Atmos. Chem. Phys. Discuss., 15, C8368–C8376, 2015
www.atmos-chem-phys-discuss.net/15/C8368/2015/

Atmospheric Chemistry and Physics
Discussions

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 #2

Received and published: 22 October 2015

The manuscript report the size-distribution of chemical species, particularly focusing on WSOC, OC, organic acids, carbonyl. Studied region is unique, so this report may attract readership of ACP. After reading the manuscript carefully, however, substantial revision is required on this manuscript before published in ACP. The followings are general problems I noticed.

1. Considerable amount of arguments on oxidation products were speculated without observational evidence. For example, many of discussions on the distributions of chemical species in fine mode ended with the production by in-cloud or heterogeneous processing. However, the authors did not provide any observational results on chemical reaction. Because many of the analyzed species were possibly supplied by both primary emissions and atmospheric oxidations, specific findings observed under limited conditions in literature do not secure that the reported phenomena must be those their samples underwent. More objective evaluation on other possible reasons for the observed size-distribution will substantially improve the quality of manuscript.

2. There were logic problems in some discussions. For example, LWC was calculated based on the results of inorganic concentrations. Later, the authors interpret the high correlation of LWC with the salt concentrations. The comparison is invalid because LWC is dependent-variable of the salt concentration. Poor description on the calculation of LWC is also a problem. Another example is that the authors identified substances in the fine mode as oxidation products. Contradictorily, K+, an indicator for biomass burning, also stay in the fine mode. This fact tells us that primary stuff at least partially exist in the fine mode. The authors should make discussion on the oxidation products more carefully.

3. Writing issues. I could see redundant sentences and ambiguous expressions. The authors should ask a professional editor or someone equivalent for revising the text in English.

4. Novelty issue. The current form of the manuscript does not seem to provide novel findings. Completion of discussion by citing numbers of reports can be an indication of lack of novelty, although the contents may be worthwhile with respect to publishing the size-distribution data of detailed composition of organic acids in this region. The authors should make deeper discussion by adding new aspect, such as discussion on slopes of linear regression between the chemical species.

Overall, the current form is not recommended for an article in ACP. Substantial revision is needed. Specific comments are listed below.

Specific comments

Abstract

P26510L5: Please describe specifically what “major ions” are.

P26510L12: From the L1 to L11 the authors explain the chemical species analyzed and their size-distribution. Suddenly, the statement jumped onto “These results imply that water-soluble species in the marine aerosols could act as cloud condensation nuclei. . .” After reading through the manuscript, I recommend to remove this statement because it is not the focus of this paper.

P26510L13: A similar problem. The authors suddenly started stating “The organic species are likely produced by a combination of gas-phase photooxidation...” without any scientific evidence. If there is any evidence, please state your scientific evidence briefly.

Introduction

P26511L29: The authors may have meant previously, rather than “rarely”.

Materials and method

P26512L20: The authors may want to change“Asian” to the continental.

P26512L25: Delete the sentence “Okinawa is a subtropical island..” because it seems irrelevant to the focus.

P26513L7: Please specify what the “80 mm” is.

Section 2.2: The authors should add supplier names for the solvents, reagents, and standards used.

P26514L15: It is good to state the analytical error and the detection limit. However, I did not see any statement for the detection limit of the GC analysis. Please either

consistently state the detection limits of your analysis throughout the section (I recommend it), or remove the statements. By the way, are all the data blank-corrected? I recommend the authors to mention the magnitudes of blank values and whether or not they made blank corrections.

P26514L19: “Presence of . . .” sounds a contradictory statement to the previous description. In L9, the authors acidified the sample extracts to remove inorganic carbon, implying they cared of carbonate. Meanwhile, the authors assumed carbonate in aerosol to be negligible. The treatments are inconsistent.

P26515L13: The authors may want to change “The air mass backward trajectory was” to The backward trajectories of air masses were”

P26515L17-L22: The sentences should appear in the section 3 because these are the results.

Figure 2: Although the caption says “seven-day” trajectories, each figure seems to show six-day trajectories. Correct the figure or the caption.

Results and Discussion

P26516L5-L6: The authors may want to delete the part after “because. . .” since the part is not necessary after defining what the fine and the course modes are.

P26516L12: Replace “Our sampling site Cape Hedo” with CHAAMS because the authors abbreviated the site before.

P26516L13-L15: The authors may want to rephrase the sentence “Because. . .” For example, Because the aerosols reaching to Okinawa are subjected to undergo the atmospheric oxidation during the long-range transport, the fraction of oxygenated organic species is often high. Therefore, we used the conversion factor of 2.1, instead of 1.6 for calculation of OM. P26516L16-L17: So where are the results of OM calculated? Readers will expect the results of OM after reading this sentence. The authors may show the results and make a brief discussion on it.

P26516L23-25: In the sentence "The abundant presence of NH_4^+ together with SO_4^{2-} in the same fraction demonstrated. . ..", the authors should take a step forward into the acidity of particles, if they refer "the fraction". My rough estimate from Figure 3 suggests these ions are not balanced.

P26517L3: The authors may want to change "important" to substantial or equivalent word indicating its quantity.

P26517L5-L7: Regarding "suggesting. . ..", why isn't NH_4NO_3 considered? If there is any reason to rule it out, please state it.

P26516L18-P26517L7: I could not see discussion on Figure 3. Is Figure 3 worth to show? Table 1 may be enough for the discussion the authors described.

P26517L8-L17: Aren't C2, C3, C4 emitted from primary emissions as well? Although their secondary formation can be a possibility, the authors should also refer to the fact that these can be from primary sources, unless otherwise the authors have more convincing evidence of secondary formation in these samples.

P26517L20-L28: The authors do not make discussion on the basis of their observations, but speculate the possible source of Ph, C6, and kC3 using references. Detection of these compounds is not enough to convince readers that those are the secondary origin. Unless otherwise the authors present more convincing evidence of secondary formation, I recommend to revise the discussion along with their observations (i.e., size distribution of the acids).

P26518L1-L15: The same problem with the previous one: the authors need to make discussion on their observations (the size distribution data) more strongly.

P26518L19: "It is clear. . ." is not clear to me. Please be specific why it is clear.

P26518L20: The sentence "The size distribution. . ." refers the monomodal distribution of $Na^+$and Cl^-, but the Fig. 5 clearly show the bimodal distribution. The authors should make a correction on it.

P26518L26: The authors may want to remove "smaller" and "larger". Please consider such revision in the following sentences.

P26518L28: Specifying the size of "the accumulation" would be helpful for readers to follow.

P26518L28-P26519L3: In the previous sentence, the authors concluded that the bimodal of Na^+ and Cl^- are associated with bubble bursting of the surface seawater. Suddenly, the authors state another possibility of secondary formation of NaCl. It's confusing. If the previous conclusion were supposed to be a statement for a possible source, the authors should write so. By the way, it is a bit surprising to me that NaCl is formed secondarily. Am I misunderstanding?

P26519L11-L14: The sentences explain heterogeneous production of NO_3^-. If so, why Ca^{2+} is not associated with SO_4^{2-}. According to the authors, SO_2 reacts heterogeneously with clusters to form SO_4^{2-}. The interpretation seems inconsistent.

P26519L28-P26520L2: The authors state that Fig. 5e shows "bimodal pattern". If so, the distribution of Ca^{2+} in Fig. 5c also shows a bimodal distribution as well, although the authors interpret it as monomodal. The way to interpret the data seems inconsistent.

P26520L2: The authors may want to start a new paragraph from "A unimodal size distribution. . .." and combine the next paragraph together.

P26520L5-L11: These sentences indicates that the authors neglect the growth of the particles from biomass burning during the long-rage atmospheric transport. Meanwhile, K^+ was highly correlated with LWC in fine mode (r=0.83 in Table 3), implication of water uptake. Any explanation for this contradiction?

P26520L28-P26521L4: The authors interpreted the data that high concentration of NO_3^- in the coarse mode were due to the heterogeneous reaction (R2). If so, why SO_2 did not result in so (i.e., high conc. of SO_4^{2-} in the coarse mode)? In addition, significant amount of Na+ exists in the same mode as NO3- does (i.e., 1.1-7.0 micron). What is a possible reason for the (R1) not to occur? By the way, the authors treat the negative correlation as insignificant correlation, but a negative correlation actually indicate anti-correlation where a variable y decreases as a variable x increases. If the r of -0.3 were treated as significant, the negative correlation may indicate something reactive loss of NO3- with Na+. The authors should make a discussion on it, if they treat the negative correlation as significant value.

P26521L14: Although the authors state that the high abundance of SO42- in the fine mode was due to the oxidation of SO2 gas in cloud droplets, cloud droplets are much larger 1 micron in general. Does the statement also mean that the observation site at 60 m above the sea level was covered by clouds during the study period?

P26521L21-L22: A big question arose; Doesn't the calculation for LWC require data of ambient temperature and RH, which are not referred anywhere?

Figure 6. Two plots can be combined into one.

P26522L1: Isn't the high correlation between LWC and SO42- owing to the fact that the calculated LWC was based on the concentration of SO42-, which is the major component of inorganic compounds found in particles? The same issue in L18 for NH4+.

P26522L14: The authors are skipping Figure 7 and indicating Figure 8. The order should be fixed.

P26522L28: The expression of "The occurrence of ammonium oxalate" needs to be fixed.

P26523L4-L7: This paragraph is unnecessary. The authors may want to place "(Fig. 7)" and "(Table 1)" as they discuss the data (i.e., "(Table 2)" at the end of sentence in L9.

P26523L13: In general, "a statistically significant" should be replaced with "high correlation" in this case.

P26523L16-L20: I do not understand the logic that the high correlation coefficients indicate significant contributions from two emission sources rather than one source.

P26523L28-P26524L4: The sentence is speculative without observational evidence, and the point sounds irrelevant to the focus of this manuscript.

P26523L7: Insert (Fig. 7) after "diameter".

P26523L5-L12: The authors are trying to make an argument on production of OC and WSOC in cloud-droplets during the long-range transport. However, I don't understand the logic why the observation of high correlation is the evidence of reactive production in cloud-droplets. Isn't it possible that products were formed outside of the droplets? Isn't is possible that SO42-, NH4+, and WSOC or OC were produced in different ways during the long-range transport? The authors should state the reasons for ruling out such possibilities.

P26524L22-L25: Is the LWC independent of the WSOC? If so, the comparison between LWC and the WSOC/OC ratio can be valid. Given that the comparison of WSOC with LWC is valid, I agree with that the chance that deliquescent particles become aqueous droplets increases, in turn photooxidation of OC to WSOC inside particles may occur. However, without actual observations of water content and evaluation of secondary formation of WSOC, which has been evident in numbers of publications, the discussion seems too speculative. There are more to be evaluated before speculating reactions inside droplets, such as WSOC coming from the emissions directly (as the authors refers so). The authors should add more different aspect obtained from different measurements to provide an insight into such phenomena. If the authors still want to leave the possibility, they should list the other possibility. The current form of discussion impresses me that the statements are biased.

P26525L6-L9: The sentence is confusing. The authors may want to rephrase it to direct expression, such as “The monomodal distribution suggests that the heterogeneous uptake of C2 on sea-salt particles did not occur (references).”

P26525L16-L20: As the authors point in L28 in the same page, isn’t it possible that some of C2 are derived from primary sources?

P26525L27: Omit “oxalic acid” because the authors already defined the acid as C2 in L6. There are other abbreviations defined repeatedly. Please revise.

P26526L15-L16: This seems an interesting finding. The authors may want to make a deeper discussion about this correlation by showing the plots, analyzing the slope of the regression, etc.

P26527L1: “showed additional peak at > 11.3 mm (Fig. 8c).” But I don’t see an additional peak.

P26527L7-L8: The assumption “assuming that C3 does not. . .” contradicts to the previous statement (P26526L2); “C2 is produced. . .” P26528L6 and L20: The abbreviation “Ph” is defined twice.

P26528L24-P26529L4: Why does Ph distribute to the fine mode preferentially? Figure 8 tells that C9 and Ph have different size distributions although both are oxidation products converted from the gas-phase. The authors may want to state reasons for the preferential distribution. Also, I am not sure the point that the authors are trying to make using the Ph/C9 ratios because emissions and reactivity of their precursors are different. What can we know from the ratios?

P26530L24-L27: Why does omega-C9, an oxidation product, distribute to the coarse mode, although the other oxidation products do to the fine mode? The way to interpret the size distribution seems inconsistent through the paper.

P26532L9: Omit “and thus radiating (radiative?) forcing. . ..”
