "Furukawa and Takahashi (2011) used X-ray absorption fine structure spectroscopy (XAFS) to show that most of the oxalate within aerosol particles is present as metal oxalate complexes, especially as Ca and Zn oxalate complexes. Xing et al. (2013) also suggest the formation of a stable Zn oxalate complex in the aerosol phase in urban aerosols over China. These complexes are weakly water soluble and very stable, which prevents oxalate from being oxidized by OH in aerosol water. These effects are not included in the model due to the lack of detailed information, but it is clear that their inclusion could increase the amount of oxalate in aerosol water.".

7) Several model studies, e.g., Lim et al., (2010 and references therein) have shown that oligomers are not stable and decrease over time, likely due to further oxidation by OHaq. Neglecting their further oxidation, as done in the current study (cf p. 29644, l. 15), leads to an overestimate of their mass. Given that kinetic data are available, I suggest including their photochemical loss.

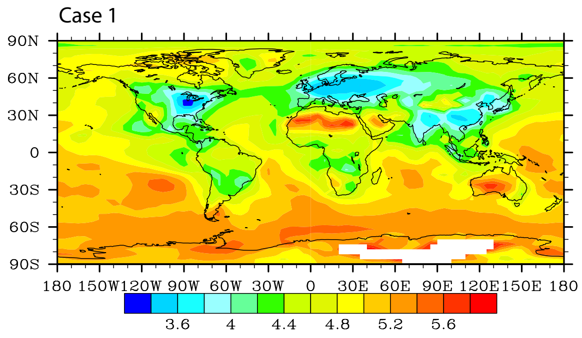
Reply: Actually we have included the further oxidation of oligomers by OHaq in Case 3 (see the reaction R38, R42, R53, and R54 in Table S5, exactly following Lim et al. (2010). We don't include these reactions in Case 1 because the uptake parameter represents the probability that a molecule impacting the aerosol surface will result in uptake and formation of a species which does not evaporate, and this already takes into account the chemical reactions including the loss of oligomers inside the aerosol implicitly. This explanation has been added to the revised manuscript as follows:

“ We do not include the chemical destruction in the Case 1, because the uptake parameter represents the probability that a molecule impacting the aerosol surface will result in uptake and formation of a species which does not evaporate, and this already takes into account the chemical reactions including the loss of oligomers inside the aerosol implicitly. But in the Case 3 where we use the multiphase reaction scheme for aqSOA formation in aerosol water, we do include the further oxidation of oligomers by OHaq in Case 3 (see the reaction R38, R42, R53, and R54 in Table S5, exactly following Lim et al. (2010). ”.

8) Using the explicit scheme, the loss of oxalate by OHaq will strongly depend on the pH value (R4-6 in Table S3)

. How is pH predicted in the current model and how does it compare to observations (or any measured proxy for pH, e.g. NH4/SO4)? Could differences in predicted pH also explain (part of) the differences between the current and previous model studies?

Reply: Aqueous H^+ concentration is predicted explicitly in the model, using the same method as that for other aqueous species (e.g. aqueous OH) concentrations and by assuming ion neutrality. We will add a plot of the predicted annual mean pH in cloud near 971 hPa and a table of comparisons of pH values with measurements reported in literature in the Supplement as follows.



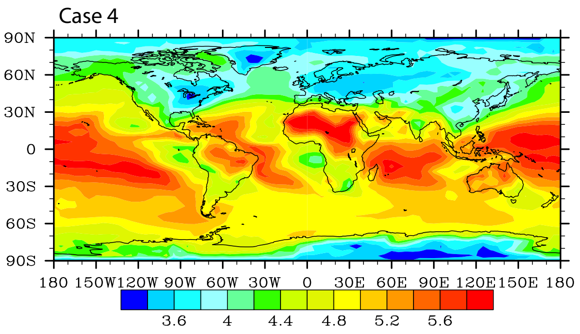


Table 2. Comparison of measured pH values in cloud water with modeled pH values

Measured pH values	Location	Time	Reference	Modeled pH (Case 1)	Modeled pH (Case 4)
Average=4.10	Tai Mountain, China	Summer, 2007	Shen et al. (2012)	3.77	3.87
Average=3.77	Tai Mountain,	Summer,	Shen et al.	3.77	3.87

	China	2008	(2012)		
Average=3.68	Tai Mountain, China	Spring, 2007	Shen et al. (2012)	4.33	3.92
Average=4.34	Tai Mountain, China	Spring, 2008	Shen et al. (2012)	4.33	3.92
3.5~3.8	Whiteface Mtn, NY, U.S.	July and August	Faust et al. (1993)	3.99	4.20
3.5~4.0	Shenandoah Park, VA	August	Faust et al. (1993)	3.89	4.61
5.6~5.8	Corvallis, OR	Nov. and Jan.	Faust et al. (1993)	4.33	4.12
2.7~3.8	Whiteface Mtn, NY, U.S.	July, 1998	Moore et al. (2004)	3.96	4.29
5.5~7.0	Davis	December 1998–January 1999)	Moore et al. (2004)	4.20	4.12
4.5~5.5	Puy de Dôme, France	February-April, 2001 and February-May, 2002	Marinoni et al. (2004)	3.74	3.70
3.6~5.8	Puy de Dôme, France	February, 2002	Sellegri et al. (2003)	3.61	3.37
4.6~6.6	Sydney, Australia	July-August, 1976	Scott (1978)	4.63	4.78

From the above comparisons, the model predictions agree with the measured pH values very well at Tai Mountain, Whiteface Mountain, and Shenandoah Park sites, while the model tends to predict more acidic conditions at Corvallis, Davis, the Puy de Dôme sites and the Sydney sites. We believe, however, more measurements of pH are needed to form conclusions about the adequacy of the model prediction of pH.

Previous model studies didn’t report the cloud pH values, so we cannot compare our predicted pH values to those in previous model studies.

We added the following to the manuscript:

“The formation and loss of oxalate by OHaq depends strongly on the pH value (see reactions R2-6 in Table S3), because the rate constants of oxidations of glyoxylic acid and oxalic acid are smaller than those of their anions (i.e., glyoxylate and oxalate) and the relative abundance of these acids and their anions depends on pH values. We have briefly compared our predicted pH values with observations from the literature. The results agree with predictions at some locations, but show that the model is too acidic in other locations. We would expect the oxalate concentrations to vary little if pH values were increased, because both formation rate and the destruction rate of oxalate would increase.

This weak dependence of aqSOA formed in cloud has been observed in a parcel model including a multiphase reaction mechanism similar to what we use in this work (Ervens et al., 2008)."

9) The uptake rates of both oxidants (OH, NO3) and organics from the gas into the aqueous phase will depend on the available surface area, both if the explicit chemistry scheme and the 'gamma approach' are used. For simplicity, an average cloud droplet size of 10 um is assumed (p. 29638, l. 3). For aerosol, it is not even clear whether a single size or a wet size spectrum is applied: It is stated that the 'effective radius' is calculated for sulfate aerosol. In radiation calculations, 'effective radius' usually refers to the ratio of the third to second moment of a size distribution, i.e. a single size characterizes the population. Is this really what you mean or is 'effective radius' here simply the 'wet radius' based on relative humidity and hygroscopicity? In any case, ideally the potential sensitivity or uncertainty in predicting realistic wet particle and cloud drop size distributions (also in the context with comment 2) and its impact on aqSOA prediction should be pointed out.

Reply: The effective radius of wet sulfate aerosol is used. It is the ratio of third to second moment of the wet sulfate aerosol size distribution. As stated on line 4-5, page 29638, the aerosol effective radius is humidity dependent. We will clarify this by revising the sentence on line 3-5, page 29638, to "In addition, an effective cloud droplet radius of 10 μm is assumed for all clouds, while the effective radius for aqueous sulfate particles (the ratio of third to second moment of the wet sulfate aerosol size distributions) is calculated explicitly according to their relative humidity dependent size distributions.".

Liu et al. (2012) studied the sensitivity of aqSOA formation in cloud to the cloud droplet size. They found that the global total aqSOA production depends weakly on assumptions of cloud droplet size when the cloud water content is unchanged. Waxman et al. (2013) studied the sensitivity of aqSOA formation in aqueous aerosol to aerosol size distributions. Little size dependence was reported for the case using the multiphase reaction scheme, but the uptake method showed a strong sensitivity to size distribution because of changes in the surface to volume ratio. We will add a discussion of these uncertainties in predicting realistic wet particle and cloud drop size distributions in Section 3.6 as follows: "There are other uncertainties in the treatment for aqSOA formation. Liu et al. (2012) used a global model to study the sensitivity of their predicted aqSOA in cloud to cloud lifetime, cloud droplet size and cloud fraction. They found that the predicted aqSOA was sensitive to the cloud lifetime and cloud fraction while it depended only weakly on the cloud droplet size. Waxman et al. (2013) studied the sensitivity of aqSOA formation in aerosol to aerosol size distributions. Little size dependence was reported for the case using the multiphase reaction scheme, but the uptake method showed a strong sensitivity to size distribution because of changes in the surface to volume ratio."

Specific comments
Abstract: It should be made clearer that all numbers refer to 'predicted' masses etc.

Reply: We will revise the sentence on line 7-8, page 29630, to "The predicted net global SOA production rate in cloud water ranges from 19.5 Tg yr^{-1} to 46.8Tg yr^{-1} while that in aerosol water ranges from −0.9 Tg yr^{-1} to 12.6 Tg yr^{-1}".

p. 29632, l. 5: Organic acids, such as oxalic, by itself have a fairly high vapor pressure. However, their salts have a sufficiently low vapor pressure to keep them in the condensed phase.

Reply: To emphasize the role of their salts, we will change the sentence on line 3 to "Water-soluble and polar gases are taken up by the aqueous phase and can be oxidized in water leading to the production of low volatility substances (e.g., organic acids and especially their corresponding salts, oligomers, and organosulfates). While organic acids have high vapor pressures, we account for the formation of low volatility substances in the model by using low vapor pressures for glyoxylic acid, oxalic acid, and pyruvic acid as have all other models."

p. 29632, l. 20: Do you mean 'most abundant'? Or most important 'for what'?

Reply: Yes, we meant 'most abundant'. So we will change it to "the most abundant of which is oxalic acid".

p. 29632, l. 24f: This sentence seems somewhat out of place or redundant. The formation of aqSOA from MVK and MACR occurs via oligomerization or formation of other products that have been discussed in previous sentences.

Reply: we will delete this sentence in the revised manuscript.

p. 29633, l. 25: In the study by Ervens and Volkamer (2010), a surface-dependence or mixed sulfate/organic seed particles was found. Such particles are likely the best proxy for ambient particles, as opposed to particles composed of a single compound.

Reply: We will revise these sentences as follows: "but Ervens and Volkamer (2010) found no correlation between the SOA volume increase and the seed aerosol surface area for most of seed aerosols used the laboratory study by Volkamer et al. (2009). Instead, the SOA volume increase was shown to be linear to the total water mass on these seed particles, implying that SOA was formed as a result of a bulk process. On the other hand, the positive correlation between the SOA volume increase and the surface area observed for mixed sulfate/ fulvic acid seed particles in the study by Ervens and Volkamer (2010) suggests that a surface process dominates on these mixed particles. Additionally, Waxman et al. (2013) found that a surface limited uptake process could explain the observed gas-phase glyoxal mass in Mexico City much better than a bulk phase process did."

p. 29634, l. 5: Not really clear what 'in addition' refers to here. Maybe it can be just *deleted.*

Reply: we will delete ‘in addtion’.

p. 29635, l. 17: In many of these lab studies, the reaction mechanisms are derived based on detailed product studies and temporal concentration profiles. I suggest changing ’estimate’ to ’derived’ or ’developed’.

Reply: We gather you meant on page 29634. We will change ‘so that sufficient information exists to estimate their reaction mechanisms’ to ‘so that sufficient information exists to develop a complete mechanism.’.

p. 29636, l. 8: Is the wet or dry surface of sulfate aerosol used to predict epoxide formation?

Reply: It is the wet surface of sulfate aerosol. We will clarify this by changing the sentence by “In addition, we also accounted for SOA formation due to heterogeneous reactions of epoxides on the surface of wet sulfate aerosol by assuming an uptake coefficient of 0.0029.”

p. 29636, l. 10: Why is the used mechanism the ’most realistic one’?

Reply: Because this gas-phase mechanism can capture the observations of OH and the first generation products of isoprene-OH reactions better than the other two mechanisms used in Lin et al. (2012). We will revise this sentence to “Here, we used Simulation C in Table 1 in Lin et al. (2012), since this mechanism was shown to best capture the observations of OH and the first generation products of isoprene-OH reactions. ”.

p. 29639, l. 5: This is a quite bold statement. I suggest replacing ’generally’ by ’relatively’.

Reply: We will replace ‘generally’ with ‘relatively’ in the revised manuscript.

p. 29639, l. 23: There is a huge body of literature that suggests that the Henry’s law constant of glyoxal (and likely related compounds) is strongly enhanced in aerosol. water, e.g. (Kroll et al., 2005; Volkamer et al., 2009). Many laboratory studies, e.g. (Lim et al., 2010), for aqSOA formation in aerosol water are performed for high glyoxal concentrations (_ mM) that can be only achieved with such enhanced ’effective Henry’s law constants’. Are any of such effects taken into account in the present study?

Reply: We don’t include these effects in Case 3, but we parameterized first-order photochemical reaction rate k used in Case 2 based on the Ervens and Volkamer (2010) paper which did include the ionic strength effect on Henry’s law constants implicitly. To test the potential effect of using an enhanced effective Henry’s law constants, we added a sensitivity test for Case 3, increasing the effective Henry’s law constants of glyoxal and methylgloyxal by 3 orders of magnitude due to their interactions with salts (Kampf et al., 2013). In this sensitivity case, the chemical production rate of glyoxal oligomer is 4.65×10^{-1} Tg/yr, and the chemical destruction rate is 2.70×10^{-1} Tg/yr, so the net production rate is 1.95×10^{-1} Tg/yr. The net production rate for methylglyoxal oligomer is 8.68×10^{-2} Tg/yr. An increase of 3 orders magnitude for effective Henry's law constants increases the net production rate of glyoxal oligomer by about one order of magnitude and the net production rate of methylglyoxal oligomer by a factor of 58. The increase in net production rate leads to an increase in oligomer burden by a factor of 4.4. However, these enhanced net production rates and burdens are still smaller than those predicted in the Case 1 which uses an uptake method for the aqSOA formed in aqueous aerosol. We will discuss the ionic strength effect on the effective Henry's law constant and the results of the sensitivity test described above in Section 3.6.

p. 29640, l. 13: Is there a threshold for LWC above which aqSOA in aerosol water is considered? I.e. do you mean 'deliquesced' by 'aqueous' here?

Reply: Yes. There is a threshold relative humidify for the formation of aerosol LWC. The deliquescence relative humidity (DRH) for pure sulfate aerosol is set to be 0.80. We note that the DRH has been shown to decrease in the mixed particles of sulfate and SOA (Brooks et al., 2002; Smith et al., 2012), thus the use of 0.80 as the DRH may underestimate to some extent the formation of aqSOA in aqueous aerosol. We will clarify this in the revised manuscript.

p. 29641, l. 8: This is ambiguous: Do you really predict (methyl)glyoxal concentrations based only on Henry's law or is the full kinetic uptake described (as stated earlier in the manuscript)?

Reply: Sorry for the confusion. We use the kinetic uptake to predict glyoxal and methylglyoxal concentrations, which include Henry's law as well as other kinetic parameters (e.g., gas diffusion coefficients, accommodation coefficients, and etc.). To clarify this, we will revise the sentence as follows: "In case 1, we used the detailed multiphase reaction scheme (Eq. 1a, b) to predict the production of glyoxylic acid, oxalic acid and pyruvic acid in both cloud water and aerosol water together with the kinetic uptake described in Sect. 2.2.1 to predict the concentrations of glyoxal and methylglyoxal in cloud water. In aerosol water we used the surface-limited uptake of glyoxal and methylglyoxal to predict the formation of oligomers from these species."

*p. 29642, l. 11f: Does this mean that only 0.00175% (3.5% * 5%) of dust aerosols contribute to dissolved iron? Are the resulting predicted iron concentrations comparable to measured ones in cloud water?*

Reply: Yes, only 0.00175 of dust aerosols contribute to dissolved iron. We don't expect the use of a global uniform fraction to be able to predict accurately the spatial variations of iron concentrations in cloud water, because the iron solubility depends on the cloud pH values, dust mineralogical composition, chemical aging on the dust aerosol, and etc. (Han et al., 2012). To consider all these effects, we need to employ a kinetic iron dissolution model (e.g., Johnson and Meskhidze, 2013**).** However, the simple method we used in the paper is able to give us a first-order approximation of dissolved iron content in cloud water. And our work is the first attempt to explore the potential effect of iron chemistry in cloud on oxalate concentrations. There are very few measurements available in the literature for iron concentration in cloud. We are listing in the table below the comparison of modeled dissolved iron concentrations with measurements reported in the literature. As it is shown in the table, the iron concentration in cloud varies several orders even at the same location. The simulations in our model are within the range of observations at puy de Dôme Station, Whiteface Moutain, and Great Dun Fell, while the model overestimate the measurements at Mt. Elden site and at San Pedro Hill site.

References	Measured dissolved iron (μ mol/L)	Modeled dissolved iron (μ mol/L)	Location
Parazols et al., 2006	0.1-9.1	1.43	puy de Dôme Station, France.
Hutchings et at., 2009	4.7-30.4	595	Mt. Elden, Arizona, U.S.A.
Arakaki and Faust, 1998	0.08-1.57	0.29	Whiteface Mountain, New York, U.S. A.
Sedlak et al., 1997	0.06-1.6	0.45	Great Dun Fell, U.K.
Erel et al., 1993	3-20	100.6	San Pedro Hill, CA, U.S.A

We will add the following in the revised manuscript:
“This scheme cannot describe the spatial and time variations in dissolved Fe as predicted in models that include a kinetic description of Fe dissolution (Johnson and Meskhidze 2013, Ito and Feng, 2010) but is able to provide a first-order approximation of the dissolved iron content in cloud water.”

p. 29647, l. 12: This is not a comparison to the ’real atmosphere’ but a model-model comparison.

Reply: We will change the sentence to “or/and that the bulk phase reactions adopted from Ervens and Volkamer (2010) may not include the full set of reactions of glyoxal that are accounted for in the uptake parameter method”.

p. 29648, l. 6: Does the lifetime of oxalate referred to here only describe its lifetime with regards to deposition? Depending on pH and OHaq (and Fe) levels, its chemical life time might be much shorter.

Reply: Yes. The lifetime is only with respect to deposition. We will revise the sentence to “The lifetime of oxalic acid with respect to deposition in case 4 is longer than that in case 1 (5.0 days in case 4 vs. 2.3 days in case 1),…”.

p. 29649, l. 1ff: Can you quantify the relative contributions of the OH reaction vs Fe-complex photolysis for oxalate destruction? How do these proportions compare to recent findings by Sorooshian et al. (2013)?

Reply: Globally, Fe-complex photolysis accounts for 21.7 Tg/yr of oxalate destruction, while the destruction rate through OH and NO_3 reactions is 1.20 Tg/yr. This significant sink of oxalate by Fe-complex photolysis is consistent with the finding by Sorooshian et al. (2013) who observed that oxalate concentrations are negatively correlated with observed Fe concentrations. We note that Sorooshian et al. (2013) did not report the proportions of the OH reaction vs. Fe-complex photolysis for oxalate destruction, so we can't compare the proportion in our model with their results. However, Sorooshian et al. (2013) used a box model to simulate the oxalate formation with and without Fe chemistry. They found that the oxalate concentration would decrease when increasing the dissolved iron concentration, and gradually level off at 15% of the concentration predicted without consideration of Fe chemistry. Our model results show the oxalate concentration with iron is about 44% of that predicted without iron. We will state these results in the revised manuscript.

p. 29649, Section 3.6: This section is extremely vague and at most qualitative and does not add much to our understanding of uncertainties or underlying mechanisms of aqSOA formation. It should be updated and improved in light of my numerous comments in this review regarding uncertainties in the assumed aqSOA approaches.

Reply: This section quantifies the relative contribution of cloud water vs. aerosol water to the total aqSOA in different cases, and shows large differences between different cases in predicting the relative importance of cloud water vs. aerosol water. As we stated in our replies above, we will further improve this section by discussing the uncertainties in the assumed aqSOA approaches. And we will add to the following to the end of this section in the revised manuscript.

" There are additional uncertainties that need to be explored in the treatment of aqSOA formation. Liu et al. (2012) used a global model to study the sensitivity of their predicted aqSOA in cloud to cloud lifetime, cloud droplet size and cloud fraction. They found that the predicted aqSOA was sensitive to the cloud lifetime and cloud fraction while it depended only weakly on the cloud droplet size. Waxman et al. (2013) studied the sensitivity of aqSOA formation in aerosol to aerosol size distributions. Little size dependence was reported for the case using the multiphase reaction scheme, but the uptake method showed a strong sensitivity to size distribution because of changes in the surface to volume ratio.

Furukawa and Takahashi (2011) used X-ray absorption fine structure spectroscopy (XAFS) to show that most of the oxalate within aerosol particles is present as metal oxalate complexes, especially as Ca and Zn oxalate complexes. Xing et al. (2013) also suggest the formation of a stable Zn oxalate complex in the aerosol phase in urban aerosols over China. These complexes are weakly water soluble and very stable, which prevents oxalate from being oxidized by OH in aerosol water. These effects are not included in the model due to the lack of detailed information, but it is clear that their inclusion could increase the amount of oxalate in aerosol water.

Many studies have suggested a 2~3 order of magnitude enhancement of effective Henry's law constant for glyoxal between cloud conditions and aerosol conditions (Kroll et al., 2005; Volkamer et al., 2009; Kampf et al., 2013). To test the potential effect of this enhancement, we added a sensitivity test based on Case 3 but increasing the effective Henry's law constants of glyoxal and methylgloyxal by 3 orders of magnitude. In this sensitivity case, the chemical production rate of glyoxal oligomer is 4.65×10^{-1} Tg/yr, and the chemical destruction rate is 1.95×10^{-1} Tg/yr, leading to a net production rate of 1.95×10^{-1} Tg/yr. The net production rate for methylglyoxal oligomer is 8.68×10^{-2} Tg/yr. Thus, an increase of 3 orders magnitude for the effective Henry's law constants increases the net production rate of glyoxal oligomer by one order magnitude and the net production rate of methylglyoxal oligomer by a factor of 58. The increase in net production rate leads to an increase in oligomer burden by a factor of 4.4. However, these enhanced net production rates and global burdens are still smaller than those predicted in the Case 1 which uses an uptake method used for the production of aqSOA in aqueous aerosol.

The comparison of Case 2 and Case 3 with Case 1 shows that the use of a multiphase reaction scheme for aerosol water decreases the global total aqSOA burden by around 50%. In the case which increases the effective Henry's law constant by 3 orders magnitude, the aqSOA burden is lower than that predicted in Case 1 by 42%. The replacement of diagnostic cloud field with GFDL AM3 cloud field causes the burden to increase by 16%. In the case including iron chemistry in cloud, the burden is predicted to be smaller than that in Case 1 by11%. The use of the uptake parameter method for both cloud water and aerosol water in Case 6 predicts a 185% larger burden than Case 1. "

p. 29652, l. 26: While on a different scale, there are numerous process model studies available that report detailed oxalate and LWC measurements, together with oxalate predictions, e.g., (Sorooshian et al., 2006; Wonaschuetz et al., 2012)

Reply: We will clarify this by changing this sentence to "However, there is only limited information available in the literature where measured oxalate concentrations were reported together with cloud water content (e.g., Sorooshian et al., 2006; Wonaschuetz et al., 2012). "

p. 29653, 1st paragraph: What is the predicted ratio of aqSOA/total SOA?

Reply: The predicted ratio of aqSOA concentrations to total SOA concentrations ranges from 9.5% in Case 2 to 33.5% in Case 6 on a global basis. We will add this information after the first sentence in this paragraph.

p. 29254, l. 8: Not clear. I assume you do not compare to measurements during pre-industrial times (?)

Reply: We will remove two sentences between line 5 and line 8, page 29254, since they cause confusion and don't help to understand the reason for model-measurement discrepancy .

p. 29655, l. 26: What is the highest and lowest O/C ratio among the 26 SVOCs? How much variability would either limit introduce to the predicted overall O/C?

Reply: Among the 26 SVOCs, the highest O/C ratio is 3.0, and the lowest is 0.3. The SVOC with the highest O/C ratio contributes less than 1% to the total SVOCs globally, while the compound with the lowest O/C ratio accounts for less than 5%. Thus we don't think these two limits are important for the overall O/C. Nevertheless, the sentence will be changed to: "We estimate the average O/C ratio for the SOA from aerosol phase reactions of condensed SVOCS to be around 0.687, with values for some of the SVOCs with smaller burdens ranging from 3.0 to 0.3.".

p. 29657, l. 25: Such a missing oxalate source was also suggested by Rinaldi et al. (2011)

Reply: We will add Rinaldi et al. (2011) in the sentence as follows: "Consistent with the findings of Myriokefalitakis et al. (2011) and Rinaldi et al. (2011), the comparison of oxalate for marine sites…".

p. 29657, l. 28: Add here that also the understanding of oxalate sinks and reservoirs (e.g. salts) needs to be improved.

Reply: We will revise it as follows: "This underestimation indicates that further study is needed to understand oxalate formation and sinks and as well as the formation of oxalate-containing reservoirs (e.g. salts).".

Table 1: Case 1: This is not clear. Isn't the gas/particle transfer described by the kinetic approach? This, of course, does include Henry's law constants but would also account for possible 'non-equilibrium' situations.

Reply: We will change to "a kinetic approach is used for all gas/particle transfer".

Table 3: Caption should be improved: "Predicted global average production rates by individual reactions : : :" (or similar).

Reply: We will change the caption to "Predicted global average production rates in cloud water by the individual reactions for Case 1".

Table 5: Should that be 'aqSOA' in the caption?

Reply: We will replace 'SOA' with 'aqSOA' in the caption.

Figure 2: Aren't these plots the same for all Cases except Case 4? Or is there any feedback between chemistry and LWC?

Reply: They are the same for all Cases except Case 4. “Plots are for Case 1” will be changed to “Plots are for Case 1, but are similar for all Cases except Case 4”.

Figure 6: How do the results by Myriokefalitakis compare to your predictions? Can they be added to the figures in order to show if there is a systematic or random difference between model predictions?

Reply: To discuss the predictions and comparisons of oxalate with measurements in Myriokefalitakis et al. (2011), we will add a paragraph on line 12, page 29652, as follows: “The global oxalate burden in the simulation that Myriokefalitakis et al. (2011) predicted in case S1 is 5 times larger than the burden in Case 1 in our predictions. This is partly because Myriokefalitakis et al. (2011) increased the solubility of glyoxal and methylglyoxal in cloud water by 2 orders of magnitude, which is at the high end of measured values, causing a larger oxalate source. Also, Myriokefalitakis et al. (2011) included a set of additional reactions performed by Carlton et al. (2007) under higher glyoxal concentration conditions than those present in real cloud water, which results in more oxalate formation. In addition, a longer oxalate lifetime with respect to deposition was predicted by these authors. The larger oxalate burden in Myriokefalitakis et al. (2011) leads to a closer agreement with measurements over rural sites. However, the simulations in Myriokefalitakis et al. (2011) did not include iron chemistry in cloud which can decrease oxalate concentrations significantly (compare Case 1 and Case 5).”.
It is hard to add their comparisons to our figures because we don’t have their simulation data.

Table S3 and S4: The products of GLY, MGLY, and PRV with NO3 are not discussed in the paper by Herrmann et al. (2005). While I assume that there is no study that reports them, a comment (footnote) should be added stating that they have been assumed to be identical to those of the OH reaction.

Reply: We will add a footnote to clarity that the products of GLY, MGLY, and PRV with NO_3 are assumed to be the same as those of the OH reaction.

Table S4, R1 and R3: As written, it suggests a second order rate constant. The original value by Creighton is expressed as first order rate constant. Is this accounted for in the reaction scheme used here? If so, ’+ H2O’ should be set in parentheses.

Report: Thanks. We will set ‘+H2O’ in parentheses.

Technical comments
p. 29632, l. 20: to be part

Reply: We will change it.

p. 29632, l. 22: Add ’water’ after ’cloud’ (otherwise it might also include interstitial air)

Reply: We will add it in the revised manuscript.

p. 29633, l. 23: ..there IS still a range

Reply: We think it should be ‘there are still a range of methods…’, since “methods” are plural.

p. 29635, l. 9: Should that be ’of SOA’ or are you saying that in the new model, SOA can actually condense on both sulfate and SOA particles?

Reply: We will change it to ‘of SOA’. Thanks.

p. 29638, l. 26: remove ’from’

Reply: We will delete it.

p. 29640, l. 19: Define MW

Reply: Right after the end of this sentence, we will add ‘, in which MW is the molecule weight of glyoxal or methylglyoxal’.

p. 29642, l. 2: in the Supplement

Reply: We will change it to ‘in the Supplement’.

p. 29648, l. 25: ’Fe(III) complexes’. (Fe(III) salts are not photolysed)

Reply: We will change it to “Fe(III) oxalate complexes”.

p. 29650, Section 4: If the authors find a meaningful way to compare their model results to observations and decide to keep this section, I suggest dividing it into multiple subsections (e.g. 4.1. Oxalate; 4.2 AMS or PM measurements; 4.3 O/C ratio)

Reply: We will divide it into three subsections: 4.1. Oxalate; 4.2. AMS measurements; 4.3. O/C ratios.

p. 29657, l. 8: dominates

Reply: We will change ‘dominate’ to ‘dominates’.

p. 29657, l. 14: Overall

Reply: We will revise ‘Over all’ to ‘Overall’.

p. 29658, l. 7: two tropical

Reply: We will change ‘twotropical’ to ‘two tropical’.

- Supplement: Check all super- and subscripts (e.g. Table S2, R10, R33; Table S4, R43-45) - Table S2: Column header: K298 (Mn S-1) should be replaced by k298 (Mn s-1) - Table S2, R51 seems wrong (charge balance)

Reply: We will check them all and correct them.

References not already present in the original manuscript or the reviewer's comments

Arakaki, T. and Faust, B. C.: Sources, sinks and mechanisms of hydroxyl radical (OH) photoproduction and consumption in authentic acidic continental cloud waters from Whiteface mountain, New York: The role of the Fe(r) (r = II, III) photochemical cycle, J. Geophys. Res., 103, 3487–3504, 1998.

Brooks, S. D., Wise, M. E., Cushing, M., and Tolbert, M. A.: Deliquescence behavior of organic/ammonium sulfate aerosol, J. Geophys. Res., 29(19), 1917, doi:10.1029/2002GL014733, 2002.

Erel, Y., Pehkonen, S. O. and Hoffmann, M. R.: Redox chemistry of iron in fog and stratus clouds, J. Geophys. Res., 98(D10), 18423, doi:10.1029/93JD01575, 1993.

Faust, B. C. and Allen, J. M.: Aqueous-phase photochemical formation of hydroxyl radical in authentic cloudwaters and fogwaters, Environ. Sci. Technol., 27(6), 1221–1224, doi:10.1021/es00043a024, 1993.

Han, Q., Zender, C. S., Moore, J. K., Buck, C. S., Chen, Y., Johansen, A. and Measures, C. I.: Global estimates of mineral dust aerosol iron and aluminum solubility that account for particle size using diffusion-controlled and surface-area-controlled approximations, Global Biogeochem. Cycles, 26(2), GB2038, doi:10.1029/2011GB004186, 2012.

Hutchings, J. W., Robinson, M. S. and McIlwraith, H.: The Chemistry of Intercepted Clouds in Northern Arizona during the North American Monsoon Season, Water Air Soil Pollut., 199, 191–202, 2009.

Ito, A. and Feng, Y.: Role of dust alkalinity in acid mobilization of iron, 10, 9237-9250, doi:10.5194/acp-10-9237-2010, 2010.

Johnson, M. S. and Meskhidze, N.: Atmospheric dissolved iron deposition to the global oceans: effects of oxalate-promoted Fe dissolution, photochemical redox cycling, and dust mineralogy, Geosci. Model Dev., 6, 1137–1155, doi:10.5194/gmd-6-1137-2013, 2013.

Kampf, C. J., Waxman, E. M., Slowik, J. G., Dommen, J., Pfaffenberger, L., Praplan, A. P., Prevot, A. S. H., Baltensperger, U., Hoffmann, T., and Volkamer, R.: Effective Henry's law partitioning and the salting constant of glyoxal in aerosols containing sulfate, Environ. Sci. Technol., 43, 4236–4244, 2013.

Marinoni, A., Laj, P., Sellegri, K. and Mailhot, G.: Cloud chemistry at the Puy de Dôme:

variability and relationships with environmental factors, Atmos. Chem. Phys., 4, 715–728, doi:10.5194/acp-4-715-2004, 2004.

Moore, K. F., Sherman, D. E., Reilly, J. E., and jr. Collet, J. L.: Drop size-dependent chemical composition in clouds and fogs. Part I: Observations, Atmos. Environ., 38, 1389–1402, 2004.

Parazols, M., Marinoni, A., Amato, P., Abida, O., Laj, P. and Mailhot, G.: Speciation and role of iron in cloud droplets at the puy de Dôme station, J Atmos Chem, 54(3), 267–281, doi:10.1007/s10874-006-9026-x, 2006.

Scott, W. D.: The pH of cloud water and the production of sulfate, Atmos. Environ., 12, 917-921, 1978.

Sedlak, D. L., Hoigné, J., David, M. M., Colvile, R. N., Seyffer, E., Acker, K., Wiepercht, W., Lind, J. A., and Fuzzi, S.: The cloudwater chemistry of iron and copper at Great Dun Fell, UK, At- mos. Environ., 31, 2515–2526, 1997.

Shen, X., Lee, T., Guo, J., Wang, X., Li, P., Xu, P., Wang, Y., Ren, Y., Wang, W., Wang, T., Li, Y., Carn, S. A., and Collett Jr, J. L.: Aqueous phase sulfate production in clouds in eastern China, Atmos. Environ., 62, 502–511, doi:10.1016/j.atmosenv.2012.07.079, 2012.

Sellegri, K., Laj, P., Marinoni, A., Dupuy, R., Legrand, M., and Preunkert, S.: Contribution of gaseous and particulate species to droplet solute composition at the Puy de Dôme, France, Atmos. Chem. Phys., 3, 1509-1522, doi:10.5194/acp-3-1509-2003, 2003.

Smith, M. L., Bertram, A. K. and Martin, S. T.: Deliquescence, efflorescence, and phase miscibility of mixed particles of ammonium sulfate and isoprene-derived secondary organic material, Atmos. Chem. Phys., 12, 9613–9628, doi:10.5194/acp-12-9613-2012, 2012.

Xing, L., Fu, T. M., Cao, J. J., Lee, S. C., Wang, G. H., Ho, K. F., Cheng, M. C., You, C. F. and Wang, T. J.: Seasonal and spatial variability of the OM/OC mass ratios and high regional correlation between oxalic acid and zinc in Chinese urban organic aerosols, Atmos. Chem. Phys., 13, 4307–4318, doi:10.5194/acp-13-4307-2013, 2013.