

***Interactive comment on “Distributions of low molecular weight dicarboxylic acids, ketoacids and  $\alpha$ -dicarbonyls in the marine aerosols collected over the Arctic Ocean during late summer” by K. Kawamura et al.***

**K. Kawamura et al.**

kawamura@lowtem.hokudai.ac.jp

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Reply to Anonymous Referee #1

We thank the anonymous reviewer for his/her detailed and constructive comments on our manuscript. Below are the point-by-point replies to the comments and suggestions.

This study presents data on dicarboxylic, and ketoacids and dicarbonyls concentrations in ambient aerosol collected above the Arctic Ocean. While many studies on  
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these compounds have been published before at different locations, data from such clean environments are not available yet. This particular location is only marginally impacted by anthropogenic emissions and long transport and processing times affect the ratios of dicarboxylic acids resulting in different results than found at other locations. In addition, isotope studies ( $^{14}\text{N}$ , and  $^{13}\text{C}$ ) have been performed and are used to infer assumptions on sources of the dicarboxylic acids. The authors conclude that the main sources of the target organics are terrestrial from transport from North America or from biological activity. This study represents a continuation of many previous ones of the same group. Thus, the methodology is robust and the results are put in context with their previous studies. The data set is new and thus the study warrants publication. However, I have several comments that should be considered in before acceptance.

Major comments 1) The conclusions are somewhat vague and should be more concisely expressed. What is the role of biological activity vs terrestrial sources? The direction of argumentation appears to change over the course of the paper and between the sections about diacid abundances and isotope ratios.

Authors' Reply: The sentence in the conclusion section was modified by adding a phrase “long-range transport of continental aerosols and their precursors”. Please see page 15, lines 363-366 in the revised MS.

2) While the authors cite about 30 of their own papers, they completely neglect any other studies from other groups that have measured the same compounds. While these other studies might not be that complete in species characterization, trends of typical species are discussed there in the context of additional locations. I suggest adding a more balanced discussion of known data. A few exemplary studies that should be taken into account include [Röhl and Lammel, 2001; Wang et al., 2002; Yao et al., 2002; Römpf et al., 2006; Sorooshian et al., 2006; van Pinxteren et al., 2009; Kitanovski et al., 2011] but I urge the authors to do a more comprehensive literature search in order to give a fairer and broader perspective of the role of diacids in atmospheric aerosols that gives credit to international colleagues who do similar research.

Reply: Following the comments, we referred most of the references in the revised MS.

3) The authors generalize the role of the target compounds to climate impact even though these compounds only contribute  $\sim$ 1% to the total aerosol mass. Examples for such statements are included in the introduction 'diacids ... can act as CCN' or the last two sentences of the conclusions that imply that diacid loading might later the radiative impact. Even if the amount of these organics doubles, the radiative impacts as well as the CCN activity of particles will not change to any measurable degree. CCN are mostly composed of inorganic compounds that nearly completely control the activity; a 1-2% addition of other material does not matter much. I think the merit in the current study should be expressed in a different form by presenting the organic acids/dicarbonyls as tracer compounds for photochemical processing, possibly in the aqueous phase. Recently there has been a huge body of literature (e.g. summarized by [Ervens et al., 2011]) that suggests that photochemical processing of organic in (aqueous) aerosols can affect organic mass and properties. Thus, I suggesting at least mentioning the thought that diacids only represent proxies that are routinely measured for a possibly much larger fraction of the aerosol and thus such studies that lead to understanding underlying processes might concern a significant fraction of the aerosol mass.

Reply: Thanks for the helpful comments. One new paragraph was added in the Introduction section as the second paragraph with the scope of dicarboxylic acids and related compounds as organic tracers to understand photochemical processes in the atmosphere. In the paragraph, we cited some literatures suggested by the referee. Please see lines 64-78 in the revised MS.

Minor comments p. 10124, l. 19: What do you mean by 'without any size cut'? Can you be more specific about the size range of collected particles?

Reply: The term "TSP" was added in the sentence. Please see line 108.

p. 10127, l. 3-10: Reword these sentences as it is not clear which values are compared

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here. What are the aerosol that are referred to in the first sentence and how do they differ to the marine aerosols referred to in the 2nd sentence? In the 3rd sentence, the values in the brackets should be moved after 'winter aerosols' and 'spring aerosols' to make it easier to read.

Reply: The sentences have been reworded following the referee's comments. Please see lines 171-179.

p. 101218, l. 4: What is the 'P' in POC?

Reply: The term "particulate" is added in line 198.

p. 10128, l. 20-23: The last part of the sentence ('and subsequent . . .') is redundant and misleading. I suggest deleting it.

Reply: The term "(NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, HNO<sub>3</sub>, NO<sub>3</sub>-)" was deleted.

p. 10130, l. 17: should that read 'Fig. 4'?

Reply: Corrected.

p. 10132, l. 3-11: Again it seems that the authors first highlight their own work on FeOx photolysis and only add one more sentence that basically says the same (FeOx complexes get depleted in UV-A light). This whole section should be discussed in more detail and more balanced. Questions that should be taken into account: - Do Fe levels in atmospheric aerosols support your hypotheses? - Could simply the oxidation of oxalate by OH explain the same trend? - how about other Fe-carboxylate photolysis processes? Do you e.g. see small depletion of Fe-malonate? Relate your findings to data by e.g., [Cunningham et al., 1988; Faust and Zepp, 1993] and related literature

Reply: To answer the reviewer's questions, we added few phrases and sentences. Please see lines 308-324. In order to discuss the Fe-oxalate reaction, we referenced one paper that reported Fe concentrations in Arctic aerosols (Gong and Barrie, Science of Total Environment, 342, 175-183, 2005). We also added one sentence on the

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possible decomposition of malonic acid referring the paper of Faust and Zepp (1993). Two references (Cunningham et al., 1988; Faust and Zepp, 1993) recommended by the referee were included in the revised MS. Concerning the isotopic fractionation of malonic acid, we cannot answer the referee's question because we conducted the laboratory experiment only for oxalic acid in Pavuvuri and Kawamura (2012). This should be the future target of the experiment. Thanks for your comments.

p. 10133, l. 25: The only species highlighted is the abundance of azelaic acid and oxalaic acid and their possible photochemical formation and loss, respectively. Is this what you are referring here to by 'photochemical production and degradation'? Be more specific.

Reply: This sentence was deleted and the next sentence was a bit modified as "We found a depletion of oxalic acid in the marine aerosols under foggy and cloudy conditions, which is possibly interpreted by selective degradation of oxalate-Fe complex in aqueous phase". See lines 366-368.

p. 10134, l. 10: Reword this sentence.

Reply: The sentence was reworded as "However, isotopic compositions of oxalic acid suggested that photochemical aging is not so serious as the marine aerosols studied in the lower latitudes including tropics". Please see lines 374-376.

Figure 4: The labels on the x-axis are way too small!

Reply: Yes, their sizes are small in the present style, but I expect that the figure would be enlarged when published and there is no problem.

Technical comments - to my knowledge, both 'arctic' and Arctic' is acceptable as adjective. However, one form should be used consistently.

Reply: Arctic is used now.

p. 10123, l. 13: photochemically p. 10124, l. 2, l. 2: remove 'a' (permafrost thaws)

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p. 10124, l. 4: These. . . p. 10124, l. 7: 'for the measurements' seems redundant p. 10125, l. 24: chromatograph . . . spectrometer p. 10126, l. 14: TC and TN should be defined here (and not in the next section) p. 10131, l. 26: succinic acid p. 10132, l. 6: delete 'bifunctional' p. 10133, l. 20: dicarbonyls Figure 6: 'dicarbonyls' (in legend)

Reply: Thanks for the careful reading. All the corrections were made in the revised MS.

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