Reply to Referee 3:

Notes: Referee comments are printed in italic, author replies in plain text. All page and line references refer to the original manuscript (not the revised version).

General comments

This paper reports a data set of size-resolved dicarboxylic acids (DCAs) obtained at several continental sites in Germany. Based on these datasets together with backtrajectory analysis and principal component analysis, the authors suggest that low molecular DCAs formed via gas-phase reactions can be important as well as those formed via aqueous-phase reactions. They also suggested that the formation of DCAs is significant in anthropogenically-influenced air masses under high photochemical conditions. The present work may provide valuable data sets in our understanding on formation processes of DCAs, which is an important component of water-soluble organic aerosols. The manuscript likely fits with the scientific scope of ACP. However, I have many concerns on the manuscript. Overall, the manuscript lacks quantitative discussion (see comments below), which makes discussion rather weak throughout the manuscript. Although a large data set presented is valuable, there are a number of important issues that need to be worked out. I recommend its publication in ACP after some major revisions.

Author reply:

We thank the reviewer for taking the time to read and critically comment our manuscript. All raised issues are addressed in the following.

Specific comments

(1) The authors suggest that formation of DCAs in the gas phase occurs on "short" timescales, whereas the formation in the aqueous phase occurs on "longer" timescales. However, the terms "short" or "longer" are rather qualitative. The authors should discuss the timescales for each process.

Author reply:

We agree with the reviewer that terms like "short" and "long" are too qualitative and added a few sentences to indicate what we think might be the timescales of formation in PC 1 and 2. It has to be noted, though, that a really quantitative discussion of this issue does not seem to be feasible to us from the data presented in this study.

Addition to PC 1 (P32105 L21):

"Based on these indications, the timescale of gas-phase DCA formation might be estimated to lie in the range of minutes to hours, depending on the photochemical conditions. A real quantitative discussion of formation kinetics is, however, not feasible from the data of the present study."

Modification in PC 2 (P32106 L18):

"… it can be assumed that DCA production takes place on a slower timescale (hours to days) as compared to PC 1."

(2) The analysis presented in this manuscript much relies on trajectories. According to

"mean trajectory length" in Fig.2, the horizontal scale which the authors discuss seems to be a few thousand km. How about the influence of local (or urban-scale) emissions on source apportionment especially at urban sites? What is horizontal resolution of meteorological data used in the trajectory calculation? Is the resolution high enough to resolve the effect of local-scale emissions of DCA precursors?

Author reply:
The horizontal resolution of meteorological input data for back trajectory calculation is 1 degree and thus not high enough to resolve local emissions. We added information on the meteorological grid resolution to the experimental section (P32099 L17) and inserted the following sentence into the PC1 section (P32105 L21, see also response to reviewer 2): "In fact, local emissions cannot be resolved by the coarse resolution of trajectory calculation."

(3) Based on size-resolved DCA concentrations and its correlations with concentrations of sulfate and other tracers, the authors defined PC2 as anthropogenically-influenced DCAs possibly formed via aqueous-phase reactions. What are the RH values along the trajectories and at the sampling site to support aqueous-phase reactions? The authors mentioned RH for PC1 which is suggested to represent gas-phase formation of DCAs, but not for PC2. The discussion should be more systematic.

Author reply:
The mean RH along the trajectories was between approx. 60 and 80 % for nearly all samples, while the mean RH at the sampling site usually lied in between 50 and 90 %. We had done PCA runs with these two parameters included, but then decided to not include them into the final version, as the number of parameters in Table 2 (PCA) is already quite high and RH did not give any additional information. As stated in the discussion of PC 1 (P32104 L25-26) RH is anticorrelated to the solar flux. Therefore, in the previous PCA runs with RH included, both RH along the trajectory and RH at the receptor site showed negative loadings on PC 1 (-0.81 and -0.66, respectively) and insignificant loadings on PC 2 (corresponding to the insignificant loadings of the solar flux parameters in PC 2). RH alone does thus not help to support aqueous phase reactions in PC 2 and the importance of aqueous phase chemistry can only be indirectly deduced from the correlation with sulphate and the size distribution characteristics (as done on P32106 L26 – P32107 L8). We therefore state in the manuscript (P32107 L9-10) that more direct evidence of aqueous phase formation would be desirable, which is, however, not available from the data of the present study. It also has to be noted, that RH alone might not be sufficient to judge on the importance of aqueous reactions, as it is rather the available liquid water than the RH, which determines aqueous chemistry. Liquid water content for aerosol particles is a function of both RH and hygroscopic material, while for clouds it depends on the supersaturation and CCN concentrations.
In order to make our points somewhat clearer, we made the following modifications in the revised manuscript:
P32104 L25-26: removed insert in brackets and instead added the following to P32106 L1: "Regarding RH, it has to be noted that it is strongly anti-correlated to the solar flux parameters in our

dataset and its inclusion to the PCA leads to strong negative loadings for both RH along the trajectory as well as RH at the receptor site (data not shown). Regarding particle sizes,…"

P32107 L8: added the following:

"Both lines of thought (correlation with aqueous phase formed sulfate and aqueous phase production leading to a "droplet mode") are supported to some extent by PC 2 as well (high loadings of DCAs and sulfate as well as highest loadings in "droplet mode" size range). RH during sampling did not help to further elucidate the role of aqueous chemistry in our data set, as PCA runs with RH included resulted in insignificant loadings to PC2."

(4) The authors have combined all the data for the PCA calculation. However, relative importance of sources and formation pathways may be different in different seasons, at different sites. Is the authors' major conclusion (importance of gas-phase formation of DCAs) representative for any seasons at any sites in central Europe?

Author reply:

We fully agree that the relative importance of formation pathways will be different in different seasons. Gas-phase formation (PC 1) will be most important in summer, as the high radiation needed to drive the photochemistry is obviously not available in winter. PC 1 is inherently linked to high radiation, which we clearly state in the PC 1 section (P32104 L23-24), in the discussion of the main sources (P32109 L24), and in the Conclusions (P32113 L19). To avoid any misunderstanding, we now also include it in the abstract (P32094 L11):

"…photochemical formation during intense radiation days in polluted air masses, likely occurring in the gas phase on short timescales…".

With regards to the different sites, it is quite probable that at any central European site where the "prerequisites" for PC 1 are met (intense radiation and some anthropogenic influence, cf. RTIs) gas-phase formation might be important. As the true nature of gas-phase precursors and their possibly complex interactions cannot be resolved with data from this study, this will need to be addressed in future studies, though. Our dataset is not large enough to obtain statistically robust results for all of the different sampling sites individually, which is why we pooled the data in the first place.

To make these points clearer, we added the following paragraph to the Conclusions (P32113 L14):

"The relative importance of these sources will be different in different seasons with photochemical gas-phase formation being most important in summer. How it differs between different sites likely depends on the nature of precursors and their possibly complex interactions and will need to be addressed in future studies."

(5) If the gas-phase formation in 0.05-0.14 µm is really important for the abundance of DCAs (Table 2), then, why the size distributions show that DCAs showed the peak in accumulation mode (0.14-1.2 µm) (Fig. 1)? Doesn't this mean that the aqueous-phase formation of DCAs is the most important to control the abundance of DCAs?

Author reply:

Overall, and especially so when looking at average distributions like in Figure 1, aqueous-phase formation of DCAs is indeed likely to be the most important process controlling DCA abundance in particles. This is exactly what we stated both in the abstract (P32094 L14-16) and in the Discussion of main sources section (P32112 L1-4).

Under certain conditions, however, our results suggest gas-phase formation to have an important influence as well. On P32110 L5-14 we discussed this importance and derived an upper estimate of about one third to one half of total PM10 DCA concentrations which can possibly related to gas-phase formation under appropriate conditions. The importance of gas-phase formation is different within different particle size ranges, which is one of the indications to distinguish between the two formation processes.

(6) If the photochemistry and anthropogenic sources are important factors to determine the amount of gas-phase DCAs, the authors should show concentrations of gas species (O3, NOx, CO, SO2) in the text and Table 1.

Author reply:

We understand the wish of the reviewer to see the trace gas concentration data, but would rather not like to include it into Table 1, which is quite packed already. We therefore prepared a plot similar to Figure 2, which we will upload as Supporting information together with the revised version of the manuscript (a reference to it will be added to the experimental section on P32099 L8). Discussing the concentration data in the text is not really necessary, in our opinion. To us, the interesting feature is not so much the absolute concentration level but rather how the trace gas concentrations correlate with the different PCA components. This can already be seen from their loadings in Table 2.

In addition, I suggest the authors to use some indicators of photochemical aging (e.g., the observed ratios of oxalate/DCAs, sulfate/(sulfate+SO2), etc.) and discuss these indicators in comparison with the trajectory analysis to show their consistency.

Author reply:

We thank the reviewer for this suggestion. Following his/her suggestion we calculated (on a molar basis) the suggested ratios of PM10 oxalate/total DCAs and PM10 sulfate/(sulfate+SO2) and included these ratios into a PCA run. This resulted in insignificant loadings of both ratios to PC 1 (0.09 and -0.11), while for PC 2 a positive loading (0.43) was obtained for the sulfate ratio and a negative loading (-0.62) for the DCA ratio. If these ratios are taken as indicators of a "photochemical age" of the sampled air masses, then gas phase formation (PC 1) seems to be independent of it, while the results for aqueous phase formation (PC 2) are contradicting. We are sceptical, whether such simple ratios are really suitable to describe the complex processes leading to the observed concentration patterns. For the oxalate/DCAs ratio, for example, it very likely depends on a large variety of different source processes for the individual acids and can thus not easily interpreted in the context of this study. For the sulfate/(sulfate+SO2) ratio, it is not clear at all, whether the emission strength of SO2 is in any way correlated to the emission strengths of DCA precursors. Emission of SO2 into an aged air mass (containing high sulfate and DCA concentrations) would imply a decreased photochemical age, even though DCA concentrations might still be very high. Due to such difficulties in the interpretation of these ratios, we would rather refrain from using them in the present study.

(7) P. 32098, L. 22-28: The authors should address the reproducibility of this analytical method for individual DCAs. The authors should also show more QA/QC data to provide more information on their method for DCAs analysis.

Data on reproducibility has been added to P32098 L23. For more information on the used analytical method we would like to refer to the cited Neusüß et al. paper, where the method has been introduced and described in full detail.

P. 32099, L. 7-10: Please add more information on the gas measurement, such as instruments/methods used, measurement uncertainty, etc.

Author reply:

The following information has been added (P32099 L7-8):

"Mixing ratios of the trace gases ozone (O_3), nitrogen monoxide (NO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and carbon monoxide (CO) were measured at all sites except Falkenberg using commercial standard trace gas monitors from different manufacturers. Principles of detection were UV absorption (O_3), UV fluorescence (SO_2), and chemiluminescence (NO_x). The gas monitors were calibrated on a regular basis."