

Interactive comment on “Dicarboxylic acids, oxoacids, benzoic acid, α -dicarbonyls, WSOC, OC, and ions in spring aerosols from Okinawa Island in the western North Pacific Rim: size distributions and formation processes” by D. K. Deshmukh et al.

Anonymous Referee #3

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General comment:

The manuscript presents the concentrations of size resolved organic and inorganic compounds in aerosols collected at a sampling site located in Okinawa Island, Japan. The aerosol data in the region is rare so the data presented here is useful to the readers of ACP. The chemical analysis appears to be performed well, however, the conclusions drawn from the data are often speculative. I listed a series of specific comments that I

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would like the authors to address before it can be recommended for the publication in ACP.

Specific comments:

The authors use seven day back trajectories to identify the source regions of air masses, and attributed the origins of organic and inorganic species to the continental Asia. How did the precipitation affect the transport of these species? Were all seven days unaffected by precipitation events? This needs to be discussed in the revised manuscript.

Pp. 26517 line 22: Phtalate plasticizers may also be emitted from various plastics used in the heavily populated or industrialized regions in China, and transported to Okinawa.

Pp. 26519 line 19: Can the authors exclude the contribution of local limestone dust here? As far as I know, the islands of Okinawa are largely made of limestone that originates from coral. This should be discussed here.

Pp. 26521 line 28: The uptake coefficient of SO₂ to an aqueous particle depends strongly on a pH value the particle as well. Have the authors determined the pH value of the particles in this range? If so, is it acidic, neutral, or basic? This needs to be included in the discussion.

Pp. 26522 line 3: Why should the size distribution of MSA be the reason for the contribution of DMS oxidation to the formation of sulfate during the long range transport? How have the authors excluded the contribution of local DMS emission sources? A better explanation is necessary here.

Pp. 26522 line 10 onwards: I think this section needs to be written in a better way. The uptake of gas-phase NH₃ to form particle-phase NH₄⁺ is not affected by the presence of SO₄²⁻, rather the pH value of the particle-phase. When the counter ions other than H⁺ are present in the particles, NH₄⁺ is very unlikely to be present unless (NH₄)₂SO₄ is thermodynamically favorable. What the authors meant here is most likely that acidic

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sulfate can form from the oxidation of gas-phase SO₂, leading to nucleating particles. The uptake of ammonia neutralized freshly nucleating particles, forming ammonium sulfate, and this is thermodynamically more stable than, for example, ammonium nitrate.

Pp. 26522 line 21: What do the authors mean by heterogeneous reactions? Do the authors mean the reactive uptake?

Pp. 26522 line 26: What is the excess amount of ammonium over sulfate? What does ISORROPIA II tell about the composition of particles? Is excess ammonium significant enough to produce ammonium oxalate?

Pp. 26523 line 11: What do the authors mean by primary combustion products? Do they originate from internal combustion engines or biomass burning? The former is unlikely to produce a large amount of WSOC.

Pp. 26524 line 3: In what way do the fossil fuel combustion and biomass burning in East Asia influence the climate over the western North Pacific? Do the authors mean direct forcing or indirect forcing? The term climate means the statistics of the weather conditions over 30 years. Can the author really indicate their influence on the climate from this data? The authors should be more specific about the mechanisms impacting the climate over the region.

Pp. 26524 line 3: How do the authors know that it is formed in cloud processing? Did the air masses collected at the sampling site pass through clouds? Can the authors provide evidence for this (e.g. satellite images and back trajectory data with vertical profiles)?

Pp. 26524 line 18: Why should the smaller particles be subjected to more intensive photochemical oxidation than the larger particles? Please add an explanation for this here.

Pp. 26524 line 22: Here, correlation does not imply causation. How do the author

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know the fractions of the WSOC produced in the aqueous phase reactions and WSOC partitioned into the particle phase? Why should the aqueous phase oxidation be more important than the gas-phase oxidation? Can the authors comment on this in the manuscript?

Pp. 26525 line 16: Can the authors comment on the formation mechanisms of C₂ diacid in the gas-phase in the manuscript? Isn't it more likely that they are produced in the aqueous-phase? This also contradicts with the sentence (Pp. 26524 line 22) that the aqueous phase oxidation is favorable for the formation of WSOC. The C₂ diacid is often the most abundant single polar organic compound, so if they are produced in the gas-phase the aqueous phase reactions may not be so important.

Pp. 26525 line 19: Here, the authors contradict the paragraph above. Is it formed from the oxidation of gas-phase precursor compounds or cloud processing of precursor compounds? Do the authors mean the oxidation of VOCs leading to C₂ diacid precursors? Then the precursors partition into an aqueous droplet, and subsequent aqueous phase oxidation forms the C₂ diacid.

Pp. 26526 line 8: The authors repeatedly indicate the higher LWC is related to more pronounced formation of C₂ diacid in the aqueous phase. I am not convinced by this explanation. What matters for their formation in the particle phase is not absolute LWC in the particle, rather the activities of precursor compounds in relation to those of oxidants. Circumstantial evidence is not sufficient to conclude that the higher LWC favors the formation of diacids in the particles.

Pp. 26526 line 15: This is only one way to produce C₂ diacid. Their good correlations do not necessarily indicate that C₂ diacid is formed from C₃-C₅ diacids. It is also plausible that they all originate from the photooxidation of a mixture of VOCs during transport.

Pp. 26529 to pp. 26533 line 3: I found this section quite repetitive and tedious to read. I suggest the authors to discuss compounds that are formed from the same

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mechanisms instead of compound classes. The authors do not need to address every single compound in the text. Instead, the authors can summarize the compounds that form from the same mechanism in a table, and discuss only about most interesting compound(s) in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 26509, 2015.

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