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## ***Interactive comment on “In-cloud oxalate formation in the global troposphere: a 3-D modeling study” by S. Myriokefalitakis et al.***

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We thank the reviewer for the careful reading of our paper and the constructive comments. We took them into consideration together with the first reviewer's comments to provide the final revised version of our manuscript.

In the revised version we have further improved our simulations (outlined now in Table 2-also in the supplement to this reply) by also accounting for NO<sub>3</sub> reactions in the aqueous phase (see new updated Table 1 now in the revised manuscript- also in the supplement to this reply) and have performed new simulations to address the reviewer's comments. All comments of the second reviewer have been addressed as follows:

Replies to general comments:

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- The average predicted oxalate fraction of 13-19% of the total organic carbon seems huge. In order to justify this number- comparisons of oxalate/sulfate, oxalate/SOA (or WSOC) and oxalate/OC should be presented in addition to the results in Figure 5 - it should be clarified what the predicted OC includes, what uncertainties it bears and how it compares to measurements.

At first, we would like to stress out that TM4-ECPL model, same with most global models, underestimates the aerosol organic carbon (OC) levels, in our case roughly by at least 50% when compared with OC observations (see Figure S3 that compares OC observations from Bahadur et al. (2009) Sciare et al. (2009) and Koulouri et al. (2008) with TM4-ECPL model results for the year 2005). In addition, according to Fig. 5, the model reasonably simulates the observed oxalate (OXL) concentrations. Thus, the underprediction of OC levels and not the overprediction of OXL concentrations appears to be the main reason for the high OXL to OC ratio calculated by the model. Furthermore, in the new TM4-ECPL calculations performed following the reviewer comments (see below) the oxalate mass fraction is slightly revised towards lower values (10-16%). Note however that this value, as clearly mentioned in the paper, refers to organic aerosol mass and not to OC mass.

As mentioned in our replies to reviewer 1 and shown in figures S2 and S4 in the supplement to that reply, TM4-ECPL calculated OXL correlates well with the computed sulfate ( $\text{SO}_4^{2-}$ ). The revised simulations have further improved this correlation. Figure S4 shows comparisons of calculated and observed values of OXL/WSOC (water soluble organic carbon), OXL/OC, OXL/ $\text{SO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ , WSOC, OC and OXL (for this figure the OC is accounted and not the organic mass) indicating that the model performs reasonably well at several monitoring stations.

In our reply to the point 6 of the reviewer #1 we report the components of secondary organic aerosol (SOA). Accounting also for the primary OC and its aged forms we use a total of 19 tracers in our model to simulate organic aerosol components that are grouped in 8 major categories: SOA from anthropogenic volatile organics (SOAa), SOA

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from biogenic volatile organics (SOAb), methanesulfonic acid (MSA), marine amines salts, oxalate (OXL), aged SOA, primary anthropogenic OC, primary marine OC. Figure S1 now shows the annual mean total OC distribution and the contribution of the various components of OC to this distribution as computed by our model for surface, middle troposphere and the zonal mean.

- The base case simulation S1 assumes Henry's Law constants for SOA precursors (glyoxal, methylglyoxal, etc) to be higher by two orders of magnitude than Henry's Law constants KH in pure water because of the 'ionic strength effect in cloud water'. However the ionic strengths in the laboratory experiments that are referred to (Ip et al., 2009) was much higher than encountered in cloud water (micromolar). In addition, the generalization of the increase in KH for all compounds seems an exaggeration as (i) for methylglyoxal no such effect is known, (ii) for glyoxylic and glycolic acid this enhancement factor seems to be too high.

Although cloud droplets do not consist of pure water but contain a range of water soluble species e.g. sulfate, ammonium, chloride etc, most of the effective Henry values provided in literature are representative for pure water. Herrmann (2003) presented ionic strength (I) values for remote, continental and polluted clouds ranging between 1E-4 M and 1.7E-1 M. Ip et al. (2009) suggested an increase of Henry's law constant of glyoxal (GLY) by 50 times in the presence of sulfate at I=3E-2 M, compared to pure water. However, they found that increasing I to 2.25E-1 M, the effective Henry was enhanced to more than 109 M atm-1. This ionic strength is in the range – close to the higher values - reported by Hermann (2003) for polluted clouds, In the present study for the base simulation (S1), in order to represent the atmospheric conditions we assume an increase because of cloud ionic strength effect for GLY and for glycolaldehyde (GLYAL) and methylglyoxal (MGLY) by 2 orders of magnitude, that is within the range of reported enhancement for GLY. Although for MGLY such effect is not known, our assumption can be justified by the similar to GLY chemical structure and behavior of MGLY. For organic acids no enhancement of KH has been applied.

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- I am afraid that the KH values for acids in table S3 'double count' the acid dissociation and thus imply a too strong partitioning of glyoxylic acid into the aqueous phase which would directly affect the oxalic acid formation, in particular above the ocean where aerosol is likely to be basic and thus an overly high effective Henry's Law constant KH(eff) would be calculated by the applied approach. The intrinsic KH for glyoxylic acid is 28.67 (Ip et al., 2009) and only the effective KH(eff), i.e. including dissociation Kdiss is on the order of 1E4  $KH(\text{eff}) = KH \left(1 + Kdiss/[H^+]\right)$  The same is true for KH of oxalate. Correcting KH(eff) for oxalate might not impact the model results significantly as it is assumed in the model that all oxalate remains in the particle phase. However, even this latter assumption might be an overestimate for realistic conditions as it has been shown that oxalate does exist in the gas phase and thus is not fully contained in the particles.

We are aware that for acids, effective Henry includes the dissociation effect (Kdiss) and therefore we did not take into account the  $(1 + Kdiss/[H^+])$  factor in our calculations. In table S3 we present the effective Henry values KH(eff) taken into account in the model's calculations and not the intrinsic KH. Therefore, we have corrected the title of table S3 in the supplementary material following also the comment by the first reviewer.

- The value of the Henry's Law constant of OH (9000 M atm<sup>-1</sup>) is the highest reported in the literature. Values that are based on thermodynamic calculations (cf Sander et al.) are at least two orders of magnitude smaller and should be preferred over estimated ones. The applied value crucially biases the oxalate formation rate in the aqueous phase as it increases the OH aqueous concentration.

Following the reviewer's recommendations, we revised all our simulations using a Henry law constant of 30 M atm<sup>-1</sup> (at 298 K; from Sander, 1993) which has been also used in earlier box-model studies (e.g. Barth et al., 2003). As a sensitivity test (Simulation S1.5 listed in new Table 2) we compared these results with the simulation using the high Henry value of 9000 M atm<sup>-1</sup> used by Lelieveld and Crutzen (1991). This comparison showed that the adoption of the higher OH Henry's law constant leads to

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an enhancement by about 17% in the OXL formation.

- The authors make the assumption that in aerosol water 20% of the predicted SOA yield is oxalate. The assumption behind this value should be further explained (e.g. by means of Figure 9, Lim et al., ACP 2010).

Lim et al. (2010) have shown that the yield of oxalic acid formation from GLY aqueous phase chemistry is highly variable and depends on GLY and OH radical concentrations. For instance, they conclude that at cloud relevant GLY concentrations mainly oxalic acid is formed, whereas at aerosol relevant GLY concentrations, GLY-SOA is predominated by oligomers with yields of over 80%. Therefore, they recommended the use of explicit chemistry instead of the adoption of a yield in chemistry-transport models where short lived species concentrations can show variability higher than an order of magnitude. In the present global modeling study (simulation S3) we assume that in clouds GLY oxidation is producing OXL whereas during daytime GLY oxidation in aerosol water produces SOA that consists of 80% oligomers and 20% OXL. This yield is used as an upper limit of OXL production in the aerosol water. A relevant comment is added in the revised manuscript.

#### Replies to specific comments

- p. 488, l. 20: The statement that SOA model generally underestimate SOA mass is somewhat outdated. More recent simulations that include semivolatile species predict a much better model/observation comparison than the cited factor of 5-100.

Indeed, global models have made large improvements the past few years reducing the large discrepancies between observations and model results (see also Figure S3). Such improvement include consideration of marine organic aerosol (OA) components (e.g. Myriokefalitakis et al., 2010; Vignati et al., 2010) and of the oxidation of intermediate volatility organic compounds and the semi-volatile character of primary OA (Pye and Seinfeld, 2010; Jathar et al., 2011), reduced the discrepancies of model results with observations. Most of the models are actually able to simulate the order of magni-

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tude of OA in the troposphere. However the general statement of the underestimation of organic aerosol mass by most models remains valid. This comment is added in the revised version.

- p. 489, l. 1: The study by Weber et al. does not suggest a specific mechanism (gas or aqueous phase) for the formation of water-soluble organic carbon.

In the revised version we removed this reference since the recent work of this group is discussed 2 pages later (reference to Hennigan et al. 2009).

- p. 489, l. 18: the formation of low-volatility compounds has not been observed but rather 'suggested' based on observations.

We replaced 'observed' by 'suggested'

- p. 489, l. 20: The study by Ervens and Volkamer is not a laboratory study. Better to cite 'Volkamer et al., ACP, 2009' here.

We changed the reference 'Ervens and Volkamer, 2010' to 'Volkamer et al., 2009'.

- p. 490, l. 25 : This text seems redundant as the formation of organosulfates etc is mentioned before.

We prefer to keep the text in order to distinguish the three major SOA formation pathways in the aqueous-phase (organic acids, oligomers and organosulfates).

- p. 491, l. 2: Hennigan et al., 2008b reports on the WSOC/NO<sub>3</sub> ratios, not on aqueous phase processes.

The reviewer is right. We have removed the reference.

- p. 491, l. 7-10. This sentence seems a bit out of place here.

We moved this sentence two paragraphs later, where the importance of OXL and the other low molecular weight dicarboxylic acids is mentioned.

- p. 493, Section 2: - Some brief information on the organic aerosol module might be

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useful. What precursors are included? How do model predictions compare to observations?

With the exception of the SOA formation from multiphase chemistry that is presented here, all other OA parameterizations have been published in detail previously. The most detailed references are Tsigaridis et al. (2006) and Myriokefalitakis et al. (2010). Myriokefalitakis et al (2010) provide all parameters used by the two product model used to calculate SOA. Briefly, TM4-ECPL accounts for soluble and insoluble forms of anthropogenic and marine primary OA that age chemically by reaction with O<sub>3</sub> as described in Tsigaridis and Kanakidou (2003). SOA is chemically formed by gas phase oxidation of terpenes and other reactive volatile organics (represented by a- and b-pinenes), isoprene and aromatics (represented by toluene and xylene) and dimethylsulfide. SOA is also allowed to age chemically by reaction with OH radical as in Tsigaridis and Kanakidou (2003). We added this information in the introduction of the model description.

The comparison of calculated OC with observations is included in the supplementary material Figures S3 and S4.

- Does ISORROPIA include water uptake by organics? If so, what assumptions are made on OA hygroscopicity? If not, how would affect the results (e.g. SOA formation in aerosol water)?

ISORROPIA in TM4-ECPL does not include water uptake by organics, and the organic phase is assumed to not contribute to aerosol water. We acknowledge that this underestimates water uptake, but not significantly (except in regions where organics completely dominate the aerosol mass). This is because water uptake of SOA on a per-mass basis is much lower than that of sea-salt and ammonium sulfate .

The water uptake associated with organics can be expressed in terms of changes of the hygroscopicity parameter  $k$ . Assuming that the  $k$  of SOA is  $\sim 0.1$ , that the  $k$  of the inorganics range between that of ammonium sulfate (0.6) and sea-salt (1.25), and

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that the density of SOA, sulfate and sea-salt are 1.4, 1.76, 2.1 respectively, one can compute the k of the composite aerosol as:

$$k = k_{org} \cdot E_{org} + k_{inorg} \cdot E_{inorg}$$

where  $k_{org} = 0.1$ ,  $k_{inorg} = 0.6-1.25$  and E's are the volume fraction of the constituents ( $E_{org} = \rho_{org} \cdot m_{org} / (\rho_{org} \cdot m_{org} + \rho_{inorg} \cdot m_{inorg})$ ), with  $\rho$ ,  $m$  being the density and mass of the species, respectively.

Neglecting the contribution of organics to k leads to an underestimation of the aerosol kappa by 20-30% for an aerosol with organic mass fraction of 80%, however drops to 10% or lower for mass fraction of 60% or lower. This means that only in the heart of the Amazon boundary layer we should expect to see some significant underestimation of aerosol water, hence an important underestimation of OXL formation. Outside the boundary layer the contribution of SOA to total aerosol mass is small, hence its associated water uptake is at most a few percent. To put these numbers into context, the ZSR correlation used to predict water uptake in ISORROPIA-II has an estimated error of  $\sim 10\%$ . Hence the organic water uptake is within the uncertainty of ZSR for most of the atmosphere, even when completely neglecting the contribution of organic aerosols.

It is now explicitly mentioned in the text that ISORROPIA in TM4-ECPL does not include water uptake by organics, and the organic phase is assumed to not contribute to aerosol water. Based on the OA levels and contributions to the total aerosol mass calculated by TM4-ECPL, this approximation is expected to produce some underestimation in aerosol water and hence underestimation in OXL formation, only in the heart of the Amazon boundary layer. Outside the boundary, the contribution of water soluble organic to total aerosol mass is small, hence its associated water uptake at most a few percent. Such organic water uptake is within the uncertainty of ZSR for most of the atmosphere. ZSR is correlation used to predict water uptake in ISORROPIA-II has an estimated error of  $\sim 10\%$ .

- p.494, l.9: How is GLX (glyoxylic acid) partitioning treated outside of clouds? Is

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vapor-pressure related partitioning assumed?

We assume that GLX remains in the particulate phase after cloud evaporation in this study.

- p. 494, l. 18: Strictly, SO<sub>2</sub>, CO<sub>2</sub> are not acids.

We rephrased the sentence 'For pH > 4.3 the dissolution and subsequent dissociation of CO<sub>2</sub>, SO<sub>2</sub>, and NH<sub>3</sub> are also taken into account (Jeuken et al., 2001).'

- p. 494, l. 20: Are organic salts captured by ISORROPIA (e.g., ammonium oxalate)?

Organic salts are not taken into account by ISORROPIA. This omission of organic acids is expected to result in slightly lower water acidity than when considering organic acids. This is now clearly mentioned in the text. Consideration of organics in ISORROPIA is planned for future studies.

- p. 495, l. 25: Rework as the ionic strength and composition of cloud water can certainly be better constrained than the effect of these parameters on the solubility of organics.

We rephrased as follows: 'Nevertheless, the effect of the ionic composition and strength of cloud droplets on Henry law constants is largely uncertain, therefore an additional simulation (S1.1) was carried out, which neglects any water ionic composition impact on effective Henry law constants.'

- p. 495, l. 28: I do not understand this sentence. What is meant by 'interstitial cloud'?

Has been corrected to 'interstitial aerosol'

- p. 496, l. 21: why do you assume here a fraction of 1% oxalate? In the introduction, references were cited that suggested 0.1%.

Yamasoe et al. (2000) showed that OXL accounts for about 0.1% of the total aerosol mass emitted during the burning processes, while Schmidl et al. (2008) found that

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the average concentration of OXL in smoke from the burning of wood ranges between 0.1-0.3% of the total emitted mass and about 400 times lower compared to OC emitted mass. For simulation S2 we assumed as an upper limit a fraction of 1% of POC to be emitted as OXL. However, even these elevated OXL emissions are too low to affect significantly OXL concentrations. In the revised S2 simulation we considered a fraction of 0.2% according to an average value of OXL/OC fraction from biomass burning processes (almost 400 times lower than that of OC concentrations; Schmidl et al., 2008). However, this change does not alter any of our conclusions.

- p. 497, l. 2: the rate constant depends both on ammonium activity and pH which not necessarily implies ionic strength (ionic strength could be also introduced by ions other than ammonium)

We replaced the phrase 'ionic strength' with 'pH'

- p. 497, l. 14: In the study by Ervens and Volkamer, it was discussed that SOA formation is either initiated by photochemical processes or it occurs in the dark (on much longer time scales) which can be described by a reversible uptake and higher Henry's Law constants. Mixing both approaches, i.e. applying reaction 14 (Table S1) AND higher KH does not seem reasonable to describe a photochemical scenario.

In simulation S3 we take into account GLY formation in aerosol water using a rate of 4s-1 that describes photochemical processes according to Ervens and Volkamer (2010). For this simulation we did not use higher KH constants, as incorrectly referred in the text. We have corrected this part.

- p. 498, l. 21f: It is interesting that you predict almost the same amounts of oxalate from glyoxal and methylglyoxal even though the latter only forms oxalate by a process of more steps (i.e. methylglyoxal  $\rightarrow$  pyruvic acid  $\rightarrow$  acetic acid  $\rightarrow$  oxalate vs glyoxal  $\rightarrow$  glyoxylic  $\rightarrow$  oxalate). Can you comment on that? Are the methylglyoxal concentrations higher?

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According to TM4-ECPL calculations, Methylglyoxal (MGLY) burden is about 0.1 Tg, about 5 times higher than that of GLY (0.02 Tg; see Myriokefalitakis et al., 2008). MGLY in the gas-phase is calculated to be produced mainly by isoprene (~80%) and terpenes oxidation (~15%) and only 5% by anthropogenic NMVOC, mainly acetone and aromatics. Our results are in general agreement with the Fu et al. (2008) study who calculated the global burden of GLY and MGLY using the GEOS-Chem model to be 0.015 and 0.025 Tg, respectively. In the revised TM4-ECPL simulation (S1), OXL is calculated to be produced by about 56% from GLY, (~18 Tg yr-1), 20% from GLYAL (~6 Tg yr-1) and about 24% (~8 Tg yr-1) from MGLY. MGLY is therefore calculated to be an important OXL precursor in the aqueous-phase. Although there is no direct OXL formation from MGLY, the higher gas-phase concentration of MGLY compared to GLY makes MGLY the second most important precursor of OXL.

- p. 499, l. 16: Where does the value of 4.7e7 come from? In the table the highest value is 1.9e8.

We thank the reviewer for pointing us this typographic error in the text. The value in the Table is the correct one and is now also used in the text.

- p. 500, l. 2: Clarify. The Figure caption says 'annual mean', not monthly mean.  
'monthly mean' has been changed to 'annual mean'

- p. 500, l. 12: Is the statement on higher aqueous phase OH concentrations in summertime a model result? Higher biogenic concentrations in summer might suppress OH concentrations.

Indeed, higher biogenic concentrations during summer compete with OH photochemical production, with the net result depending on the location's characteristics.

TM4-ECPL model output provides the total OH radical concentration (e.g. OH(tot)=OH(g) + OH(aq); see Supplementary material Eq. 4) instead of the concentrations in the gas and aqueous phases. Figure S5 depicts the ratio of OH total con-

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centrations in June to those in January for surface and the zonal mean, as calculated by the TM4-ECPL model.

Hermann et al. (2005) calculated that the most important sources of OH radicals in the droplets are (i) the Fenton reaction between  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  accounting for about 33%, (ii) the photolytic decomposition of  $\text{H}_2\text{O}_2$  with a contribution of about 25% and (iii) uptake of OH radicals into the droplets which accounts for about 21% of the total source of OH in the droplets. In TM4-ECPL we account for the last two mechanisms of OH sources in the aqueous phase that are both driven by photochemistry and account for about 63% and 37% of the OH sources in the aqueous-phase, respectively, on an annual basis. It is therefore expected that the aqueous-phase OH radical concentrations are strongly supported by the gas-phase OH concentrations and their transfer to the aqueous-phase.

According to our calculations, the OH radical formation in the aqueous phase in January is by about 2.5% higher than in June on the global scale. This is due to i) a 7.8% higher OH water uptake in January compared to June, which may be attributed to the impact of biogenic emissions on the gas-phase OH radical concentrations during summer, and ii) a 7.3% lower formation of OH radicals in the aqueous-phase by the photolysis of  $\text{H}_2\text{O}_2$  in January than in June. However, in the Northern Hemisphere, OH aqueous-phase formation is calculated to be more than 2 times higher in June compared to January. The uptake of gas-phase OH radicals in the aqueous phase in June is also enhanced by about 2 times and the production of OH radicals by the  $\text{H}_2\text{O}_2$  photolysis in the aqueous-phase is calculated to be almost 2.5 times higher than in January.

In order to avoid a possible misinterpretation, we rephrased the text as follows: 'According to TM4-ECPL calculations, the summertime OXL peak in the Northern Hemisphere (NH) can be attributed to about two times higher aqueous-phase OH radical production than during winter. Summertime aqueous-phase OH radical concentrations in the NH are supported both by higher gas-phase OH radical uptake in the aqueous-phase ( $\sim 2$

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times) and by enhanced aqueous-phase OH production due to more intense in-cloud H<sub>2</sub>O<sub>2</sub> photolysis (~2.5 times). Note, however, that on the global scale the seasonality is reversed, since the aqueous-phase OH radical production in June is about 2.5% lower than in January, which may be attributed to the higher biogenic VOC emissions occurring during the warm season, that suppress OH radical concentration in the gas-phase.'

- p. 500, l. 16: Can you give a number on the contribution of aqueous phase H<sub>2</sub>O<sub>2</sub> photolysis to the total OH(aq) concentration? In general, this contribution is thought to be less than direct uptake (cf Herrmann et al., *Atmos. Environ.* 2005).

As above mentioned, Herrmann et al. (2005) calculated that the most important sources of OH radicals in the droplets are (i) the Fenton reaction between Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> accounting for about 33%, (ii) the photolytic decomposition of H<sub>2</sub>O<sub>2</sub> with a contribution of about 25% and (iii) uptake of OH radicals into the droplets which accounts for about 21% out of the total source of OH in the droplets. According to TM4-ECPL calculations that neglect the Fe<sup>2+</sup> reaction about 63% of the aqueous-phase OH radicals originate from direct uptake from the gas-phase and about 37% from H<sub>2</sub>O<sub>2</sub> aqueous-phase photolysis. Photolysis of NO<sub>3</sub><sup>-</sup> and the reaction of O<sub>3</sub>(aq) with O<sub>2</sub><sup>-</sup> do not significantly contribute to OH radical formation in the aqueous phase (~0.11%).

- p. 501, l. 1-5: The other SOA contributions should be discussed here. What are the main precursors? What assumptions are made in the partitioning e.g. which fraction of (organic?) aerosol mass is assumed to absorb newly formed SOA?

We now provide an outline of the various OA components and their precursors in the model description (details have been already published in cited references of our group; see also reply to reviewer's comment p493). We also include Figure S6 with the major groups of the OA components in the supplementary material.

- Table 1: - do you mean 'GLY concentrations above the ocean'? 'Oceanic' implies glyoxal concentration in ocean water.

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We replaced 'Oceanic' by 'above the ocean'

- Table 2: Can you comment on the fact that in some lines 'net chemical production' -'deposition' does not add up to zero?

This is a rounding up decimals issue that has been corrected.

- Figure 6: Add the information that the model results shown are from simulation S3. Why has this case been chosen for comparison?

-In Fig. 5 of the ACPD version of the paper we have chosen to compare model results from simulation S3 with observations, because that simulation had a better seasonality when compared to that of measurements. However, to avoid confusion, in the revised version we compare the base case simulation (S1) results with the available measurements. This change does not affect the outcome of the study.

Supplemental information:

- Table S1: - R19 and 20: The products should be 0.85 GLX- + 0.15 HCHO (not HCOO-)

We have corrected this typo in the reactions Table – This does not affect the simulations, since it was correct in the model.

- R25: Why' + 2 OH'?

The reactions are taken from Lim et al. (2005) sup. material. For the undissociated OXL the oxidation requires 2OH radicals, where for the monoanion and bionion OXL only one OH radical. For the present study we assume that the produced CO2- reacts fast with O2 to produce CO2 and O2-. The two steps of this reaction have been therefore neglected and an overall reaction has been taken into account.

- Footnote h: What is the maximum value of  $j(H_2O_2)$  that has been assumed? I.e. under what conditions is  $k \approx 4 \text{ s}^{-1}$ ?

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The photolysis rate of  $\text{H}_2\text{O}_2$  in the gas phase varies hourly and is calculated on line by the model as described by Landgraf and Crutzen (1998) and Lelieveld et al. (2002), based on the IUPAC recommendations (Atkinson et al., 2006), as summarized in Myriokefalitakis et al (2008). The photochemically driven reaction rate ( $k$ ) applied to simulate the glyoxal degradation in the aerosol water was scaled to follow the  $\text{JH}_2\text{O}_2$  diurnal variability calculated by the model and average globally and annually at 4s<sup>-1</sup>.

- Table S2: It should be  $\text{HO}_2 \leftrightarrow \text{O}_2^- + \text{H}^+$ , not  $\text{OH}^- + \text{H}^+$

We corrected the equilibrium reaction products.

-p. 5, l. 81-86: How sensitive are the results towards the assumed droplet diameter for the calculated uptake rate? If there is a huge sensitivity, wouldn't it be more appropriate to assume different droplet diameters above land and ocean?

The droplet diameters differ with location. Herrmann (2003) reports that the droplet radius varies between  $\sim 3.6$  and  $>16.5$   $\mu\text{m}$  for remote clouds, 1 and 15  $\mu\text{m}$  for continental and  $\sim 1$ -25  $\mu\text{m}$  for polluted clouds. For this study we used an average cloud droplet radius of 5  $\mu\text{m}$ , which is more representative over continents where the emissions of OXL precursors occur, rather than over oceans, where a cloud droplet radius of 10  $\mu\text{m}$  would be more representative. Gas transfer to small droplets is faster than to large droplets due to the larger surface-to-volume ratio of smaller droplets. Lelieveld and Crutzen (1991) also suggested small sensitivity of the results to the changes in droplet sizes, since gas-transfer processes are generally much faster than the chemical processes involved. However, for the revised simulations, we followed the recommendations of the reviewer using a cloud droplet radius of 5  $\mu\text{m}$  over land and cloud droplet radius of 10  $\mu\text{m}$  over oceans. This is now mentioned in the model description section. The comparison of this simulations with the one using a unified cloud droplet radius of 5  $\mu\text{m}$  shows that the use of different droplets radius over ocean and land does not significantly change the formation of OXL ( $\sim 2\%$  enhanced OXL formation when using a fixed cloud droplet radius of 5  $\mu\text{m}$ ). A comment is also added in the revised version

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All language and typographic corrections have been performed.

References additional to those in the ACPD manuscript:

Bahadur, R., Habib, G., Russell, L. M.: Climatology of PM2.5 organic carbon concentrations from a review of ground-based atmospheric measurements by evolved gas analysis, *Atmos. Environ.*, 43, 9, 1591-1602, doi:10.1016/j.atmosenv.2008.12.018, 2009.

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