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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aircraft observations of water-soluble dicarboxylic acids in the aerosols over China" *by* Yan-Lin Zhang et al.

Anonymous Referee #2

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The manuscript by Zhang et al studied distributions of organic compounds obtained by aircraft measurements in China and argued that contribution of aqueous-phase photochemistry to SOA formation is significant using various correlation analyses. Potentially this work will make an important contribution to SOA studies particularly in East Asia and be suitable for ACP readership. But some of authors' arguments are confusing, misleading, and not clearly supported by evidence. Most of all, the organization is not effective. I highly recommend that authors should work on organization by bringing the LWC-oxalic acid analysis (currently in the end) to the front in Results and Discussion (Section 3) so that readers are clear about the main point of this manuscript is aqueous chemistry contribution to SOA. This will minimize confusions from paragraphs (Line 279-283, Line 283-285 and Line 291-299). Then, authors can discuss biogenic/anthropogenic influences on oxalic acid formation and aqueous

chemistry. Provide biogenic/anthropogenic emission data if available. Provide NOx measurements, too for isoprene arguments. Take an advantage of referencing most recent papers. Below I provide comments. There are also numerous technical errors (e.g., grammatical errors, typos), which need to be corrected.

Line 38: Authors should clarify LMW. For example, is LWM less than 300? Or is a C5 diacid still LMW?

Line 41: LWM diacids -> Aerosols

Line 43: contribute from -> contribute to the wide range from

Line 56: is -> are

Line 62-64: This is a modeling study of cloud chemistry. There is no evidence yet from lab or field studies supporting this argument. There should be more discussions. Authors may discuss the mechanism of isoprene photooxidation focusing on partitioning of water soluble photooxidation products into the aqueous phase leading to oxalic acid formation.

Line 74: I don't see a verb in the sentence.

Line 89: I am not clear about this. What are the examples of chemical constraints? And what more need to be considered?

Line 101: identified -> observed

Line 175-178: C5 and C6 diacids are the ozonolysis products in smog chamber studies. How does that support photooxidation (OH radical reaction or photolysis) of anthropogenic precursors? If cloud (photo)chemistry was involved, authors need to state that. Besides, authors should provide evidence (or reference) of higher oxidation capacity in the areas (or polluted areas) during the summer than winter.

Line 188-200: OH reactions of water soluble organic compounds in the aqueous phase clearly produce malonic and succinic acid (Tan et al., EST, 2009). Authors should

include this in their discussion. How does aqueous photooxidation affect C3/C4?

Line 219-222: It seems this statement contradicts the previous statement (Line 184-186).

Line 221: Does “the low troposphere” means the ground level?

Line 232-233: Again, provide evidence or reference.

Line 245: I would note that C2 is oxalic acid. Let readers know that Cn is n-numbered carbon diacid somewhere in the text.

Line 248-250: Remove wC2 if you mean HCO-COOH is glyoxylic acid, which is an oxidation product of pyruvic acid, glyoxal, and methylglyoxal. Also reference Lim et al., ACP 2013, which show a full mechanism for aqueous OH reactions.

Line 252-255: I doubt this is true. Oxalic acid is the most dominant product for glyoxal with the high yield (Tan et al. EST, 2009; Lim et al., ACP, 2010). But it is not for methylglyoxal. So, the given correlation analysis cannot tell whether C2 is biogenic

Line 256-259: The same goes here. Is there any evidence support that winter is more anthropogenically influenced (e.g., seasonal emission inventory)?

Line 267-268: 2-methyltetrols are also isoprene SOA tracers. This means oxalic acid correlated with some of isoprene SOA tracers, not all.

Line 269: Are you sure there are diepoxy derivatives from isoprene? None of Paulot et al. Science, 2009 and Surratt et al. PNAS, 2010 reports that. If it is a typo, then change it to epoxy derivatives.

Line 270: further oxidation -> further gas-phase oxidation. There is no aqueous chemistry involved here.

Line 272-274: NOx is critical in isoprene-OH reactions. In the presence of NOx, methacrolein and MVK form. In the absence of NOx, ISOPOOH forms and further

ISOPOOH reactions produce IEPOX. To support your conclusion, you should provide NOx measurements.

Line 279-283: This statement is confusing. Are you saying oxalic acid is formed via gas-phase oxidation without aqueous reactions and lifted up to FT? But, there is no evidence of oxalic acid formation from gas-phase oxidation of isoprene or monoterpene. Besides, recent lab and field studies suggest that IEPOX contributes to SOA via aqueous chemistry (Nguyen et al. ACP, 2010; Budisulistiorini et al., ACP 2015; Pye et al., EST, 2013).

Line 281: What is the boundary layer height? Is this 2 km, the lower FT?

Line 283-285: It is difficult to conclude like this unless authors provide compelling evidence of aqueous chemistry leading to oxalic acid.

Line 291-299: These statements are also confusing. Why should oxalic acid be considered for SOA? Note that oxalic acid itself is not SOA due to high vapor pressure. I would agree if you argue that oxalic acid is evidence of aqueous chemistry. Then, you need to discuss how water soluble compounds formed from biogenic and anthropogenic sources; how they partition into wet aerosols or cloud waters; and how OH radicals formed and initiated aqueous-phase photooxidation. Besides, you mentioned C5 and C6 are from anthropogenic sources. But this chemistry is initiated by ozone and not related to aqueous chemistry. How is including this chemistry likely to reduce the discrepancy between model predictions and measurements of OA?

Line 308: Do you mean higher altitude at low FT?

Line 314: Specify “other species.” Can they also provide evidence of aqueous chemistry like oxalic acid.

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