Reply to Referee 1:

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).

This study reports on size-resolved aerosol composition data collected in Germany with a focus on dicarboxylic acids, which represent an important class of organic species. Analysis of the data includes PCA to help with source apportionment. Back-trajectory data are also used. The topic of this work is of interest to this journal. While the methods are not novel, the results are of importance to help with process-level understanding of the formation mechanisms of organic acids. The key conclusions reached about organic acids include the following: (i) a key source is photochemical formation in polluted air masses likely occurring in the gas phase on short time scales; and (ii) a key source includes secondary reactions likely occurring in the aqueous phase on longer time scales. The results support the conclusions. The methods used are described well and proper credit is given to related work. The title is appropriate. The paper is written well and the tables and figures are good. I recommend publication of the work.

Author reply:
We thank the reviewer for his/her positive judgment of our work.

Reply to referee 2

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).

This paper presents results from size-resolved measurements of dicarboxylic acids from filter samples collected at several inland sites in Germany. This data is combined with results from a newly developed statistical back-trajectory analysis technique. Principal component analysis (PCA) is then used to the combined data set to determine the important factors that drive the dicarboxylic acid concentrations.
Dicarboxylic acids are the most abundant group of organic compounds that contribute to the total organic aerosol. Secondary organic aerosol formation, a process that is still not well understood, is likely an important source of these acids. This suggests that it is important to measure these acids and include them in atmospheric chemistry models. This paper is providing data that many in the atmospheric community would be interested in.

Author reply:
We thank the reviewer for his/her kind remarks on our manuscript. All issues raised by this reviewer are being addressed in the following.

Overall, this is a good paper. It is generally well written and easy to follow. My only question is on the interpretation of the correlation of a PCA factor with the mean trajectory length. If this correlation is negative then wouldn't that mean that the emissions were local and/or fresh? It seems to me that the negative relationship observed for both PC1 and PC2 vs. mean trajectory length is being interpreted differently for the two different factors. This, along with a handful of other comments, are outlined in more detail below and need to be addressed before the paper can be considered for publication.

Author reply:
A negative loading of the mean trajectory length to a given PCA factor does not necessarily mean that the emissions were local and/or fresh. As can be seen from Figure 2, the mean trajectory lengths in this study were all well above 1000 km, thus even air masses with the shortest back trajectories carry emissions from a large area. In fact, local emissions cannot be resolved by the coarse resolution of trajectory calculation. The negative correlation of back trajectory length indicates rather short trajectories for PC1 and PC2, which – at the given sites of sampling – translates to higher residence times above continental areas as compared to marine areas (where long trajectories usually originate). Thus, it supports the positive loadings of some of the continental land cover classes in PC1 and PC2.
To make this point clearer, we inserted the following paragraph into the PC1 section (P32105 L21): "The negative loading of mean trajectory length to PC1 indicates comparatively short back trajectories, thus rather high residence times above continental areas as compared to marine areas (where longer trajectories spend much of their travelling time for the given sampling sites of this study). It has to be noted, though, that all back trajectories of sampled air masses are well above 1000 km in mean trajectory length (Figure 2). The negative loading of this parameter does therefore not indicate a local influence of emissions. In fact, local emissions cannot be resolved by the coarse resolution of trajectory calculation."

General Comments:
1.It is not clear what citation order is being employed. When a group of references are mentioned by the authors it can vary from being listed in chronological order, alphabetical order, or no order at all. Either of the first two are fine to use, but the same format should be used throughout the entire text.
Author reply:
The referee made a valid point here. Referencing order in groups of references has been corrected to chronological throughout the manuscript.

Specific Comments: 1.Introduction Page 32095, Line 4 – Suggest adding of before Cigarette
Page 32096, Line 4 – Suggest removing the by before about 21%
Page 32097, Line 2 – Suggest changing the respective to their respective

All three corrections were done as suggested.

2.Materials and methods 2.1Sampling Page 32097, Line 14 – What does the abbreviation DWD stand for? It is not defined.

DWD: Deutscher Wetterdienst, German weather service. As it is not really relevant here, the abbreviation DWD has been removed.

Page 32097, Line 18 – Should institute be capitalized?

Yes. No changes made.

Page 32097, Line 25 – Suggest removing (aluminum)

Done.

Page 32098, Line 1 – The chemical formula used is not defined

“H_2O_2” has been replaced by “hydrogen peroxide solution”

Page 32098, Line 5 – Suggest adding an as before evaporation
C11251

Done.

Page 32098, Line 6 – I am not sure what the d after bounce is referring to.

The “d” has been removed.

Page 32098, Line 8 - Suggest adding an of after downstream

Done.

2.2Measurements Page 32099, Line 7 – The chemical formulas used are not defined

Definitions have been included.

2.3Back trajectory Page 32099, Line 11 – To stay consistent with the rest of the text suggest adding a comma between back and trajectory
A comma between “back” and “trajectory” would not make sense. We believe the referee actually wanted to suggest a comma after “In this study”, which has been inserted.

Page 32100, Line 6 – Suggest adding an as after regarded
2.4Principal component analysis Page 32101, Line 5 – Suggest changing was analyzed to were analyzed
Page 32101, Line 7 – Suggest changing do thus not to thus do not
3.Results and discussion 3.1PM10 concentrations and size distributions of DCAs Page 32101, Line 19 – Suggest adding by after differ

All done.

Page 32102, Line 13 – The abbreviation GC/MS is not defined. Also, suggest adding a the before GC/MS.

Definition of GC/MS included and “a” added.

3.3.1PC 1: anthropogenically influenced gasSOA Page 32105, Line 18 – To stay consistent with the rest of the text suggest adding a comma between back and trajectory

“back trajectory” as a term does nowhere in the manuscript have a comma in between. We’re afraid we don’t really see where a comma should be placed in this line. No changes made.

3.3.2PC 2: anthropogenically influenced aqSOA Page 32106, Line 1 – anthropogenically is misspelled

Corrected.

Page 32106, Lines 8-11 – The authors mention that PC2 is anticorrelated to the mean trajectory length and likely represents aged air masses with long residence times. I am not sure I completely follow this. If a component is negatively correlated with trajectory length couldn’t this mean that the air masses are local (i.e., they aren’t traveling far and therefore aren’t related to the air mass path taken)?

See answer above. The air masses are still travelling far. The anticorrelation of mean trajectory length with PC2 means PC2 likely represents aged air masses with long residence times *above continental areas* (P32106, L8-11) as compared to trajectories with larger lengths and thus longer times above the oceans.

Also, PC1 is anticorrelated with mean trajectory length and the authors suggest it be local and from quick formation.

The suggestion of PC1 being local and from quick formation is based on the similarity of the two solar flux parameters (as stated on P32105 L13-21), not on the negative loading of mean trajectory length. We hope it is clearer now with the modifications indicated in the above reply.

3.3.3PC 3: traffic Page 32107, Line 19 – Suggest changing presumable to presumably C11252
3.3.5PC 5: sea salt Page 32108, Line 8 – Suggest adding a the before total
3.3.6PC 6: soil Page 32109, Line 3 – Suggest changing does likely not to does not Likely

All done.

3.4Discussion of main DCA sources Page 32110, Lines 14-16 – I am not sure I completely follow this sentence. I think the authors are trying to indicate that condensed phase reactions could also occur, but would likely be lower than gas phase oxidation. If so, then I would suggest rephrasing this sentence.

This sentence refers to the estimation above that about upt to one third to one half of total DCA concentration can be attributed to gas phase sources under appropriate conditions (P32110 L12-13). As this estimation is based on the crude assumption of impactor stage 1 and stage 2 DCA concentrations being formed solely from gas phase oxidation processes (P32110 L10-12), a (very probable) contribution of condensed phase reactions to these stage 1 and stage 2 DCA concentrations would mean that the actual contribution of gas phase processes is likely lower. We slightly modified the sentence as follows:
"Given, however, that condensed phase reactions likely contribute to DCA concentrations in these particle sizes (impactor stages 1 and 2) as well, the contribution of gas phase sources to total DCA concentrations will likely be lower, though."

Page 32110, Line 18 – Suggest changing is incorporated to are incorporated

Done.

Page 32110, Line 22 – The chemical formula used is not defined
Page 32111, Line 6 – The chemical formula used is not defined

Definitions are now included.

Page 32111, Line 9 – Suggest adding an of before other

Done.

Page 32112, Line 10 – I am not sure I understand the use of the word manifold in this sentence. Are the authors trying to indicate that the precursors of dicarboxylic acids are numerous?

Indeed, yes. "Manifold" has been replaced by "numerous".

Page 32112, Line 12 – To stay consistent with the rest of the text suggest adding a comma between back and trajectory
No changes made as we don't see where a comma might be missing here. Between "back" and "trajectory" it would not make sense.

Page 32112, Line 15 – What does the abbreviation RTI stand for? It is not defined.

RTI: residence time index. It is defined on P32099 L27.

4.Conclusions Page 32113, Lines 7 and 12 – To stay consistent with the rest of the text suggest adding a comma between back and trajectory

Again, no changes made. See above.

References Page 32119, Line 20 – Believe Krivacsy should have accent marks
Page 32120, Line 4 – Believe Gelencser should have accent marks
Page 32120, Line 25 – Believe Meszaros, Gelencser, and Krivacsy should have accent marks

Here and anywhere else, correct accent marks have been added to Krivácsy, Gelencsér, and Mészáros.

Page 32122, Line 20 – Simoneit is misspelled

Corrected.

Page 32124, Line 22 – Believe Muller should have accent marks

Here and anywhere else, correct accent marks have been added to Müller. In addition, "Bruggemann" has been corrected to "Brüggemann".

Tables Table 1 -It is not defined what the abbreviation bdl stands for

bdl: below detection limit. It is defined in the first row of remarks below Table 1

-In reference column, believe Meszaros should have accent marks

Done.

Figures Figure 1 -I not sure if the units for the y-axis are correct. Should it be ng/m3/um?

No, as logDp is dimensionless. Actually, a more correct notation would be log(Dp/1µm). You cannot take the logarithm of a unit.
However, we realized that the axis label might be more accurately expressed as ΔM/ΔlogDp (ng m^{-3}) and modified it accordingly. Also, we changed the Figure caption to "Mean mass size distributions …"

Figure 2 -m2 in the y-axis units for the Solar Flux at receptor plot should be m-2
Done.

-Incaption, to stay consistent with the rest of the text suggest adding a comma between back and trajectory

No changes made. See above.

Figure 3 -In caption, I think screen should be scree

Yes, indeed. Corrected now.

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."