

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 2.1 Sampling 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

“H₂O₂” 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.

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

Definitions have been included.

2.3 Back 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

2.4 Principal 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 3.1 PM10 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.

3.3.1 PC 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.

3.3.2 PC 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 up 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 $\Delta M/\Delta \log D_p$ (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.