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Atmospheric Chemistry and Physics Discussions

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 have addressed all of them as follows:

1. Clarifications on measurements are now provided:

The most common technique used to quantify oxalate in the atmosphere is aerosol sampling on filters (Teflon or quartz) with subsequent extraction and analysis by Ion-Chromatography (IC) or Gas-Chromatography (GC) coupled with Mass Spectrometer (MS). GC/MS analysis requires esterification of the carboxylic groups, procedure that shows different acid recovery depending on the ester type. Kawamura et al. (2010) compared oxalate levels in Arctic aerosols measured by IC and GC/MS employing dibutyl esters and found comparable results. A supporting table (Table S4) will be provided in the revised supplementary material indicating the location, type (surface/ship/aircraft), observation period, oxalate mean concentration over the period, filter type, analytical technique used and reference. A few additional data and references have been included, although more may exist. This table (S4) will be referenced in the caption of Fig. 6. The data have been extracted from the referenced publications with the exception of those from the CARBOSOL stations and from Finokalia, Amsterdam island and Alert stations that have been communicated to us by the experimental groups.

2. Comparison between the model results and measurements.

The oxalate observations reported in literature that are used in the present study for the model evaluation show large variability both in the sampling duration (from a few minutes to several days) and in the timing of the sampling (daytime or nighttime). He and Kawamura (2010) have shown that nighttime observations of oxalic acid over polluted areas are about 1.3 times higher than the daytime ones. However, the investigation of the diurnal variability of oxalate is out of the scope of this work and will be addressed in a future study. Furthermore, most of the data used for Fig. 6 concern relative long samplings, over several days, and have therefore trapped both daytime and nighttime levels of oxalate. Note also that the aim of the comparison in Fig. 6 is not to make a point-by-point evaluation of our 3D global model results, but to provide a quick outlook of the model ability to capture the order of magnitude of observed oxalate levels in the atmosphere. This is achieved by comparing monthly averaged model output for simulation S3 with the mean concentrations reported for the specific month at each location, as stated in page 506, lines 11-12.

3. Meteorological conditions using by the model and measurements.

Since TM4-ECPL is an off-line model, it does not compute meteorology but is using as input ECMWF meteorology that assimilates observations (including Liquid Water

Content (LWC), clouds and precipitation distributions) and varies every 3 hours. Therefore the model uses "typical" LWC values for the studied locations. An outlook of the adopted cloud LWC is provided in Fig. 1a,b. In addition there is no relevant information reported in most of the used literature to allow such point-by-point comparison.

3. Page 506, line 11: Remove "all measurements" as not all measurements are shown here that are reported in the literature.

Some additional references have been added. 'All' will be removed.

4. Figure 5-6: Can the authors compare (between model and obs) any parameters other than oxalate, such as oxalate:sulfate ratio in Fig. 3E? This would be a meaningful comparison to present.

We have tentatively examined the oxalate to sulfate correlation as derived i) from observations found in literature and ii) from our model results. Although OXL and SO4= correlate both in the observations (r=0.7) and in the TM4-ECPL model results (r=0.6), this comparison (Figure S2 will be added in the supplementary material) indicates 3 times higher slope (mean OXL/SO4= ratio) and also higher intercept in the observations than reproduced by our model. The good correlation points to the importance of multiphase chemistry for both aerosol components but might also indicate an underestimation of the sources or/and an overestimation of sinks of OXL by TM4-ECPL. Relevant discussion will be added in the revised manuscript in section 4, at the end of the 3rd paragraph.

5. Is there any relationship between the points with greatest disagreement and specific regions or season?

As stated in page 506 lines 20-25, correlations have been investigated per group of stations (urban, rural, marine) and additional ANOVA (analysis of variance) has been performed. We have re-calculated the correlations, accounting for the additional data in Figure 5, and the model was found to better simulate the marine (slope=0.63±0.06,

r2=0.68, N=49, a=0.05, F =102, p-value=2.3E−13), and rural (marine and rural together: slope=0.64±0.07, r2=0.45, N=112; a=0.05, F =91, p-value=4.4E−16) observations than the urban ones (no correlation). Overall, as can be seen by the slopes of the correlations, the model tends to underestimate OXL observations. This indicates that the model either misses OXL sources (primary and secondary) or possibly overestimates OXL sinks. We have now performed additional ANOVA analysis of variance for the monthly data shown if Fig 5 (seasonality) for all simulations performed and each monitoring station. These statistics will be provided in a new Table S5 in the supplementary materials. They show that the model reproduces reasonably (0.48< r <0.85) the seasonality at most studied location except in Azores and K-Pustza stations, most probably due to important contribution from unaccounted regional sources like formation from the degradation of higher fatty acids or in the polluted atmosphere.

6. Page 501, line 5-6: Contribution of OXL to SOA mass and other SOA components.

TM4-ECPL calculates on-line the chemical production of 12 SOA components that can grouped in anthropogenic SOA (SOAa), biogenic SOA (SOAb), methanesufonic acid (MSA), Marine Amines Salts and Oxalate (OXL). The contribution of each of them to the SOA mass depends on time and space. SOAb is calculated to be the most important SOA component in the model near the surface, reaching about 80% in the highly forested areas (e.g Amazon basin) and about 50% in the northern hemisphere. OXL, that has a high OM:OC ratio, is also calculated to be an important contributor to SOA mass. Although in TM4-ECPL, OXL is mainly driven by isoprene (about 79%), high fractions of OXL to SOA total mass are calculated over oceans, possibly due to long range transport of oxidation products of terrestrial biogenic VOC and subsequent cloud processing, as well as to the multiphase processing of the marine VOC emissions. In the free troposphere (∼500 hPa), OXL and SOAb are calculated to contribute most and almost equally to the SOA mass. This happens because of 1) the increasing partitioning of SOAb gaseous precursors to form SOAb due to the lower temperature in the free troposphere and 2) the increasing LWC in the middle troposphere (Fig. 1b) that favors OXL production. As far as it concerns the other SOA components, SOAa contributes the most in the northern hemisphere where the emissions of the SOAa precursors are the highest. The abundance of SOAa to SOA total mass from surface to the free troposphere varies between ∼20% and ∼40%. On the other hand, the major marine SOA components (MSA and Marine Amines) are localized over the oceanic regions with contribution to the total SOA mass of up to ∼50%. Note, however, that high contribution is not necessarily tied to high absolute levels, since over ocean SOA levels are significantly lower than over land. Appropriate discussion will be included in the revised version and Figure S1 will be included in the supplementary material.

7. Being quantitative in these (Pg 501, line 9; Pg 503, line 15), and other areas would be more meaningful to the reader.

We rephrase these sentences to make them more quantitative: “The OXL to nss-SO42- mass ratios shown in this figure indicate that nss-SO42- is about 9 times higher than OXL in terms of mass in the NH continental polluted regions but not in the tropics, where OXL reaches half the mass of nss-SO42- over terrestrial biogenic sources (e.g., Amazon Basin and Central Africa).” Furthermore, in order to investigate the ability of the model to reproduce the seasonality in OXL levels, we have also performed ANOVA analysis for the monthly varying data shown in Fig. 5 (see also points above). Thus discussion will be included in the text.

8. Technical Corrections:

All English and typographic corrections have been performed.

Reference.

He, N. and Kawamura, K.: Distributions and diurnal changes of low molecular weight organic acids and α-dicarbonyls in suburban aerosols collected at Mangshan, North China, Geochem. J., 44, e17-e22, 2010.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C1068/2011/acpd-11-C1068-2011-supplement.pdf

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