Biogeosciences Discuss., 9, C3675–C3680, 2012
www.biogeosciences-discuss.net/9/C3675/2012/

Biogeosciences Discussions

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

Anonymous Referee #1

Received and published: 30 August 2012

This study presents data on dicarboxylic, and ketoacids and dicarbonyls concentrations in ambient aerosol collected above the Arctic Ocean. While many studies on 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 (14N, and 13C) 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.

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 [Röhrl and Lammel, 2001; Wang et al., 2002; Yao et al., 2002; Römpp 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.

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 measureable degree. CCN are mostly composed of inorganic compounds that nearly completely control the

BGD

9, C3675–C3680, 2012

CCN 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.

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?

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

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

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

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

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

BGD

9, C3675–C3680, 2012

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

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.

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

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

Technical comments

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

p. 10123, l. 13: photochemically

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

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)

BGD

9, C3675–C3680, 2012

References

Cunningham, K. M., M. C. Goldberg, and E. R. Weiner (1988), Mechanisms for aqueous photolysis of adsorbed benzoate, oxalate, and succinate on iron oxyhydroxide (goethite) surfaces, Environmental Science & Technology, 22(9), 1090-1097, 10.1021/es00174a015.

Ervens, B., B. J. Turpin, and R. J. Weber (2011), Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, Atmos. Chem. Phys., 11(21), 11069–11102, doi:10.5194/acp-11-11069-2011.

Faust, B. C., and R. G. Zepp (1993), Photochemistry of Aqueous Iron(III)-Polycarboxylate Complexes: Roles in the Chemistry of Atmospheric and Surface Waters, Environ. Sci. Technol., 27, 2517-2522.

Kitanovski, Z., I. Grgić, and M. Veber (2011), Characterization of carboxylic acids in atmospheric aerosols using hydrophilic interaction liquid chromatography tandem mass spectrometry, Journal of Chromatography A, 1218(28), 4417-4425, 10.1016/j.chroma.2011.05.020.

Röhrl, A., and G. Lammel (2001), Low-Molecular Weight Dicarboxylic Acids and Glyoxylic Acids: Seasonal and Air Mass Characteristics, Environ. Sci. Technol., 35, 95-101.

Römpp, A., R. Winterhalter, and G. K. Moortgat (2006), Oxodicarboxylic acids in atmospheric aerosol particles, Atmospheric Environment, 40(35), 6846-6862, 10.1016/j.atmosenv.2006.05.053.

Sorooshian, A., F. J. Brechtel, B. Ervens, G. Feingold, V. Varutbangkul, R. Bahreini, S. Murphy, J. S. Holloway, E. L. Atlas, K. Anlauf, G. Buzorius, H. Jonsson, R. C. Flagan, and J. H. Seinfeld (2006), Oxalic acid in clear and cloudy atmospheres: Analysis of data from International Consortium for Atmospheric Research on Transport and Trans-

BGD

9, C3675–C3680, 2012

formation 2004, J. Geophys. Res., 111(D23), doi: 10.1029/2005JD006880.

van Pinxteren, D., E. Brüggemann, T. Gnauk, Y. Iinuma, K. Müller, A. Nowak, P. Achtert, A. Wiedensohler, and H. Herrmann (2009), Size- and time-resolved chemical particle characterization during CAREBeijing-2006: Different pollution regimes and diurnal profiles, J. Geophys. Res., 114(D2), D00G09, 10.1029/2008jd010890.

Wang, G., S. Niu, C. Liu, and L. Wang (2002), Identification of dicarboxylic acids and aldehydes of PM10 and PM2.5 aerosols in Nanjing, China, Atmos. Environ., 36, 1941-1950.

Yao, X., M. Fang, and C. K. Chan (2002), Size distributions and formation of dicarboxylic acids in atmospheric particles, Atmospheric Environment, 36(13), 2099-2107, 10.1016/s1352-2310(02)00230-3.

Interactive comment on Biogeosciences Discuss., 9, 10121, 2012.