

To

Prof. Veli-Matti Kerminen
Editor
Atmospheric Chemistry and Physics (ACP)

RE: Submission of revised manuscript entitle “**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**” for publication in Atmospheric Chemistry and Physics

Reference: MS No.: acp-2015-568

Dear Prof. Kerminen,

Thanks for the decision letter on our manuscript. We have revised the manuscript meticulously following the referees' comments and suggestions. The authors greatly appreciate the critical and useful comments by anonymous referee's that significantly improved the quality of our manuscript. Our responses and changes are included in the response letter as blue color. The changes in the revised manuscript are highlighted in yellow. Please find the response letter and revised manuscript.

We believe that revised manuscript is acceptable for publication in ACP.

Thanking you.

Sincerely yours,

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Responses to the Comments of Referee #2

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.

Response: We thank the referee's careful reading and helpful comments, based on which we tried to improve the quality of our manuscript as follows.

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.

Response: The manuscript has been rigorously checked for its correctness towards interpretation and discussion of the data observed. Other possible reasons for the observed size distribution of water-soluble inorganic ions as well as diacids and related compounds have been discussed in the revised MS. Please see lines 220-223, 225-234, 341-347, 434-441 and 503-506 as well as our responses given below.

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.

Response: The discussion on the results of correlation analysis between LWC and salt concentrations has been removed and the contents have been rephrased accordingly. A detail description for the calculation of LWC has been now provided in section 2.4. We agree that diacids and related compounds can also be produced primarily from combustion sources such as biomass burning in East Asia and long-range transported to Okinawa. Interestingly, we found significant positive correlations of K^+ with diacids and related compounds in fine mode. We have discussed this points in the revised MS. Please see lines 169-175, 419-421, 434-441 and 503-506 as well as our responses given below.

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.

Response: We have removed the redundant sentences and ambiguous expressions. The revised MS has been edited for the English language.

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.

Response: Thank you for very important comment. Based on the referee's suggestion and

comments, we added the following sentences.

“It is important to understand whether anthropogenic or biogenic organic precursors are oxidized to increase the atmospheric level of shorter-chain (C₂-C₅) diacids and related compounds (ω C₂ and Gly) in fine mode of Okinawa aerosols. The strong correlation of C₂-C₅ diacids with Ph ($r = 0.83-0.90$) was found in fine mode. This result suggests that anthropogenic precursors are more important sources of C₂-C₅ diacids than biogenic precursors in fine mode. The weak correlations of C₂-C₅ diacids with C₉ ($r = 0.09-0.38$) further suggest that biogenic precursors such as unsaturated fatty acids are not a major source of shorter-chain diacids in fine mode. The higher influences of anthropogenic VOCs than biogenic VOCs can also be evidenced by a lack of correlation ($r = 0.25-0.36$) between C₂-C₅ diacids and MeGly in fine mode. Myriokefalitakis et al. (2011) proposed that about 80% of MeGly is formed in the atmosphere by the oxidation of biogenic VOCs such as isoprene. Strong correlations of ω C₂ and Gly with Ph ($r = 0.90$ and 0.85) also suggest that anthropogenic precursors are their major sources in fine mode of Okinawa aerosols.”

Please see lines 606-617 in the revised MS.

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.

Response: The major ions measured in this study have been included in the abstract. Please see line 13-14 in the revised MS.

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.

Response: Removed.

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.

Response: Thanks for your suggestion. We have revised the text as “Strong correlations of C₂-C₅ diacids, ω C₂ and Gly with sulfate were observed in fine mode ($r = 0.86-0.99$), indicating a commonality in their secondary formation. Their significant correlations with liquid water content in fine mode ($r = 0.82-0.95$) further suggest an importance of the aqueous-phase production in Okinawa aerosols. They may have also been directly emitted from biomass burning in fine mode as suggested by strong correlations with potassium ($r = 0.85-0.96$), which is a tracer of biomass burning.”

Please see lines 19-24 in the revised MS.

Introduction

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

Response: Changed. Please see line 61 in the revised MS.

Materials and method

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

Response: Changed. Please see line 79 in the revised MS.

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

Response: Deleted.

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

Response: We rephrased to “quartz fiber filter (QFF, 80 mm in diameter). Please see line 90 in the revised MS.

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

Response: Suppliers are now provided. Please see lines 148-150 in the revised MS.

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.

Response: We added few phrases on the detection limit in GC analysis and field blanks. Please see lines 112-113 and 146-148 in the revised MS.

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.

Response: We are sorry for the mistake. We acidified the aerosol extract with 1.2 M HCl to remove inorganic carbon. To keep the consistency, we have removed the phrase “Presence of carbonate carbon.....assumed to be negligible” in the revised MS.

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

Response: Changed. Please see line 152 in the revised MS.

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

Response: The sentences “Okinawa was strongly affected by continental.....oceanic air masses” have been moved in the section 3.1. Please see lines 189-192 in the revised MS.

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

Response: The air masses shown in Figure 2 are the seven-day backward trajectories at 500 m a.g.l. for the samples (OKI-1 to OKI-5) collected in Okinawa. To our understanding, reviewer might have confused on the dates we provided for the samples OKI-1 to OKI-5 in Figure 2 (OKI-1: 18-23 March 2008; OKI-2: 23-28 March 2008; OKI-3: 28 March-02 April 2008; OKI-4: 02-07 April 2008; OKI-5: 10-13 April 2008). The dates given in each panel in Figure 2 are the starting and ending date of collection of aerosol samples in Okinawa. To avoid any confusion, we have rephrased the caption of Figure 2 as follows.

“**Figure 2.** NOAA HYSPLIT seven-day backward air mass trajectories at 500 m a.g.l. for the aerosol samples (OKI-1 to OKI-5) at Okinawa Island. The dates given in each panel in figure are the starting and ending date of collection of aerosol samples in Okinawa Island.”

Please see Figure 2 in the revised MS.

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 coarse modes are.

Response: Deleted.

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

Response: Corrected. Please see line 183 in the revised MS.

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.

Response: We have rephrased the sentence in the revised MS. A brief discussion on organic matter (OM) in Okinawa aerosols has been now provided in the revised MS as “OM was enriched in fine size fractions than the coarse size fractions (Figure 3). The elevated level of OM in fine fractions in Okinawa (Table 1) suggests a substantial contribution of organic aerosols primarily from combustion sources and secondarily from photochemical processes during long-range atmospheric transport. The OM in fine mode aerosol in Okinawa might be consists of oxygenated organic compounds such as diacids, ω -oxoacids and α -dicarbonyls.” We also provided the fine and coarse mode concentrations of OM in Table 1.

Please see lines 184-188, 194-198 and Table 1 in the revised MS.

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.

Response: We calculated the equivalent ratios of total cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) to anions (Cl^- , NO_3^- and SO_4^{2-}) for size-segregated aerosols. We also calculated the equivalent ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ for fine modes. We deleted the sentence “The abundant presence of NH_4^+ together with SO_4^{2-} in the same fraction demonstrated.....” from section 3.1 and results are included in section 3.2 in the revised MS as follows.

“Average equivalent ratios of total cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) to anions (Cl^- , NO_3^- and SO_4^{2-}) in fine fractions varied from 0.75 for the size bin of 0.65-1.1 μm to 0.86 for the size bin of 1.1-2.1 μm , indicating that fine mode aerosols in Okinawa were apparently acidic.”

Please see lines 379-382 in the revised MS.

“The average $\text{NH}_4^+/\text{SO}_4^{2-}$ equivalent ratios in fine mode particles in Okinawa varied from 0.36 for the size bin of 1.1-2.1 μm to 0.81 for the size bin of 0.43-0.65 μm , indicating that NH_3 was not abundant enough to neutralize all SO_2 and hence H_2SO_4 and NH_4SO_4 were present in addition to $(\text{NH}_4)_2\text{SO}_4$ in fine mode.”

Please see lines 386-389 in the revised MS.

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

Response: Corrected. Please see line 208 in the revised MS.

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

Response: Based on the comment, we added the following sentences in the revised MS.

“The reaction of NH_3 with H_2SO_4 is favored over its reaction with HNO_3 . The average $\text{NH}_4^+/\text{SO}_4^{2-}$

equivalent ratios in fine mode particles in Okinawa varied from 0.36 for the size bin of 1.1-2.1 μm to 0.81 for the size bin of 0.43-0.65 μm , indicating that NH_3 was not abundant enough to neutralize all SO_2 and hence H_2SO_4 and NH_4SO_4 were present in addition to $(\text{NH}_4)_2\text{SO}_4$ in fine mode. Interestingly, the average $\text{NH}_4^+/\text{SO}_4^{2-}$ equivalent ratios in coarse mode particles ranged from 0.01 for the size bin $>11.3 \mu\text{m}$ to 0.09 for the size bins of 2.1-3.3 and 3.3-4.7 μm , suggesting that coarse mode aerosols in Okinawa were also NH_4^+ -poor. This result further indicates that there was not enough NH_3 to neutralize HNO_3 , and thus shortfall of NH_3 may be the restrictive factor for the formation of NH_4NO_3 in Okinawa aerosols.”

Please see lines 385-395 in the revised MS.

However, the sentence “Very small amount was nitrate through the reaction of gaseous HNO_3 onto pre-existing alkaline particles” has been rephrased as “Substantial amount of NO_3^- was detected in coarse mode, suggesting a formation of $\text{Ca}(\text{NO}_3)_2$ or NaNO_3 in coarse fractions through the reactive adsorption of gaseous HNO_3 onto pre-existing alkaline particles.”

Please see lines 209-211 in the revised MS.

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.

Response: We added two phrases concerning Figure 3. Please see lines 194 and 199-200 in the revised MS.

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.

Response: Based on the comment, we added few sentences on the primary sources of diacids as follows.

“They can also be emitted from primary sources such as fossil fuel combustion and biomass burning. Fossil fuel combustion and biomass burning also emit numerous VOCs to the atmosphere, which are ultimately oxidized to diacids via gas and aqueous-phase oxidation.”

Please see lines 220-223 in the revised MS.

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).

Response: Following the reviewer's suggestion, we have revised the text in section 3.1 as follows.

“Ph and C₆ diacids originate from various anthropogenic sources and thus they can be used as anthropogenic tracers. Ph primarily originates from coal burning and vehicle emission whereas photooxidation of aromatic hydrocarbons such as naphthalene (NAP) and o-xylene derived from incomplete combustion of fossil fuel form Ph via secondary processes (Kawamura and Kaplan, 1987). Moreover, the abundant presence of Ph may also be caused by enhanced emission of phthalates from plastics used in heavily populated and industrialized regions in China and the subsequent long-range atmospheric transport to Okinawa. Phthalic acid esters are used as plasticizers in resins and polymers (Simoneit et al., 2005). They can be released into the air by evaporation because they are not chemically bonded to the polymer.”

Please see lines 225-234 in the revised MS.

“The high abundances of Ph and C₆ diacids in Okinawa suggest the significant influence of anthropogenic sources in East Asia via long-range transport of aerosols over the western North Pacific Rim.” Please see lines 235-237 in the revised MS.

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

Response: Following the referee's suggestion, we reorganized the discussion in section 3.1 as follows.

“Such continental air masses can also bring C₉ via atmospheric processing of biogenic unsaturated fatty acids during long-range transport. The abundant presence of C₉ indicates that atmospheric oxidation of biogenic unsaturated fatty acids also occurs in Okinawa aerosols during long-range transport.”

Please see lines 244-247 in the revised MS.

“ωC₂ and Gly are the oxidation product of several anthropogenic and biogenic VOCs and primary generated by fossil fuel combustion and biomass burning (Zimmermann and Poppe, 1996; Volkamer et al., 2001), and are further oxidized to C₂ diacid (Myriokefalitakis et al., 2011). The predominance of ωC₂ and Gly indicates their importance as key precursors of C₂ in Okinawa aerosols.”

Please see lines 250-254 in the revised MS.

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

Response: We have rephrased the sentence as “Na⁺ and Cl⁻ are mainly derived from the ocean surface as sea salt particles in the marine atmosphere.”

Please see lines 257-258 in the revised MS.

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.

Response: We are sorry for this error. We have corrected “unimodal distribution” to “bimodal distribution”. Please see line 259 in the revised MS.

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

Response: Removed. Please see line 263 in the revised MS.

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

Response: This sentence has been deleted.

P26518L28-P26519L3: In the previous sentence, the authors concluded that the bi-modal 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?

Response: We are sorry for this mistake. The bimodal distribution of Na⁺ and Cl⁻ in Okinawa are associated with the bubble bursting of surface seawater. Therefore, the phrase “The accumulation of these specieslong-range transport” has been deleted in the revised MS.

P26519L11-L14: The sentences explain heterogeneous production of NO₃⁻. If so, why Ca²⁺ is not associated with SO₄²⁻. According to the authors, SO₂ reacts heterogeneously with clusters to form SO₄²⁻. The interpretation seems inconsistent.

Response: Please see our response to the comment **P26520L28-P26521L4** as below.

P26519L28-P26520L2: The authors state that Fig. 5e shows “bimodal pattern”. If so, the distribution of Ca²⁺ 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.

Response: We are sorry for this error. This problem has been solved. Please see line 299 in the revised MS.

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

Response: Done. Please see lines 299-314 in the revised MS.

P26520L5-L11: These sentences indicate that the authors neglect the growth of the particles from biomass burning during the long-range 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?

Response: Based on the comment, a brief description was added in the revised MS as follows.

“Freshly emitted biomass burning aerosol particles usually exist at the size of 0.1-0.5 μm and thus the peak of K^+ at 0.65-1.1 μm shows that the fine mode K^+ in Okinawa was associated with aged aerosols. Fresh biomass burning aerosols emitted in East Asia might have undergone growth to a relatively large size by absorbing water vapor from the atmosphere during long-range atmospheric transport to Okinawa. The peak of K^+ at 0.65-1.1 μm in fine mode is conceivably a result of a combination of K^+ derived from fresh biomass burning with other water-soluble species such as SO_4^{2-} during long-range transport. This interpretation is supported by the fact that K^+ showed a positive correlation with LWC ($r = 0.83$) in fine mode.”

Please see lines 300-307 in the revised MS.

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_4^{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 NO_3^- 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 indicates 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 NO_3^- with Na^+ . The authors should make a discussion on it, if they treat the negative correlation as significant value.

Response: Following the reviewer's comments, we reorganized the discussion as below.

“The size distribution of SO_4^{2-} also depends on the concentration of NH_4^+ , richness of NH_3 in the air, and the presence of coarse mode particles. SO_4^{2-} and NH_4^+ often coexist in fine mode because H_2SO_4 condenses on this mode as fine particles that have more surface area (Jacobson, 2002). Although NH_3 was not abundant enough to neutralize all SO_4^{2-} , most of SO_4^{2-} was neutralized by NH_3 in fine mode and exists in the form of NH_4HSO_4 in addition to $(\text{NH}_4)_2\text{SO}_4$. Hence, SO_4^{2-} is enriched in fine mode rather than being associated with dust particles. An enrichment of NO_3^- in the dust fraction in our study is supported by the laboratory studies of Hanisch and Crowley (2001a) and (2001b), who found a large and irreversible uptake between HNO_3 and various authentic dust samples including samples from Chinese dust region.”

Please see lines 396-404 in the revised MS.

“We found that coarse mode Na^+ , which is derived from sea salts, is negatively correlated ($r = -0.30$) with the coarse mode NO_3^- . Although this correlation is not significant ($p = 0.51$), the negative correlation may indicate some reactive loss of NO_3^- from sea salt particles in coarse mode in Okinawa.”

Please see lines 327-330 in the revised MS.

P26521L14: Although the authors state that the high abundance of SO_4^{2-} in the fine mode was due to the oxidation of SO_2 gas in cloud droplets, cloud droplets are much larger than 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?

Response: Based on the comments, we rephrased the paragraph as below.

“A unimodal size distribution of SO_4^{2-} was observed with a peak at 0.65-1.1 μm . The occurrence of SO_4^{2-} at the size of 0.65-1.1 μm cannot be explained by gas-phase nucleation or condensation of SO_2 . It has also been suggested that in-cloud process produce SO_4^{2-} as larger particles by the oxidation of SO_2 in cloud droplets (Gao et al., 2012), which can become fine particle after the dryness of cloud droplets. This result suggests that the peak of SO_4^{2-} at 0.65-1.1 μm in Okinawa is involved with oxidation of SO_2 with OH radical and O_3 in aerosol aqueous-phase.”

Please see lines 341-347 in the revised MS.

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

Response: Ambient temperature (T) and relative humidity (RH) are required for the calculation of liquid water content (LWC) using ISORROPIA II model. These points are added in the revised MS as below.

“ISORROPIA II implies the Zdanovskii-Stokes-Robinson equation and treats only the thermodynamics of K^+ - Ca^{2+} - Mg^{2+} - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosol system to estimate the LWC. Therefore, the measured organic species such as diacids and related compounds are not included in ISORROPIA II. The model was run as “reverse problem”, in which temperature, relative humidity and aerosol phase concentrations of water-soluble inorganic ions were used as input for the estimation of aerosol LWC.”

Please see lines 169-175 in the revised MS.

Figure 6. Two plots can be combined into one.

Response: Figure 6 has been modified accordingly. Please see Figure 6 in the revised MS.

P26522L1: Isn't the high correlation between LWC and SO_4^{2-} owing to the fact that the calculated LWC was based on the concentration of SO_4^{2-} , which is the major component of inorganic compounds found in particles? The same issue in L18 for NH_4^+ .

Response: Yes, high correlations of LWC with SO_4^{2-} and NH_4^+ suggest that abundant presence of these ions in fine mode increased the amount of LWC in fine mode of Okinawa aerosols. Therefore, we deleted the phrase “The high LWC at 0.65-1.1 μmatmospheric transport in East Asia” and made appropriate modifications accordingly in the revised MS. Please see lines 348-349, 354-357 and 405-406.

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

Response: We have fixed it. Please note that Figure 8 has been referred as Figure 7 in the revised MS.

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

Response: Referee #3 also commented on this issue. As suggested by referee #3, we calculated the equivalent ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ in size-segregated aerosols to evaluate the excess amount of NH_3 that can react with oxalic acid (C_2) to form ammonium oxalate in fine fraction of Okinawa. The equivalent ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ varied from 0.36 for the size bin of 1.1-2.1 μm to 0.81 for the size bin of 0.43-0.65 μm in fine mode. These values suggest that NH_3 was not sufficient to neutralize all SO_2 and hence there was no NH_3 to further react with C_2 to form ammonium oxalate in fine mode. Therefore, the sentences “The occurrence of ammonium oxalate.....biomass burning aerosols” has been deleted in the revised MS. However, the significant positive correlation between C_2 and NH_4^+ ($r = 0.89$) in fine fraction suggested that C_2 is also a secondary photochemical product. This point has briefly been mentioned in the revised MS. Please see lines 501-503.

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.

Response: We deleted the suggested paragraph and correction has been made in the revised MS. Please note that Figure 7 has been referred as Figure 8 in the revised MS. Please see line 411.

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

Response: Corrected. Please see line 415 in the revised MS.

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

Response: We have revised the sentence as follows.

“This result suggests that direct emission from biomass burning or fast oxidation of biomass burning-derived precursors contribute significantly to the formation of fine mode WSOC in Okinawa aerosols during long-range transport.”

Please see lines 419-421 in the revised MS.

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

Response: Based on the comment, we rephrased the sentence as follows.

“Because WSOC is an important fraction of OC in Okinawa aerosols, high loadings of WSOC in aerosols of continental air mass origin suggest that both fossil fuel combustion and biomass burning in East Asia may have a significant influence on the composition of water-soluble organic aerosols over the western North Pacific Rim.”

Please see lines 428-431 in the revised MS.

P26523L7: Insert (Fig. 7) after “diameter”.

Response: Please note that this should be in Page-26524 and Line-7. The correction has been made in the revised MS. Figure 7 has been referred as Figure 8 in the revised MS. Please see line 434.

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 it 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.

Response: Following the comments, we rephrased the sentences as follow.

“Primary emission from fossil fuel combustion and biomass burning and secondary production from photooxidation of VOCs are considered to be the major sources of OC in atmospheric aerosols (Aggarwal and Kawamura, 2009; Jung et al., 2010). Primary emission from biomass burning or photooxidation of biomass burning derived precursors might be a dominant source of fine mode OC in Okinawa aerosols. This interpretation is supported by the fact that OC showed strong correlation ($r = 0.95$) with K⁺ in fine mode. The fine mode OC showed significant positive correlations with SO₄²⁻ ($r = 0.93$) and NH₄⁺ ($r = 0.91$), suggesting secondary photochemical formation characteristics of OC in fine mode in Okinawa.”

Please see lines 434-441 in the revised MS.

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.

Response: Please note that concentration of WSOC is not included in ISORROPIA II model for the estimation of LWC. LWC calculated using ISORROPIA II in our study is independent of WSOC. Therefore, we believe that the correlation between LWC and WSOC/OC ratio can give some information about the possible aqueous-phase production of WSOC from OC during long-range transport. However, the actual observation of LWC for the aerosol samples is not possible at this stage. Therefore, we rephrased the text and included other possibilities for the production of WSOC in fine mode as follows.

“WSOC also contribute to aerosol LWC although their ability to absorb water is significantly less than that of inorganics (Ansari and Pandis, 2000). Speer et al. (2003) and Engelhart et al. (2011) also noted that inorganic aerosols are associated with 62-80% of aerosol LWC. Moreover, organic species are not taken into account in ISORROPIA II for the calculation of LWC. It is noteworthy that WSOC/OC ratio and LWC significantly correlate in the fine mode with $r = 0.87$ whereas the negative correlation was found in the coarse mode ($r = -0.19$), suggesting the possibility of photochemical production of WSOC from OC in aerosol aqueous-phase in fine mode of Okinawa aerosols. There may also be other important sources of fine mode WSOC in Okinawa aerosols such as primary emission from biomass burning and secondary formation via gas-phase photochemical reactions during long-range atmospheric transport (Hagler et al., 2007; Lim et al., 2010). The strong correlation of WSOC with K^+ in fine mode suggests a substantial contribution of biomass burning to fine mode WSOC in Okinawa aerosols.”

Please see lines 464-475 in the revised MS.

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).”

Response: To avoid any confusion, we rephrased the sentence. Please see lines 485-486 in the revised MS.

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?

Response: Following the comment, we added few sentences as below.

“The fine mode C_2 can also be produced primarily from fossil fuel combustion and biomass burning in East Asia and long-range transported to Okinawa. C_2 diacid showed a significant positive correlation with fine mode K^+ ($r = 0.85$), indicating that biomass burning contributed significantly to fine mode C_2 diacid in Okinawa aerosols.”

Please see lines 503-506 in the revised MS.

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

Response: Omitted.

P26526L15-L18: 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.

Response: We appreciate the referee's suggestion for discussion based on slopes of linear regression between the measured species. The authors understand that inclusion of this parameter can give some important information about the formation processes of diacids and related

compounds in size-segregated aerosols. The scatter plots for some major diacids and related compounds are given below. We found that there is no significant difference on the slopes of linear regression lines among most of chemical species (excluding the correlation of oxalic acid with glutaric acid and glyoxal) in fine and coarse modes. Although this is probably because of small numbers ($N = 5$) of data sets in this study, we are not sure that discussion on slopes of linear regression lines will scientifically sound for this paper or not due to small number of data sets. Therefore, we decided not to include any discussion on the slopes of the linear regression in the revised MS.

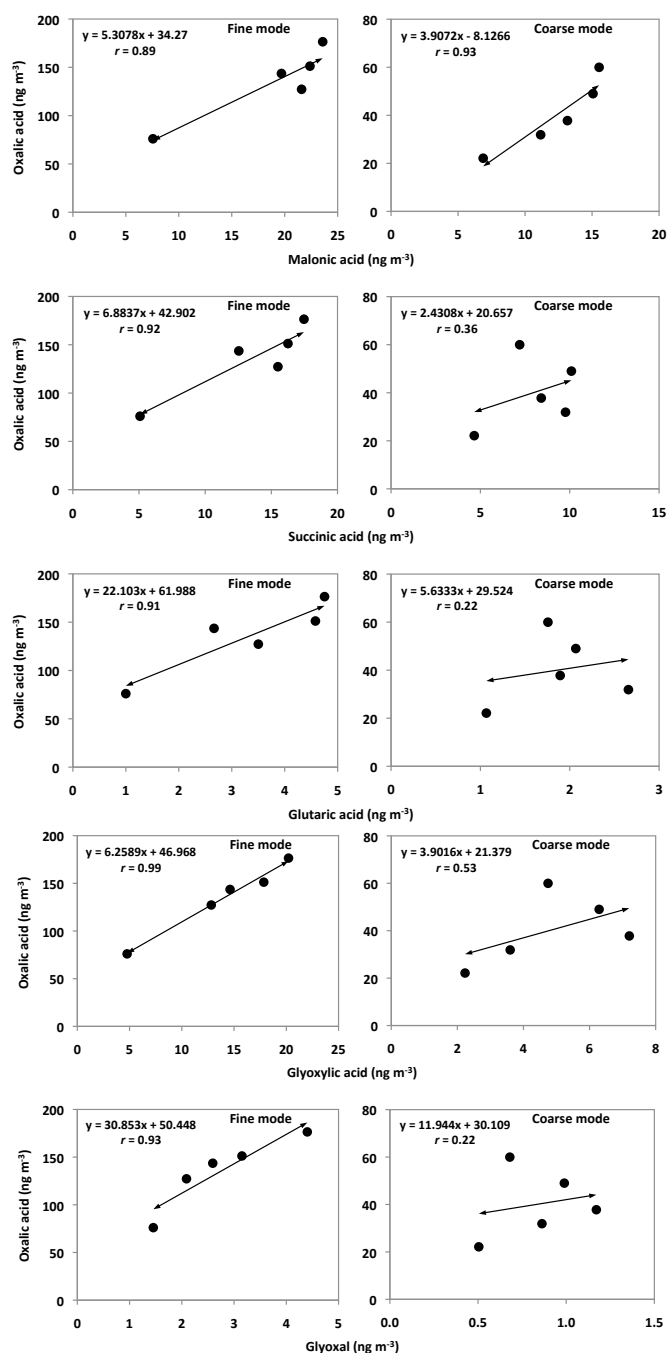


Figure: Linear regression of oxalic acid (C_2) with malonic (C_3), succinic (C_4), glutaric (C_5), glyoxylic acid (ωC_2) and glyoxal (Gly) in fine and coarse modes.

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

Response: We are sorry for this mistake. The correction was made in the revised MS. Please see lines 541-542.

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.

Response: The sentence has been rephrased as “Because C₄ is oxidized to C₃, an increase in the C₃/C₄ ratio indicates an increased photochemical processing.” The use of abbreviation has been revised in the revised MS. Please see lines 546-547, 572 and 594.

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?

Response: Based on the comments, the sentences were modified as follows.

“C₉ is a tracer of biogenic sources. Kawamura and Gagosian (1987) reported that C₉ is derived from the photooxidation of unsaturated fatty acids such as oleic (C_{18:1}) and linoleic (C_{18:2}) acids that are produced from the sea surface microlayers to the marine atmosphere with sea salt particles. These unsaturated fatty acids, which are coated in sea salt particles, predominantly reside in the coarse size range (Mochida et al., 2007; Aggarwal et al., 2010). The major peak of C₉ on coarse mode is due to the heterogeneous particle-phase oxidation of unsaturated fatty acids on the sea salt surface. We found significant correlation of C₉ with Na⁺ ($r = 0.85$) in coarse mode. This correlation is consistent with the idea that the precursors of C₉ are emitted from the ocean surface together with sea salt particles in coarse mode.”

Please see lines 559-567 in the revised MS.

“Ph is directly emitted from combustion sources and secondarily produced in the atmosphere by the photooxidation of polycyclic aromatic hydrocarbons such as naphthalene (NAP) and o-xylene derived from incomplete combustion of fossil fuel (Kawamura and Kaplan, 1987). NAP is largely exists in gas-phase and has been suggested to be a major precursor of Ph in the atmosphere (Schauer et al., 1996). The major peak of Ph on fine mode might be due to the preferential production of Ph via gas-phase photooxidation of NAP followed by subsequent condensation onto pre-existing fine mode particles during long-range transport. The high levels of NAP were found in gas-phase and aerosols in source regions in East Asia (Liu et al., 2007; Tao et al., 2007), which indicated NAP as a potential precursor of Ph diacid in Okinawa aerosols. The high levels of precursors (NAP) in the source regions might favor the significant secondary production of Ph during long-range transport in the western North Pacific. Moreover, the enrichment of Ph in fine mode further suggests that preferential origin of this diacid is related to combustion sources either by primary emission and/or secondary production from the precursor compounds, which is consistent with other anthropogenic constituents such as SO₄²⁻, NH₄⁺ and K⁺.”

Please see lines 574-588 in the revised MS.

“Ph diacid originates from various anthropogenic sources whereas C₉ diacid is produced by the oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987; Kawamura and Ikushima, 1993). Therefore, Ph/C₉ ratio is mostly used as marker to know the source strength of anthropogenic and biogenic sources of diacids. The higher Ph/C₉ ratio shows more influence of anthropogenic sources whereas lower ratio shows more influence of biogenic sources.”

Please see lines 594-598 in the revised MS.

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.

Response: Based on the suggestion, we revised the paragraph as follows.

“Although air masses during the sampling period are mostly originated from Siberia, Mongolia,

Korea and North China (Figure 2), where unsaturated fatty acids of higher plant origin are abundantly supplied to this marine receptor site, sea surface microlayers in the surroundings of Okinawa can also emit unsaturated fatty acids abundantly. The positive correlation of ωC_9 with Na^+ ($r = 0.83$) can also be seen in coarse mode. This suggests that the major peak of ωC_9 on the coarse mode may be due to the heterogeneous oxidation of unsaturated fatty acids of marine phytoplankton origin on the surface of sea salt particles. This result further suggests enhanced input of biogenic organic precursors derived from the ocean on the coarse size range in Okinawa aerosols.”

Please see lines 646-654 in the revised MS.

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

Response: Deleted.

Response to the Comments of Referee #3

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

Response: We thank the reviewer's careful reading and important comments, based on which we tried to improve the quality of our manuscript as below.

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.

Response: We agree with the referee's comment that precipitation event can affect the transport of pollutants. However, the precipitation event occurred occasionally during the sampling period in Okinawa. The total amount of precipitation was found to be 8.5 mm on March 22 for the sample OKI-1, 9.5 mm on March 25 for the sample OKI-2, 38 mm on March 30 for the sample OKI-3, 18 mm on April 03 and April 06 for the sample OKI-4 and 28 mm on April 13 for the sample OKI-5. We tried to get the satellite image of daily precipitation data for the source region. However, we did not find the daily precipitation map for the source region. Therefore, we downloaded the precipitation anomalies for March and April 2008 as the collection of aerosol samples in Okinawa was performed during 18 March to 13 April 2008.

The global map of precipitation data obtained from the website: [http://www.ncdc.noaa.gov/temp-and-precip/global-maps/200803?products\[\]=map-prcp](http://www.ncdc.noaa.gov/temp-and-precip/global-maps/200803?products[]=map-prcp) for March and April 2008, which is shown below, also shows very small precipitation in the source region such as China and Mongolia as well as Siberia. These points were briefly added in the revised MS as follows.

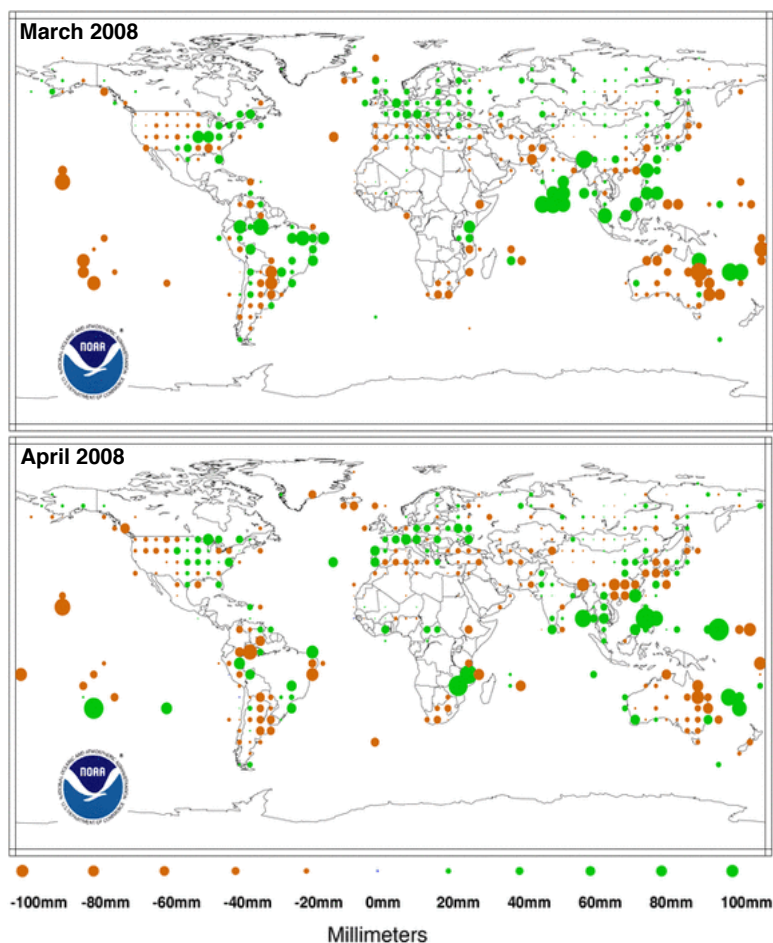
“The precipitation event occurred occasionally during the campaign with the total amounts of 8.5 mm on March 22 for OKI-1, 9.5 mm on March 25 for OKI-2, 38 mm on March 30 for OKI-3, 18 mm on April 03 and April 06 for OKI-4 and 28 mm on April 13 for OKI-5 sample set.”

Please see lines 161-164 in the revised MS.

“The scavenging of aerosols by precipitation that could result in lower concentrations of aerosol particles in Okinawa might be insignificant during the sampling periods.”

Please see lines 192-193 in the revised MS.

Precipitation Anomalies
National Climatic Data Center/NESDIS/NOAA



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

Response: Thank you for the important comment. We added following sentences in the revised MS.

“Moreover, the abundant presence of Ph may also be caused by enhanced emission of phthalates from plastics used in heavily populated and industrialized regions in China and the subsequent long-range atmospheric transport to Okinawa. Phthalic acid esters are used as plasticizers in resins and polymers (Simoneit et al., 2005). They can be released into the air by evaporation because they are not chemically bonded to the polymer.” Please see lines 230-234 in the revised MS.

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.

Response: After a review on the literature about limestone dust in Okinawa (Shimada et al., 2015), we found that there is a contribution of local limestone dust in addition to long-range transport from Siberia and Mongolia. However, as shown in Figure 5c, Ca^{2+} showed coarse mode peak in smaller size range either at 2.1-3.3 μm or 3.3-4.7 μm and thus the contribution of local dust to the coarse mode Ca^{2+} in Okinawa may be small. The recent study of Bien et al. (2014) suggested that that Ca^{2+} is mostly associated with upper coarse mode size range of $D_p > 7.0 \mu\text{m}$ when the contribution of locally produced dust is significant. Hence, we have added following sentences in the revised MS.

“There is natural limestone caves formed by elevating coral reefs in Okinawa Island. Although local limestone dust may also be re-suspended to the atmosphere by wind (Shimada et al., 2015), the contribution of local dust to the Ca^{2+} concentration in Okinawa may be small. This interpretation

can be supported by the fact that the peak of Ca^{2+} was appeared in lower coarse size range of 2.1-3.3 or 3.3-4.7 μm . It has been suggested that Ca^{2+} is likely associated with the upper coarse size range when the contribution of locally produced soil particles is significant (Bian et al., 2014). The smaller coarse mode Ca^{2+} is likely associated with long-range transported Asian dust to Okinawa. Moreover, concentrations of Ca^{2+} in coarse mode were found to be much higher in OKI-1 ($0.51 \mu\text{g m}^{-3}$) and OKI-2 ($0.60 \mu\text{g m}^{-3}$) than that in OKI-5 sample ($0.15 \mu\text{g m}^{-3}$). Backward trajectories also indicated that the air masses originated from Mongolia and Siberia are transported to Okinawa during the collection of OKI-1 and OKI-2 samples whereas OKI-5 sample has an influence of marine air masses.”

Please see lines 279-290 in the revised MS.

Pp. 26521 line 28: The uptake coefficient of SO_2 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.

Response: Unfortunately, we do not have the pH data of the water extracts of size-segregated aerosols. Moreover, indirect proxies are commonly used to represent the acidic or alkaline nature of particle. The most frequently used proxy is the “ion balance”. Average equivalent ratios of total cations to anions in fine mode varied from 0.75 for the size bin of 0.65-1.1 μm to 0.84 for the size bin of 0.43-0.65 μm . This result indicates that fine mode of Okinawa aerosols was apparently acidic.

However, we also agree with the Referee #2 comments that high LWC at 0.65-1.1 μm and high correlation (0.92) of LWC with SO_4^{2-} owing to the fact that the calculated LWC is based on the abundant presence of SO_4^{2-} in fine mode. Therefore, the sentences “The high LWC at 0.65-1.1 μmin fine mode” have been deleted and the correction has been made accordingly as follows.

“High correlation of LWC was found with SO_4^{2-} ($r = 0.92$) in fine mode. This result suggests that the enrichment of SO_4^{2-} in fine mode enhanced the LWC in fine mode of Okinawa aerosols.”

Please see lines 355-357 in the revised MS.

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.

Response: Based on the comment, we rewrote the sentences as follows.

“Size distribution of methanesulfonate (MSA^-) is similar to that of SO_4^{2-} (Figure 5i) in Okinawa. MSA^- showed a strong correlation with SO_4^{2-} ($r = 0.89$) in fine mode, suggesting that MSA^- should have similar origin with SO_4^{2-} in fine mode. Although MSA^- is believed to be produced by gas-to-particle conversion via the oxidation of dimethyl sulfide (DMS) emitted from the ocean (Quinn et al., 1993; Kerminen et al., 1997b), there is some indirect evidence that liquid-phase production might also be possible (Jefferson et al., 1998). Biomass burning also produces DMS in the atmosphere (Meinardi et al., 2003; Geng and Mu, 2006). MSA^- showed high correlation with K^+ or NH_4^+ ($r = 0.92$) in fine mode, indicating that the enhanced emission of DMS from biomass burning followed by the subsequent oxidation during long-range transport may have contributed significantly to the fine mode MSA in Okinawa. Moreover, MSA^- can also be produced in fine mode by the oxidation of DMS that is emitted from marine phytoplankton in the surrounding ocean. It is noteworthy that East Asian aerosols also travelled over the marine regions including the East China Sea, Sea of Japan and Pacific Ocean during long-range atmospheric transport.”

Please see lines 358-370 in the revised MS.

Pp. 26522 line 10 onwards: I think this section needs to be written in a better way. The uptake of gas-phase NH_3 to form particle-phase NH_4^+ is not affected by the presence of SO_4^{2-} , rather the pH value of the particle-phase. When the counter ions other than H^+ are present in the particles, NH_4^+ is very unlikely to be present unless $(\text{NH}_4)_2\text{SO}_4$ is thermodynamically favorable. What the authors

meant here is most likely that acidic 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.

Response: Following the suggestions, we revised the text as follows.

“NH₄⁺ in the Okinawa aerosols shows a unimodal size distribution with a peak at 0.65-1.1 μm (Figure 5h), indicating that NH₄⁺ is mainly formed by gas-to-particle conversion via the reaction with H₂SO₄ and HNO₃. Interestingly, the size distribution of NH₄⁺ is similar to that of SO₄²⁻ and diacids such as oxalic acid (Figure 5g and 7a). We also found a strong correlation between SO₄²⁻ and NH₄⁺ on the fine mode ($r = 0.99$).”

Please see lines 374-378 in the revised MS.

“NH₃ is an alkaline gas that neutralizes the acidic particles in the atmosphere. Kerminen et al. (1997a) proposed that particulate NH₄⁺ is secondarily formed via heterogeneous reactions of gaseous NH₃ with acidic species (H₂SO₄ and HNO₃). The reaction of NH₃ with H₂SO₄ is favored over its reaction with HNO₃. The average NH₄⁺/SO₄²⁻ equivalent ratios in fine mode particles in Okinawa varied from 0.36 for the size bin of 1.1-2.1 μm to 0.81 for the size bin of 0.43-0.65 μm, indicating that NH₃ was not abundant enough to neutralize all SO₂ and hence H₂SO₄ and NH₄SO₄ were present in addition to (NH₄)₂SO₄ in fine mode.”

Please see lines 383-389 in the revised MS.

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

Response: Following the comment, we rephrase the text as follows.

“It is notable that higher LWC in fine mode can influence the SOA formation via gas to particle conversion of organic precursors via reactive uptake on aerosols.”

Please see lines 406-408 in the revised MS.

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?

Response: Referee #2 also commented on this issue. we calculated the equivalent ratio of NH₄⁺/SO₄²⁻ in size-segregated aerosols to evaluate the excess amount of NH₃ that can react with oxalic acid (C₂) to form ammonium oxalate in fine fraction of Okinawa. The equivalent ratio of NH₄⁺/SO₄²⁻ varied from 0.36 for the size bin of 1.1-2.1 μm to 0.81 for the size bin of 0.43-0.65 μm in fine mode. These values suggest that NH₃ was not sufficient to neutralize all SO₂ and hence there was no NH₃ to further react with C₂ to form ammonium oxalate in fine mode. Therefore, the sentences “The occurrence of ammonium oxalate.....biomass burning aerosols” has been deleted in the revised MS.

ISORROPIA II gives the equilibrium concentration of chemical composition in the gas-phase, solid-phase and liquid-phase. We used ISORROPIA II to estimate liquid water content (LWC) in size-segregated aerosols. However, the significant positive correlation between C₂ and NH₄⁺ ($r = 0.89$) in fine fraction suggested that C₂ is also a secondary photochemical product. This point has been mentioned in the revised MS.

Please see line 502-503 in the revised MS.

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.

Response: To avoid any confusion, we have re-written the sentence as “Huang et al. (2006) observed that fine mode WSOC was primarily derived from combustion sources and secondarily

produced in the atmosphere by the photochemical oxidation of VOCs.”

Please see lines 411-413 in the revised MS.

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.

Response: Following the comment, we have revised the content as follows.

“Because WSOC is an important fraction of OC in Okinawa aerosols, high loadings of WSOC in aerosols of continental air mass origin suggest that both fossil fuel combustion and biomass burning in East Asia may have a significant influence on the composition of water-soluble organic aerosols over the western North Pacific Rim.”

Please see lines 428-431 in the revised MS.

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?

Response: Following the comment, we modified the sentences as below.

“Primary emission from fossil fuel combustion and biomass burning and secondary production from photooxidation of VOCs are considered to be the major sources of OC in atmospheric aerosols (Aggarwal and Kawamura, 2009; Jung et al., 2010). Primary emission from biomass burning or photooxidation of biomass burning derived precursors might be a dominant source of fine mode OC in Okinawa aerosols. This interpretation is supported by the fact that OC showed strong correlation ($r = 0.95$) with K^+ in fine mode. The fine mode OC showed significant positive correlations with SO_4^{2-} ($r = 0.93$) and NH_4^+ ($r = 0.91$), suggesting secondary photochemical formation characteristics of OC in fine mode in Okinawa.”

Please see lines 434-441 in the revised MS.

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.

Response: We modified the sentences as follows.

“Source contributions and secondary processes that may convert VOCs to a more soluble form and surface area of fine particles could cause the higher WSOC/OC ratios in fine mode. Biomass burning-derived OC is highly water-soluble and usually resides in fine mode whereas coarse mode OC contains high molecular weight organic compounds emitted by soil resuspension and emissions of pollens and fungal spores, which are less water-soluble (Wang et al., 2011; Mkoma et al., 2013). Biomass burning significantly contributed to fine mode WSOC in Okinawa and thus WSOC is secondarily produced from oxidation of biomass burning-derived VOCs (Kundu et al., 2010). However, the primary emission of fine mode WSOC from biomass burning could not be excluded. Moreover, accumulation of gas-phase precursors of WSOC may occur preferentially in the particle size with the greatest surface area (Kanakidou et al., 2005). It has been proposed that fine particles offer more surface area and thus reaction rate is more on the surface of fine particles than the coarse particles (Kanakidou et al., 2005). The higher WSOC/OC ratio in fine particles than coarse particles has also been observed in long-range transported East Asian aerosols over Northern Japan (Agarwal et al., 2010).”

Please see lines 450-463 in the revised MS.

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

Response: Please note that concentration of WSOC is not included in ISORROPIA II model for the estimation of LWC. LWC calculated using ISORROPIA II in our study is independent of WSOC. Therefore, we believe that the correlation between LWC and WSOC/OC ratio can give some information about the possible aqueous-phase production of WSOC from OC during long-range transport. However, the actual observation of LWC for the aerosol samples, as suggested by referee #2, is not possible at this stage. Therefore, we rephrased the text and included other possibilities for the production of WSOC in fine mode as follows.

“WSOC also contribute to aerosol LWC although their ability to absorb water is significantly less than that of inorganics (Ansari and Pandis, 2000). Speer et al. (2003) and Engelhart et al. (2011) also noted that inorganic aerosols are associated with 62-80% of aerosol LWC. Moreover, organic species are not taken into account in ISORROPIA II for the calculation of LWC. It is noteworthy that WSOC/OC ratio and LWC significantly correlate in the fine mode with $r = 0.87$ whereas the negative correlation was found in the coarse mode ($r = -0.19$), suggesting the possibility of photochemical production of WSOC from OC in aerosol aqueous-phase in fine mode of Okinawa aerosols. There may also be other important sources of fine mode WSOC in Okinawa aerosols such as primary emission from biomass burning and secondary formation via gas-phase photochemical reactions during long-range atmospheric transport (Hagler et al., 2007; Lim et al., 2010). The strong correlation of WSOC with K^+ in fine mode suggests a substantial contribution of biomass burning to fine mode WSOC in Okinawa aerosols.”

Please see lines 464-475 in the revised MS.

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.

Response: Following the referee's comments, we have revised the sentences as follows.

“The condensation mode of C₂ is likely produced photochemically in the gas-phase followed by condensation onto pre-existing particles at 0.1-0.5 μm (Huang et al., 2006). In the atmosphere, the gas-phase oxidation of isoprene, toluene and ethene leads to the formation of semi-volatile gaseous organic precursors such as Gly and MeGly, which are subsequently participated in aqueous-phase photochemical reaction to result in C₂ diacid (Carlton et al. 2006, 2007; Legrand et al. 2007). The fine mode peak of C₂ at the size of 0.65-1.1 μm in Okinawa aerosols suggests a preferential production of C₂ via the oxidation of precursors in the aerosol aqueous-phase during long-range atmospheric transport.”

Please see lines 493-500 in the revised MS.

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.

Response: We have revised the sentence as follows.

“We found that size distribution of C₂ diacid is similar to that of SO₄²⁻ (Figure 5g and 7a), suggesting a secondary formation of C₂ possibly in aerosol aqueous-phase.”

Please see lines 500-501 in the revised MS.

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.

Response: Laboratory experiments have proposed the formation of C₂ by aqueous-phase oxidation

of precursors such as shorter-chain diacids (C_3 - C_5) as well as ω -oxoacids (ωC_2) and α -dicarbonyls (Gly and MeGly) (Ervens and Volkamer, 2010, Pavuluri et al., 2015). One interesting finding in our study is that the precursors of C_2 (C_3 - C_5 diacids, ωC_2 and Gly) in Okinawa aerosols are also enriched in fine mode and showed high correlation with LWC. These results indicate that the enrichment of C_2 precursors and presence of LWC in fine mode favors to produce C_2 in fine mode in Okinawa. Therefore, we have revised the text and added some new sentences in the revised MS as follows.

“LWC of a particle can influence the production of C_2 via the changes in gas/particle partitioning of gaseous organic precursors and subsequent heterogeneous reaction in aerosol aqueous-phase.” Please see lines 515-517.

“A strong positive correlation ($r = 0.92$) of C_2 with LWC was found in fine mode. This result supports the possibility of aqueous phase production of C_2 via the oxidation of C_2 precursors in fine mode of Okinawa aerosols.” Please see lines 518-521.

“This result is further supported by the fact that C_3 - C_5 diacids were also enriched in the fine mode (Figure 7b-d) and showed good correlations with LWC ($r = 0.82$ - 0.89) possibly due to the enhanced secondary production from oxidation of its precursor compounds in aerosol aqueous-phase.” Please see lines 524-527.

“It is noteworthy that ωC_2 and Gly are also enriched in fine mode in Okinawa aerosols.” Please see lines 533-534.

Pp. 26526 line 15: This is only one way to produce C_2 diacid. Their good correlations do not necessarily indicate that C_2 diacid is formed from C_3 - C_5 diacids. It is also plausible that they all originate from the photooxidation of a mixture of VOCs during transport.

Response: Based on the comment, we added a new sentence as follows.

“ C_2 can also be produced by gas-phase oxidation of various VOCs including toluene, ethene and isoprene followed by subsequent oxidation in aerosol aqueous-phase during long-range atmospheric transport (Legrand et al., 2007; Lim et al., 2005).” Please see lines 527-529.

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 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.

Response: Thank you for your suggestion. However, we acknowledge that the data on size distribution of ω -oxoacids, pyruvic acid and α -dicarbonyls are sparse in the literature. ω -Oxoacids (ωC_2 - ωC_9) and α -dicarbonyls (Gly and MeGly) are important precursor of diacids in atmospheric aerosols. Therefore, their size distributions can give information about their sources and formation processes in the atmosphere.

We detected four ω -oxoacids (Table 2) in size-segregated samples. However, we have discussed the size distributions of ωC_2 and ωC_9 in the text because the size distribution of ωC_2 is similar to that of C_2 whereas ωC_9 showed size distribution similar to that of C_9 . This result suggests that ωC_2 is an important precursor of C_2 whereas ωC_9 is important for C_9 diacid in Okinawa.

We measured Gly and MeGly, which are smallest α -dicarbonyls and crucial SOA precursor because they are highly water-soluble and reactive to OH radical. Gly peaked in the fine mode whereas MeGly showed peaks in both fine and coarse modes. This result indicated their different sources and formation processes in Okinawa. Interestingly, size distribution of pyruvic acid is similar to that of MeGly, indicating their similar sources in Okinawa aerosols. Several studies suggested that Pyr is produced via the aqueous-phase oxidation of MeGly that is a gas-phase oxidation product of isoprene emitted from the ocean surface. Gly and MeGly are important precursors of C_2 diacid in aqueous-phase. Therefore, the size distributions of Gly and MeGly can

influence the size distribution of C₂ in the atmosphere.

Based on these results, we strongly believe that the discussion on sources and formation processes of these compounds via investigating their size distributions would be useful to the readers of “Atmospheric Chemistry and Physics” and also very important to the research community for future studies.

However, following the referee’s comments, we decided to delete two sentences: “A bimodal size distribution of 4-oxobutanoic acid.....on sea salt particles” and “Soil dust or sea salt particles.....diameter greater than 2.1 μm (Fig. 5a-c)” in the revised MS.

1 **Dicarboxylic acids, oxoacids, benzoic acid, α -dicarbonyls, WSOC, OC, and ions in spring**
2 **aerosols from Okinawa Island in the western North Pacific Rim: Size distributions and**
3 **formation processes**

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9 Abstract

10 Size-segregated aerosols (9-stages from <0.43 to >11.3 μm in diameter) were collected at Cape
11 Hedo, Okinawa in spring 2008 and analyzed for water-soluble diacids ($\text{C}_2\text{-C}_{12}$), ω -oxoacids ($\omega\text{C}_2\text{-}$
12 ωC_9), pyruvic acid, benzoic acid and α -dicarbonyls ($\text{C}_2\text{-C}_3$) as well as water-soluble organic carbon
13 (WSOC), organic carbon (OC) and major ions (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} , and
14 MSA^-). In all the size-segregated aerosols, oxalic acid (C_2) was found as the most abundant species
15 followed by malonic and succinic acids whereas glyoxylic acid (ωC_2) was the dominant oxoacid
16 and glyoxal (Gly) was more abundant than methylglyoxal. Diacids ($\text{C}_2\text{-C}_5$), ωC_2 and Gly as well as
17 WSOC and OC peaked at $0.65\text{-}1.1$ μm in fine mode whereas azelaic (C_9) and 9-oxononanoic (ωC_9)
18 acids peaked at $3.3\text{-}4.7$ μm in coarse mode. Sulfate and ammonium are enriched in fine mode
19 whereas sodium and chloride are in coarse mode. Strong correlations of $\text{C}_2\text{-C}_5$ diacids, ωC_2 and Gly
20 with sulfate were observed in fine mode ($r = 0.86\text{-}0.99$), indicating a commonality in their
21 secondary formation. Their significant correlations with liquid water content in fine mode ($r = 0.82\text{-}$
22 0.95) further suggest an importance of the aqueous-phase production in Okinawa aerosols. They
23 may have also been directly emitted from biomass burning in fine mode as suggested by strong
24 correlations with potassium ($r = 0.85\text{-}0.96$), which is a tracer of biomass burning. The coarse mode
25 peaks of malonic and succinic acids were obtained in the samples with marine air masses,
26 suggesting that they may be associated with the reaction on sea salt particles. Bimodal size
27 distributions of longer-chain diacid (C_9) and oxoacid (ωC_9) with a major peak in the coarse mode
28 suggest their production by photooxidation of biogenic unsaturated fatty acids via heterogeneous
29 reactions on sea salt particles.

30 **Keywords:** Water-soluble organic species, ions, size-segregated aerosols, unimodal distribution,
31 bimodal distribution, secondary aerosols.

32 **1 Introduction**

33 Tropospheric aerosol is an important environmental issue because it can dramatically reduce the
34 visibility (Jacobson et al., 2000; Kanakidou et al., 2005), affect the radiative forcing of climate
35 (Seinfeld and Pandis, 1998), and cause a negative impact on human health (Pope and Dockery,
36 2006). All of these effects strongly depend on the abundances of aerosols and their chemical and
37 physical properties in different sizes. Particles in diameter of 0.1-1.0 μm are very active in
38 scattering and absorbing incoming solar radiation and have a direct impact on climate (Ramanathan
39 et al., 2001; Seinfeld and Pankow, 2003). The knowledge of size distributions of chemical
40 components is thus essential to better understand their potential contributions to climate change and
41 pollution control. Their size distribution also provides evidences for the sources and formation
42 pathways of the atmospheric particles.

43 The emission sources and multiple secondary formation pathways of organic aerosols are not
44 well understood. Organic compounds account for up to 70% of fine aerosol mass and potentially
45 control the physicochemical properties of aerosol particles (Davidson et al., 2005; Kanakidou et al.,
46 2005). Low-molecular-weight diacids are one of the most abundant organic compound classes in
47 the atmosphere (Kawamura and Ikushima, 1993; Kawamura et al., 1996). They are primarily
48 derived from incomplete combustion of fossil fuel and biomass burning (Kawamura and Kaplan,
49 1987; Falkovich et al., 2005), and secondarily produced in the atmosphere via photooxidation of
50 unsaturated fatty acids and volatile organic compounds (VOCs) from biogenic and anthropogenic
51 sources (Kawamura and Gagosian, 1987; Kawamura et al., 1996; Sempéré and Kawamura, 2003).
52 The ability of organic aerosols to act as cloud condensation nuclei (CCN) seems to be closely
53 related to their mass-based size distributions (Pradeep Kumar et al., 2003; Ervens et al., 2007).

54 The increasing atmospheric burden of organic aerosols is associated with natural and
55 anthropogenic emissions in the continental regions. Organic aerosols are eventually transported to
56 the oceanic regions. The rapid industrialization in East Asia is expected to have important
57 influences on global atmospheric chemistry over the next decades (Wang et al., 2013; Tao et al.,
58 2013; Bian et al., 2014). Large amounts of coal burning and biomass burning in East Asia add more
59 anthropogenic aerosols altering the aerosol chemical composition in the remote Pacific atmosphere

60 (Mochida et al., 2007; Miyazaki et al., 2010; Agarwal et al., 2010; Wang et al., 2011; Engling et al.,
61 2013). Water-soluble diacids and related compounds as well as major ions are **previously** studied
62 for their size distributions in remote marine aerosols (Kawamura et al., 2007; Mochida et al., 2007;
63 Miyazaki et al., 2010), whereas their size-segregated characteristics have not been studied in
64 Okinawa Island.

65 We collected size-segregated aerosol samples with 9-size ranges in spring 2008 in Cape Hedo,
66 Okinawa. Cape Hedo is located on the northern edge of Okinawa Island and can serve as a suitable
67 site for the observation of atmospheric transport of East Asian aerosols with insignificant
68 interference from local emission sources (Takami et al., 2007). The samples were analyzed for
69 dicarboxylic acids (C_2 - C_{12}) and related compounds such as ω -oxoacids (ωC_2 - ωC_9) and pyruvic acid
70 (C_3) as well as α -dicarbonyls (C_2 - C_3) to better understand the sources and processing of water-
71 soluble organic compounds at this marine receptor site in the western North Pacific Rim. Size-
72 segregated samples were also analyzed for water-soluble organic carbon (WSOC), organic carbon
73 (OC), and major inorganic ions. The role of liquid water content of aerosol in the size distribution
74 of diacids and related compounds is discussed. The potential factors responsible for their size
75 distributions and the atmospheric implications of the size characteristics are also discussed.

76 **2 Materials and method**

77 **2.1 Site description and aerosol collection**

78 The geographical location of Okinawa Island (26.87°N and 128.25°E) and its surroundings in East
79 Asia are shown in Figure 1. Okinawa is located in the outflow region of **continental** aerosols and on
80 the pathways to the Pacific. Cape Hedo has been used as a supersite of Atmospheric Brown Clouds
81 project to study the atmospheric transport of Chinese aerosols and their chemical transformation
82 during long-range transport from East Asia (Takiguchi et al., 2008; Kunwar and Kawamura, 2014).
83 The sampling site at Cape Hedo is about 60 m a.s.l.

84 Size-segregated aerosol samples were collected at Cape Hedo Atmospheric and Aerosol
85 Monitoring Station (CHAAMS) in March 18 to April 13, 2008. This period is characterized by the
86 westerly wind in the lower troposphere, which is the principal process responsible for the transport

87 of both fossil fuel combustion and biomass burning aerosols in East Asia to the western North
88 Pacific. 9-Stage Andersen Middle Volume Impactor (Tokyo Dylec Company, Japan; 100 L min⁻¹)
89 was used for the collection of size-segregated samples. The sampler was equipped with quartz fiber
90 filters (QFF, 80 mm in diameter) that were pre-combusted at 450°C for 6 h in a furnace to eliminate
91 the adsorbed organic compounds. A total of five sets (OKI-1 to OKI-5) of size-segregated aerosol
92 samples were collected. Each sample set consists of nine filters for the sizes of <0.43, 0.43-0.65,
93 0.65-1.1, 1.1-2.1, 2.1-3.3, 3.3-4.7, 4.7-7.0, 7.0-11.3, and >11.3 μm. The filter was placed in a
94 preheated 50 mL glass vial with a Teflon-lined screw cap and stored in a freezer at the station. The
95 samples were stored in darkness at -20°C prior to analysis in Sapporo. One set of field blank was
96 collected by placing a pre-combusted QFF for 30s without sucking air before installing real QFF
97 into the sampler.

98 2.2 Analytical procedures

99 Diacids and related compounds were analyzed using the method reported in Kawamura and
100 Ikushima (1993), and Kawamura (1993). Aliquot of the filters were extracted with organic-free
101 ultrapure water (specific resistivity >18.2 MΩ-cm) under ultrasonication. The extracts were passed
102 through glass column packed with quartz wool to remove insoluble particles and filter debris. The
103 extracts were concentrated using a rotary evaporator under vacuum and derivatized to dibutyl esters
104 and dibutoxy acetals with 14% BF₃ in *n*-butanol at 100°C. Acetonitrile and *n*-hexane were added
105 into the derivatized sample and washed with organic-free pure water. The hexane layer was further
106 concentrated using a rotary evaporator and dried to almost dryness by N₂ blowdown and dissolve in
107 a known volume of *n*-hexane. A 2 μL aliquot of the sample was injected into a capillary GC
108 (Hewlett-Packard HP6890) equipped with an FID detector. Authentic diacid dibutyl esters were
109 used as external standards for the peak identification and quantification. Identifications of diacids
110 and related compounds were confirmed by GC-mass spectrometry. Recoveries of authentic
111 standards spiked to a pre-combusted QFF were 85% for oxalic acid (C₂) and more than 90% for
112 malonic to adipic (C₃-C₆) acids. The detection limits of diacids and related compounds were ca.
113 0.002 ng m⁻³. The analytical errors in duplicate analyses are within 10% for major species.

114 To measure water-soluble organic carbon (WSOC), a punch of 20 mm diameter of each QFF
115 was extracted with organic-free ultrapure water in a 50 mL glass vial with a Teflon-lined screw cap
116 under ultrasonication for 15 min. The water extracts were subsequently passed through a syringe
117 filter (Millex-GV, Millipore; diameter of 0.22 μm). The extract was first acidified with 1.2 M HCl
118 and purged with pure air in order to remove dissolved inorganic carbon and then WSOC was
119 measured using a total organic carbon (TOC) analyzer (Shimadzu TOC-V_{CSH}) (Miyazaki et al.,
120 2011). External calibration was performed using potassium hydrogen phthalate before analysis of
121 WSOC. The sample was measured three times and the average value was used for the calculation of
122 WSOC concentrations. The analytical error in the triplicate analysis was 5% with a detection limit
123 of 0.1 $\mu\text{gC m}^{-3}$.

124 Organic and elemental carbon (OC and EC) was determined using a Sunset Lab carbon analyzer
125 following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal
126 evolution protocol as described in detail by Wang et al. (2005a). A filter disc of 1.5 cm^2 was placed
127 in a quartz tube inside the thermal desorption chamber of the analyzer and then stepwise heating
128 was applied. Helium (He) gas is applied in the first ramp and is switched to mixture of He/O₂ in the
129 second ramp. The evolved CO₂ during the oxidation at each temperature step was measured with
130 non-dispersive infrared (NDIR) detector system. The detection limits of OC and EC were ca. 0.05
131 and 0.02 $\mu\text{gC m}^{-3}$, respectively. The analytical errors in the triplicate analysis of the filter sample
132 were estimated to be 5% for OC and EC. EC was detected only in fine fractions. The concentration
133 of total carbon (TC) was calculated by summing the concentrations of OC and EC in each size
134 fraction.

135 For the determination of major ions, a punch of 20 mm diameter of each filter was extracted with
136 organic-free ultrapure water under ultrasonication. These extracts were filtered through a disc filter
137 (Millex-GV, Millipore; diameter of 0.22 μm) and injected to ion chromatograph (Compact IC 761;
138 Metrohm, Switzerland) for measuring MSA^- , Cl^- , SO_4^{2-} , NO_3^- , Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+}
139 (Boreddy and Kawamura, 2015). Anions were separated on a SI-90 4E Shodex column (Showa
140 Denko; Tokyo, Japan) using a mixture of 1.8 mM Na_2CO_3 and 1.7 mM NaHCO_3 solution at a flow
141 rate of 1.2 mL min^{-1} as an eluent and 40 mM H_2SO_4 for a suppressor. A Metrosep C2-150 Metrohm

142 column was used for cation analysis using a mixture of 4 mM tartaric acid and 1 mM dipicolinic
143 acid solution as an eluent at a flow rate of 1.0 mL min⁻¹. The injected loop volume was 200 µL. The
144 detection limits for anions and cations were ca. 0.1 ng m⁻³. The analytical error in duplicate analysis
145 was about 10%.

146 Field blanks were extracted and analyzed like the real samples. However, blank levels were 0.1-
147 5% of the concentrations of real samples. The reported concentrations of organic and inorganic
148 species were corrected for the field blanks. All the chemicals including authentic standards were
149 purchased from Wako Pure Chemical Co. (Japan), except for 14% BF₃/n-butanol (Sigma-Aldrich,
150 USA).

151 2.3 Backward air mass trajectories and meteorology

152 The backward trajectories of air masses were computed for the sampling period using the Hybrid
153 Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model 4.0 developed by the National
154 Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (Draxler and
155 Rolph, 2013). The seven-day trajectories at 500 m above the ground level for the samples collected
156 in Okinawa are shown in Figure 2.

157 Meteorological data including ambient temperature, relative humidity, wind speed and
158 precipitation for each sample period were obtained from Japan Meteorological Agency
159 ([http://www/data/jma.go.jp](http://www.data/jma.go.jp)). During our campaign, the temperature, relative humidity and wind
160 speed ranged from 11.9 to 26.6°C (ave. 20.0±2.61°C), 43.0 to 91.0% (ave. 70.0±12.0%), 0.10 to
161 10.2 m s⁻¹ (ave. 3.73±1.99 m s⁻¹), respectively. The precipitation event occurred occasionally during
162 the campaign with the total amounts of 8.5 mm on March 22 for OKI-1, 9.5 mm on March 25 for
163 OKI-2, 38 mm on March 30 for OKI-3, 18 mm on April 03 and April 06 for OKI-4 and 28 mm on
164 April 13 for OKI-5 sample set.

165 2.4 Estimation of liquid water content (LWC) of aerosol

166 LWC of aerosol was calculated for the size-segregated samples collected in Okinawa Island using
167 the ISORROPIA II model (Fountoukis and Nenes, 2007). ISORROPIA II is a computationally
168 efficient and rigorous thermodynamic equilibrium model that exhibits robust and rapid convergence

169 under all aerosol types with high computational speed (Nenes et al., 1998). ISORROPIA II implies
170 the Zdanovskii-Stokes-Robinson equation and treats only the thermodynamics of K^+ - Ca^{2+} - Mg^{2+} -
171 NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosol system to estimate the LWC. Therefore, the measured
172 organic species such as diacids and related compounds are not included in ISORROPIA II. The
173 model was run as “reverse problem”, in which temperature, relative humidity and aerosol phase
174 concentrations of water-soluble inorganic ions were used as input for the estimation of aerosol
175 LWC.

176 3 Results and discussion

177 3.1 Size-segregated aerosol chemical characteristics

178 We use 2.1 μm as a split diameter between the fine and coarse mode particles. Table 1 presents the
179 concentrations of inorganic and carbonaceous species in the fine and coarse mode aerosols. Figure 3
180 shows the average concentrations of inorganic ions and organic matter (OM) in size-segregated
181 aerosols. Abundances of OM in the atmosphere are generally estimated by multiplying the
182 measured OC mass concentrations with the conversion factor of 1.6 for urban aerosols and 2.1 for
183 aged aerosols (Turpin and Lim, 2001). CHAAMS is located in the outflow region of East Asian
184 aerosols and local anthropogenic activities are insignificant. Because the aerosols reaching to
185 Okinawa are subjected to undergo the atmospheric oxidation during the long-range transport, the
186 fraction of oxygenated organic species is often high (Takami et al., 2007; Takiguchi et al., 2008;
187 Kunwar and Kawamura, 2014). Therefore, we used the conversion factor of 2.1, instead of 1.6 for
188 calculation of OM.

189 Okinawa was strongly affected by continental air masses from Siberia and Mongolia as well as
190 North China and Korea (Figure 2). It is difficult to specify the source regions of air masses for each
191 sample set because the sampling duration was 3-5 days. Each sample contains mixed continental
192 and oceanic air masses. The scavenging of aerosols by precipitation that could result in lower
193 concentrations of aerosol particles in Okinawa might be insignificant during the sampling periods.
194 OM was enriched in fine size fractions than the coarse size fractions (Figure 3). The elevated level
195 of OM in fine fractions in Okinawa (Table 1) suggests a substantial contribution of organic aerosols
196 primarily from combustion sources and secondarily from photochemical processes during long-

197 range atmospheric transport. The OM in fine mode aerosol in Okinawa might be consists of
198 oxygenated organic compounds such as diacids, ω -oxoacids and α -dicarbonyls.

199 Sulfate is the most abundant anion in fine fractions with a peak in 0.65-1.1 μm size whereas
200 chloride is the dominant anion in coarse fractions with a maximum in $>11.3 \mu\text{m}$ (Figure 3). The
201 cation budget is largely controlled by ammonium in fine fractions whereas sodium is the most
202 abundant cation in coarse fractions. The high abundance of SO_4^{2-} in fine particles suggests a
203 significant contribution of anthropogenic sources including industrial emissions in East Asia via
204 long-range transport of aerosols over the western North Pacific Rim. SO_4^{2-} is an anthropogenic
205 tracer of industrial activities whereas NH_4^+ is the secondary product of NH_3 that is largely derived
206 from the agricultural usage of nitrogen-based fertilizers (Pakkanen et al., 2001) and volatilization
207 from soils and livestock waste in East Asia (Huang et al., 2006). The dominant presences of Na^+
208 and Cl^- in coarse fractions suggest a substantial contribution from sea salt. Na^+ and Cl^- are emitted
209 from the ocean surface as relatively larger particles. Substantial amount of NO_3^- was detected in
210 coarse mode, suggesting a formation of $\text{Ca}(\text{NO}_3)_2$ or NaNO_3 in coarse fractions through the reactive
211 adsorption of gaseous HNO_3 onto pre-existing alkaline particles.

212 Diacids and related compounds detected in Okinawa are listed in Table 2 together with their
213 concentrations in the fine and coarse modes. Their molecular distributions in size-segregated
214 aerosols are shown in Figure 4. Oxalic acid (C_2) was found as the most abundant diacid followed by
215 malonic (C_3) and succinic (C_4) acids in all size-segregated aerosols. The predominance of C_2 in
216 size-segregated aerosols suggested that this diacid is produced by the photooxidation of VOCs and
217 other organic precursors in gas and aqueous-phase (Warneck, 2003; Carlton et al., 2006) during
218 long-range transport. The abundant presence of C_3 over C_4 diacid also indicates that this diacid was
219 produced via atmospheric photooxidation of organic precursors during long-range transport to
220 Okinawa (Kawamura and Sakaguchi, 1999; Kunwar and Kawamura, 2014). They can also be
221 emitted from primary sources such as fossil fuel combustion and biomass burning. Fossil fuel
222 combustion and biomass burning also emit numerous VOCs to the atmosphere, which are
223 ultimately oxidized to diacids via gas and aqueous-phase oxidation.

224 Phthalic (Ph) and adipic (C₆) acids are the next abundant diacids whereas ketomalonic acid (kC₃)
225 is more abundant than C₆ diacid in the size ranges of 0.43-0.65 μm to 0.65-1.1 μm. Ph and C₆
226 diacids originate from various anthropogenic sources and thus they can be used as anthropogenic
227 tracers. Ph primarily originates from coal burning and vehicle emission whereas photooxidation of
228 aromatic hydrocarbons such as naphthalene (NAP) and o-xylene derived from incomplete
229 combustion of fossil fuel form Ph via secondary processes (Kawamura and Kaplan, 1987).
230 Moreover, the abundant presence of Ph may also be caused by enhanced emission of phthalates
231 from plastics used in heavily populated and industrialized regions in China and the subsequent
232 long-range atmospheric transport to Okinawa. Phthalic acid esters are used as plasticizers in resins
233 and polymers (Simoneit et al., 2005). They can be released into the air by evaporation because they
234 are not chemically bonded to the polymer. Kawamura and Usukura (1993) reported that C₆ diacid is
235 an oxidation product through the reaction of cyclohexene with ozone (O₃). The high abundances of
236 Ph and C₆ diacids in Okinawa suggest the significant influence of anthropogenic sources in East
237 Asia via long-range transport of aerosols over the western North Pacific Rim.

238 Azelaic acid (C₉) is always more abundant than the adjacent suberic (C₈) and decanedioic (C₁₀)
239 acids in all the size-segregated aerosols. Kawamura and Gagosian (1987) proposed that C₉ is a
240 photooxidation product of biogenic unsaturated fatty acids such as oleic acid (C_{18:1}) containing a
241 double bond at C-9 position. Unsaturated fatty acids can be emitted from sea surface microlayers
242 and from local vegetation in Okinawa (Kunwar and Kawamura, 2014). Moreover, air masses in
243 spring are suggested to originate mostly from Russia and Mongolia as well as Korea based on
244 seven-day backward trajectory analyses. Such continental air masses can also bring C₉ via
245 atmospheric processing of biogenic unsaturated fatty acids during long-range transport. The
246 abundant presence of C₉ indicates that atmospheric oxidation of biogenic unsaturated fatty acids
247 also occurs in Okinawa aerosols during long-range transport. ω-Oxocarboxylic acids and α-
248 dicarbonyls were detected in the Okinawa aerosols. Glyoxylic acid (ωC₂) was identified as the most
249 abundant ω-oxoacid whereas glyoxal (Gly) was more abundant than methylglyoxal (MeGly) in all
250 the sizes. ωC₂ and Gly are the oxidation product of several anthropogenic and biogenic VOCs and
251 primary generated by fossil fuel combustion and biomass burning (Zimmermann and Poppe, 1996;

252 Volkamer et al., 2001), and are further oxidized to C_2 diacid (Myriokefalitakis et al., 2011). The
253 predominance of ωC_2 and Gly indicates their importance as key precursors of C_2 in Okinawa
254 aerosols.

255 3.2 Inorganic species

256 The particle size distributions of major ions are shown in Figure 5. Pearson correlation coefficients
257 (r) among the measured ions in different size modes are given in Table 3. Na^+ and Cl^- are mainly
258 derived from the ocean surface as sea salt particles in the marine atmosphere (Kumar et al., 2008;
259 Geng et al., 2009). The size distributions of Na^+ and Cl^- were found to be bimodal with two peaks
260 in coarse mode (Figure 5a and b). Their peaks at 2.1-3.3 or 3.3-4.7 μm and at $>11.3 \mu m$ suggest that
261 they are of marine origin due to bubble bursting of surface seawater. Andreas (1998) suggested that
262 the sea spray fall into two types that are defined as film and jet bubbles; film bubbles correspond to
263 the size of 0.5-5 μm whereas jet bubbles produce the size of 5-20 μm . Their coarse mode peaks at
264 2.1-3.3 μm or 3.3-4.7 as well as $>11.3 \mu m$ in Okinawa aerosols are associated with film and jet
265 bubbles. We found that size distribution of Mg^{2+} is similar to those of Na^+ and Cl^- with a significant
266 positive correlation to coarse mode Na^+ and Cl^- ($r = 0.98$), suggesting their similar origin and
267 sources.

268 A significant contribution of Ca^{2+} in coarse mode particles demonstrates its contributions from
269 soil dust (Kerminen et al., 1997a; Tsai and Chen, 2006). A lifting of soil dust in continental sites
270 followed by subsequent long-range atmospheric transport to remote marine site is also proposed as
271 an important source of Ca^{2+} (Wang et al., 2005b). Ca^{2+} showed unimodal distribution with a peak at
272 either 2.1-3.3 or 3.3-4.7 μm (Figure 5c). The coarse mode Ca^{2+} is mostly derived from crustal
273 $CaCO_3$, which heterogeneously reacts with acidic gases (HNO_3 and SO_2) (Kerminen et al., 1997a).
274 This formation mechanism is further supported by a strong correlation of coarse mode Ca^{2+} with
275 NO_3^- ($r = 0.98$). There is no correlation between Ca^{2+} and Na^+ or Cl^- (-0.12 or -0.27), revealing that
276 sea salt contribution of Ca^{2+} is negligible in Okinawa aerosols. This result suggests that the long-
277 range transport of soil dust is an important contributor of Ca^{2+} in the marine aerosols from the
278 western North Pacific Rim.

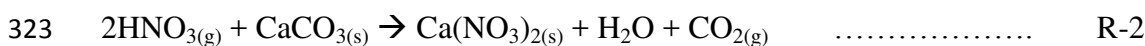
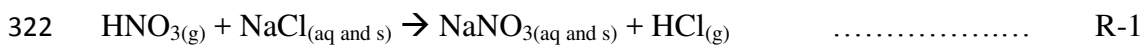
279 There is natural limestone caves formed by elevating coral reefs in Okinawa Island. Although
280 local limestone dust may also be re-suspended to the atmosphere by wind (Shimada et al., 2015),
281 the contribution of local dust to the Ca^{2+} concentration in Okinawa may be small. This
282 interpretation can be supported by the fact that the peak of Ca^{2+} was appeared in lower coarse size
283 range of 2.1-3.3 or 3.3-4.7 μm . It has been suggested that Ca^{2+} is likely associated with the upper
284 coarse size range when the contribution of locally produced soil particles is significant (Bian et al.,
285 2014). The smaller coarse mode Ca^{2+} is likely associated with long-range transported Asian dust to
286 Okinawa. Moreover, concentrations of Ca^{2+} in coarse mode were found to be much higher in OKI-1
287 ($0.51 \mu\text{g m}^{-3}$) and OKI-2 ($0.60 \mu\text{g m}^{-3}$) than that in OKI-5 sample ($0.15 \mu\text{g m}^{-3}$). Backward
288 trajectories also indicated that the air masses originated from Mongolia and Siberia are transported
289 to Okinawa during the collection of OKI-1 and OKI-2 samples whereas OKI-5 sample has an
290 influence of marine air masses. Such air mass origin again indicates a long-range transport of Asian
291 dust from East Asia to the western North Pacific.

292 Potassium is enriched in biomass burning aerosols and therefore its abundances in fine particles
293 can serve as a diagnostic tracer of biomass burning (Yamasoe et al., 2000). Moreover, contributions
294 of K^+ from sea salt and dust sources are highly variable in regional case studies with its dominance
295 in coarse mode particles. Fresh biomass burning particles mostly reside in the condensation mode at
296 0.1-0.5 μm in diameter whereas the fine mode K^+ of biomass burning origin can be subjected to in-
297 cloud processing (Kaufman and Fraser, 1997; Kleeman and Cass, 1999), in which K^+ can act as
298 effective CCN together with abundant water-soluble organic compounds.

299 A unimodal size distribution of K^+ was observed in most sets of samples (OKI-1 to OKI-4) with
300 a peak at 0.65-1.1 μm in diameter (Figure 5e). Freshly emitted biomass burning aerosol particles
301 usually exist at the size of 0.1-0.5 μm and thus the peak of K^+ at 0.65-1.1 μm shows that the fine
302 mode K^+ in Okinawa was associated with aged aerosols. Fresh biomass burning aerosols emitted in
303 East Asia might have undergone growth to a relatively large size by absorbing water vapor from the
304 atmosphere during long-range atmospheric transport to Okinawa. The peak of K^+ at 0.65-1.1 μm in
305 fine mode is conceivably a result of a combination of K^+ derived from fresh biomass burning with
306 other water-soluble species such as SO_4^{2-} during long-range transport. This interpretation is

307 supported by the fact that K^+ showed a positive correlation with LWC ($r = 0.83$) in fine mode. The
 308 fine mode nss- K^+ accounted for 95% of the total K^+ in the OKI-2 sample set and 88% of that in the
 309 OKI-3 sample set when air masses are coming from Siberia and Mongolia as well as North China.
 310 The abundant presence of fine mode nss- K^+ in the OKI-2 and OKI-3 samples further indicates the
 311 long-range atmospheric transport of biomass burning aerosols from the Asian continent to the
 312 western North Pacific Rim. The coarse mode K^+ was strongly correlated with the coarse mode Cl^- (r
 313 $= 0.90$). This result suggests that the coarse mode K^+ in the sample sets OKI-1 and OKI-5 may be
 314 derived from sea salt particles.

315 NO_x is known to be a precursor of NO_3^- , which can be converted to HNO_3 and then react with
 316 NH_3 to form NH_4NO_3 . A unimodal size distribution of NO_3^- was observed with a peak at 2.1-3.3 or
 317 3.3-4.7 μm in diameter. It should also be noted that the NO_3^- concentration in the coarse mode is
 318 much higher than that in the fine mode (Table 1). This result suggests that either dust or sea salt
 319 particle is the source of coarse mode NO_3^- in Okinawa. Coarse mode NO_3^- is the product of
 320 heterogeneous reaction of gaseous NO_2 or HNO_3 with alkaline metals such as Na^+ and Ca^{2+} as
 321 shown in Reactions 1 and 2 (Kouyoumdjian and Saliba, 2006; Seinfeld and Pandis, 2006).



324 As discussed earlier, the air masses originated from Siberia are transported over Mongolia and
 325 North China. Asian dust can be transported from the Asian continent to Okinawa. Therefore, it is
 326 possible that the gaseous HNO_3 might already have reacted with $CaCO_3$ (mineral dust particle) to
 327 form NO_3^- before arriving to Okinawa through R-2. We found that coarse mode Na^+ , which is
 328 derived from sea salts, is negatively correlated ($r = -0.30$) with the coarse mode NO_3^- . Although this
 329 correlation is not significant ($p = 0.51$), the negative correlation may indicate some reactive loss of
 330 NO_3^- from sea salt particles in coarse mode in Okinawa. NO_3^- peaked at the same particle size of
 331 Ca^{2+} . Therefore, NO_3^- in Okinawa coarse mode aerosols is probably resulted from the pickup of
 332 HNO_3 gas by soil dust particles enriched with Ca^{2+} via heterogeneous reaction near the source
 333 regions. This process is further supported by a good correlation between NO_3^- and Ca^{2+} (0.98) in the
 334 coarse mode.

335 The particle size distributions of SO_4^{2-} , which is the major source of acid deposition (Pakkanen
336 et al., 2001), have been the subject of numerous studies in the past few decades (Huang et al., 2006;
337 Kouyoumdjian and Saliba, 2006). Condensation mode SO_4^{2-} arises from gas-phase oxidation of SO_2
338 followed by gas-to-particle conversion whereas fine mode SO_4^{2-} is formed through aqueous-phase
339 oxidation of SO_2 in aerosols and cloud droplets (Seinfeld and Pandis, 1998). SO_4^{2-} on the coarse
340 mode can be attributed to a combination of sulfate and heterogeneous reactions of SO_2 on soil dust
341 or sea salt particles (Seinfeld and Pandis, 1998; Pakkanen et al., 2001). A unimodal size distribution
342 of SO_4^{2-} was observed with a peak at 0.65-1.1 μm . The occurrence of SO_4^{2-} at the size of 0.65-1.1
343 μm cannot be explained by gas-phase nucleation or condensation of SO_2 . It has also been suggested
344 that in-cloud process produce SO_4^{2-} as larger particles by the oxidation of SO_2 in cloud droplets
345 (Gao et al., 2012), which can become fine particles after the dryness of cloud droplets. This result
346 suggests that the peak of SO_4^{2-} at 0.65-1.1 μm in Okinawa is involved with oxidation of SO_2 with
347 OH radical and O_3 in aerosol aqueous-phase.

348 Secondary inorganic aerosols are major contributors to LWC (Ansari and Pandis, 1999;
349 Engelhart et al., 2011). Calculated LWC for each sample from Okinawa and average LWC in size-
350 segregated aerosols are shown in Figure 6. The most remarkable result of the calculation is the
351 different LWC among the particles of different sizes. We clearly found two peaks of LWC in fine
352 and coarse modes. The difference in LWC in size-segregated aerosols is undoubtedly due to the
353 difference in their chemical composition. We observed that the highest LWC was found at the size
354 of 0.65-1.1 μm in the fine mode in Okinawa samples. As shown in Figure 3, SO_4^{2-} and NH_4^+ are the
355 major ions among the measured inorganic species in fine fractions in Okinawa. High correlation of
356 LWC was found with SO_4^{2-} ($r = 0.92$) in fine mode. This result suggests that an enrichment of SO_4^{2-}
357 in fine mode is enhanced the amount of LWC in fine mode of Okinawa aerosols.

358 Size distribution of methanesulfonate (MSA^-) is similar to that of SO_4^{2-} (Figure 5i) in Okinawa.
359 MSA^- showed a strong correlation with SO_4^{2-} ($r = 0.89$) in fine mode, suggesting that MSA^- should
360 have similar origin with SO_4^{2-} in fine mode. Although MSA^- is believed to be produced by gas-to-
361 particle conversion via the oxidation of dimethyl sulfide (DMS) emitted from the ocean (Quinn et
362 al., 1993; Kerminen et al., 1997b), there is some indirect evidence that liquid-phase production

363 might also be possible (Jefferson et al., 1998). Biomass burning also produces DMS in the
364 atmosphere (Meinardi et al., 2003; Geng and Mu, 2006). MSA^- showed high correlation with K^+ or
365 NH_4^+ ($r = 0.92$) in fine mode, indicating that the enhanced emission of DMS from biomass burning
366 followed by the subsequent oxidation during long-range transport may have contributed
367 significantly to the fine mode MSA in Okinawa. Moreover, MSA^- can also be produced in fine
368 mode by the oxidation of DMS that is emitted from the marine phytoplankton in the surrounding
369 ocean. It is noteworthy that East Asian aerosols also travelled over the marine regions including the
370 East China Sea, Sea of Japan and Pacific Ocean during long-range atmospheric transport. This size
371 distribution of MSA^- observed over Okinawa is consistent with previous studies from the China Sea
372 by Gao et al. (1996), who suggested that MSA is produced through the oxidation of S-containing
373 species in the marine atmosphere.

374 NH_4^+ in the Okinawa aerosols shows a unimodal size distribution with a peak at 0.65-1.1 μm
375 (Figure 5h), indicating that NH_4^+ is mainly formed by gas-to-particle conversion via the reaction
376 with H_2SO_4 and HNO_3 . Interestingly, the size distribution of NH_4^+ is similar to that of SO_4^{2-} and
377 diacids such as oxalic acid (Figure 5g and 7a). We also found a strong correlation between SO_4^{2-}
378 and NH_4^+ on the fine mode ($r = 0.99$). Ion balance calculations are commonly used to evaluate the
379 acid-base balance of aerosol particles. Average equivalent ratios of total cations (Na^+ , NH_4^+ , K^+ ,
380 Mg^{2+} and Ca^{2+}) to anions (Cl^- , NO_3^- and SO_4^{2-}) in fine fractions varied from 0.75 for the size bin of
381 0.65-1.1 μm to 0.86 for the size bin of 1.1-2.1 μm , indicating that fine mode aerosols in Okinawa
382 were apparently acidic.

383 NH_3 is an alkaline gas that neutralizes the acidic particles in the atmosphere. Kerminen et al.
384 (1997a) proposed that particulate NH_4^+ is secondarily formed via heterogeneous reactions of
385 gaseous NH_3 with acidic species (H_2SO_4 and HNO_3). The reaction of NH_3 with H_2SO_4 is favored
386 over its reaction with HNO_3 . The average $\text{NH}_4^+/\text{SO}_4^{2-}$ equivalent ratios in fine mode particles in
387 Okinawa varied from 0.36 for the size bin of 1.1-2.1 μm to 0.81 for the size bin of 0.43-0.65 μm ,
388 indicating that NH_3 was not abundant enough to neutralize all SO_2 and hence H_2SO_4 and NH_4SO_4
389 were present in addition to $(\text{NH}_4)_2\text{SO}_4$ in fine mode. Interestingly, the average $\text{NH}_4^+/\text{SO}_4^{2-}$
390 equivalent ratios in coarse mode particles ranged from 0.01 for the size bin $>11.3 \mu\text{m}$ to 0.09 for the

391 size bins of 2.1-3.3 and 3.3-4.7 μm , suggesting that coarse mode aerosols in Okinawa were also
392 NH_4^+ -poor. This result further indicates that there was not enough NH_3 to neutralize HNO_3 , and
393 thus shortfall of NH_3 may be the restrictive factor for the formation of NH_4NO_3 in Okinawa
394 aerosols. Therefore, NO_3^- reacts with coarse particles that contain alkaline species (Ca^{2+}) in
395 Okinawa aerosols.

396 The size distribution of SO_4^{2-} also depends on the concentration of NH_4^+ , richness of NH_3 in the
397 air, and the presence of coarse mode particles. SO_4^{2-} and NH_4^+ often coexist in fine mode because
398 H_2SO_4 condenses on this mode as fine particles that have more surface area (Jacobson, 2002).
399 Although NH_3 was not abundant enough to neutralize all SO_4^{2-} , most of SO_4^{2-} was neutralize by
400 NH_3 in fine mode and exists in the form of NH_4HSO_4 in addition to $(\text{NH}_4)_2\text{SO}_4$. Hence, SO_4^{2-} is
401 enriched in fine mode rather than being associated with dust particles. An enrichment of NO_3^- in the
402 dust fraction in our study is supported by the laboratory studies of Hanisch and Crowley (2001a)
403 and (2001b), who found a large and irreversible uptake between HNO_3 and various authentic dust
404 samples including samples from Chinese dust region. We found that NH_4^+ showed a good
405 correlation ($r = 0.87$) with LWC in the fine mode. This result implies that the abundant presence of
406 NH_4^+ in fine mode also enhanced the LWC in fine mode of Okinawa aerosols. It is notable that
407 higher LWC in fine mode can influence the SOA formation via gas to particle conversion of
408 organic precursors via reactive uptake on aerosols.

409 3.3 Water-soluble organic carbon (WSOC) and organic carbon (OC)

410 The mass-based size distribution of WSOC is characterized by a major peak at 0.65-1.1 μm in
411 fine mode and by a small peak at 3.3-4.7 μm in coarse mode (Figure 8 and Table 1). Huang et al.
412 (2006) observed that fine mode WSOC was primarily derived from combustion sources and
413 secondarily produced in the atmosphere by the photochemical oxidation of VOCs. It is well
414 recognized that biofuel combustion and biomass burning produce a large amount of WSOC (Mayol-
415 Bracero et al., 2002). The WSOC concentrations showed high correlation with fine mode SO_4^{2-} ($r =$
416 0.96). Because production of SO_4^{2-} is strongly linked to photochemical activity, this result suggests
417 an important secondary production of WSOC in fine mode particles during long-range atmospheric
418 transport from East Asia. The WSOC concentrations also showed high correlation with K^+ ($r =$

419 0.93) and NH_4^+ (0.91) in the fine mode. This result suggests that direct emission from biomass
420 burning or fast oxidation of biomass burning-derived precursors contributes significantly to the
421 formation of fine mode WSOC in Okinawa aerosols during long-range transport.

422 Fine mode WSOC concentrations in OKI-1 to OKI-4 aerosol samples are 3-5 times higher (1.09
423 $\mu\text{g m}^{-3}$ for OKI-4 to 1.61 $\mu\text{g m}^{-3}$ for OKI-2) than that in the sample OKI-5 (0.31 $\mu\text{g m}^{-3}$). It is also
424 noteworthy that fine mode fraction of WSOC in the samples OKI-1 to OKI-4 contributed 70-75%
425 of total WSOC. We noted that the former 4 sample sets are more influenced by continental air
426 masses than the last set (Figure 2). These results suggested that WSOC is more enriched in the
427 samples with an influence of continental air masses from Siberia and Mongolia as well as North
428 China and Korea. Because WSOC is an important fraction of OC in Okinawa aerosols, high
429 loadings of WSOC in aerosols of continental air mass origin suggest that both fossil fuel
430 combustion and biomass burning in East Asia may have a significant influence on the composition
431 of water-soluble organic aerosols over the western North Pacific Rim.

432 The mass-size distribution pattern of OC is similar to that of WSOC with a major peak in the
433 size range of 0.65-1.1 μm whereas a small peak was appeared in the size range of 3.3-4.7 μm in
434 diameter (Figure 8). Primary emission from fossil fuel combustion and biomass burning and
435 secondary production from photooxidation of VOCs are considered to be the major sources of OC
436 in atmospheric aerosols (Aggarwal and Kawamura, 2009; Jung et al., 2010). Primary emission from
437 biomass burning or photooxidation of biomass burning derived precursors might be a dominant
438 source of fine mode OC in Okinawa aerosols. This interpretation is supported by the fact that OC
439 showed strong correlation ($r = 0.95$) with K^+ in fine mode. The fine mode OC showed significant
440 positive correlations with SO_4^{2-} ($r = 0.93$) and NH_4^+ ($r = 0.91$), suggesting secondary photochemical
441 formation characteristics of OC in fine mode in Okinawa.

442 A significant portion of OC may be oxidized to WSOC during the atmospheric transport from
443 East Asia to the western North Pacific. The mass ratio of WSOC/OC has been proposed as a
444 measure of photochemical processing or aging of organics especially in long-range transported
445 aerosols (Aggarwal and Kawamura, 2009). The WSOC/OC ratios varied from 0.51-0.76 with an
446 average of 0.67 ± 0.09 in the fine mode and 0.43-0.63 with an average of 0.55 ± 0.09 in the coarse

447 mode. The higher WSOC/OC ratio in fine mode suggests that organics are more significantly
448 subjected to photochemical processing in fine mode aerosols during long-range transport from the
449 Asian continent to Okinawa than coarse mode aerosols.

450 Source contributions and secondary processes that may convert VOCs to a more soluble form
451 and surface area of fine particles could cause the higher WSOC/OC ratios in fine mode. Biomass
452 burning-derived OC is highly water-soluble and usually resides in fine mode whereas coarse mode
453 OC contains high molecular weight organic compounds emitted by soil resuspension and emissions
454 of pollens and fungal spores, which are less water-soluble (Wang et al., 2011; Mkoma et al., 2013).
455 Biomass burning significantly contributed to fine mode WSOC in Okinawa and thus WSOC is
456 secondarily produced from oxidation of biomass burning-derived VOCs (Kundu et al., 2010).
457 However, the primary emission of fine mode WSOC from biomass burning could not be excluded.
458 Moreover, accumulation of gas-phase precursors of WSOC may occur preferentially in the particle
459 size with the greatest surface area (Kanakidou et al., 2005). It has been proposed that fine particles
460 offer more surface area and thus reaction rate is more on the surface of fine particles than the coarse
461 particles (Kanakidou et al., 2005). The higher WSOC/OC ratio in fine particles than coarse particles
462 has also been observed in long-range transported East Asian aerosols over Northern Japan (Agarwal
463 et al., 2010).

464 WSOC also contribute to aerosol LWC although their ability to absorb water is significantly less
465 than that of inorganics (Ansari and Pandis, 2000). Speer et al. (2003) and Engelhart et al. (2011)
466 also noted that inorganic aerosols are associated with 62-80% of aerosol LWC. Moreover, organic
467 species are not taken into account in ISORROPIA II for the calculation of LWC. It is noteworthy
468 that WSOC/OC ratio and LWC significantly correlate in the fine mode with $r = 0.87$ whereas the
469 negative correlation was found in the coarse mode ($r = -0.19$), suggesting the possibility of
470 photochemical production of WSOC from OC in aerosol aqueous-phase in fine mode of Okinawa
471 aerosols. There may also be other important sources of fine mode WSOC in Okinawa aerosols such
472 as primary emission from biomass burning and secondary formation via gas-phase photochemical
473 reactions during long-range atmospheric transport (Hagler et al., 2007; Lim et al., 2010). The strong

474 correlation of WSOC with K^+ in fine mode suggests a substantial contribution of biomass burning
475 to fine mode WSOC in Okinawa aerosols.

476 This result may also indicate that shorter-chain organic compounds with polar functional group
477 such as diacids and oxoacids as well as α -dicarbonyls may contribute more to fine mode WSOC via
478 oxidation of various organic precursors in gas and aqueous-phase during long-range transport
479 (Carlton et al., 2007; Miyazaki et al., 2010). Kawamura et al. (2005, 2007) proposed that shorter-
480 chain diacids and related polar compounds are significantly produced via photochemical oxidation
481 of various precursors and thus they are abundantly present in fine particles contributing more to
482 WSOC fraction.

483 3.4 Dicarboxylic acids

484 The size distributions of selected diacids and related compounds are shown in Figure 7. C_2 showed
485 a peak at 0.65-1.1 μm in fine mode (Figure 7a). The monomodal distribution suggests that the
486 heterogeneous uptake of C_2 on sea-salt particles did not occur (Kerminen et al., 1999; Mochida et
487 al., 2003a). The shift of smaller diacids (C_2 - C_4) from submicron to supermicron mode has been
488 observed in marine aerosols collected from the western North Pacific in spring when a strong
489 outflow of Asian dusts occurred. Mochida et al. (2003a, 2007) reported that a supermicron peak of
490 diacids was emerged by the uptake of gaseous diacids on sea salt particles based on the similarity
491 between sea salt surface area and diacids size distributions or heterogeneous oxidations of organic
492 precursors on the sea salt particles.

493 The condensation mode of C_2 is likely produced photochemically in the gas-phase followed by
494 condensation onto pre-existing particles at 0.1-0.5 μm (Huang et al., 2006). In the atmosphere, the
495 gas-phase oxidation of isoprene, toluene and ethene leads to the formation of semi-volatile gaseous
496 organic precursors such as Gly and MeGly, which are subsequently participated in aqueous-phase
497 photochemical reaction to result in C_2 diacid (Carlton et al. 2006, 2007; Legrand et al. 2007). The
498 fine mode peak of C_2 at the size of 0.65-1.1 μm in Okinawa aerosols suggests a preferential
499 production of C_2 via the oxidation of precursors in the aerosol aqueous-phase during long-range
500 atmospheric transport. We found that size distribution of C_2 diacid is similar to that of SO_4^{2-} (Figure

501 5g and 7a), suggesting a secondary formation of C_2 possibly in aerosol aqueous-phase. The good
502 correlations of C_2 with SO_4^{2-} ($r = 0.92$) and NH_4^+ ($r = 0.89$) in fine mode further supports that C_2 is
503 a secondary photochemical product. The fine mode C_2 can also be produced primarily from fossil
504 fuel combustion and biomass burning in East Asia and long-range transported to Okinawa. C_2
505 diacid showed a significant positive correlation with fine mode K^+ ($r = 0.85$), indicating that
506 biomass burning contributed significantly to fine mode C_2 diacid in Okinawa aerosols.

507 Several sources are known to C_2 in atmospheric aerosols. They include primary sources and
508 secondary formation via photooxidation of anthropogenic and biogenic precursors (Kawamura and
509 Sakaguchi, 1999). C_2 is produced by the photooxidation of C_3 (Kawamura and Ikushima, 1993). C_2
510 and C_3 are formed by the photooxidation of C_4 whereas C_4 is produced by the photooxidation of
511 glutaric acid (C_5) (Kawamura and Ikushima, 1993). The fine mode predominance of C_2 in Okinawa
512 aerosols was probably associated with an enhanced aqueous oxidation of anthropogenic precursors
513 emitted in East Asia during long-range transport. Lim et al. (2005) and Legrand et al. (2007)
514 reported the formation of diacids in aqueous-phase. Here we investigate the impact of LWC of
515 aerosols on the formation of diacids in Okinawa aerosols. LWC of a particle can influence the
516 production of C_2 via the changes in gas/particle partitioning of gaseous organic precursors and
517 subsequent heterogeneous reaction in aerosol aqueous-phase. We found that the fine mode peak of
518 C_2 is consistent with that of LWC in Okinawa samples (Figure 6b and 7a). A strong positive
519 correlation ($r = 0.92$) of C_2 with LWC was found in fine mode. This result supports the possibility
520 of aqueous phase production of C_2 via the oxidation of C_2 precursors in fine mode of Okinawa
521 aerosols.

522 The robust correlations of C_2 with C_3 - C_5 diacids ($r = 0.89$ - 0.92) indicate that they have similar
523 sources and origin or C_2 diacid might be produced via decay of longer-chain diacids during long-
524 range transport. This result is further supported by the fact that C_3 - C_5 diacids were also enriched in
525 the fine mode (Figure 7b-d) and showed good correlations with LWC ($r = 0.82$ - 0.89) possibly due
526 to the enhanced secondary production from oxidation of its precursor compounds in aerosol
527 aqueous-phase. C_2 can also be produced by gas-phase oxidation of various VOCs including toluene,
528 ethene and isoprene followed by subsequent oxidation in aerosol aqueous-phase during long-range

529 atmospheric transport (Legrand et al., 2007; Lim et al., 2005). The gas-phase photooxidation of
 530 these VOCs produce Gly and MeGly, which are easily hydrated and partitioned into the aerosol
 531 phase with lifetime less than 3 h (Legrand et al., 2007; Kampf et al., 2012). The aqueous-phase
 532 oxidation of Gly and MeGly produces ω C₂, which can further oxidize in aqueous-phase to form C₂
 533 diacid (Lim et al., 2005). It is noteworthy that ω C₂ and Gly are also enriched in fine mode in
 534 Okinawa aerosols. Their size distributions are discussed in more details in subsequent sections. Fine
 535 mode C₂ showed a significant positive correlation with ω C₂ ($r = 0.99$) and Gly (0.93) whereas weak
 536 correlation was found with MeGly (0.62). These results suggest that ω C₂ and Gly are important
 537 precursors of C₂ diacid and increased LWC in fine mode is favorable for aqueous phase oxidation
 538 of ω C₂ and Gly to result in C₂.

539 C₃ peaked at 0.65-1.1 μ m in diameter (Figure 7b), being similar to C₂ diacid (Figure 7a), except
 540 for two sets of samples (OKI-1 and OKI-5) that showed peaks at 2.1-3.3 or 3.3-4.7 μ m in the coarse
 541 mode. C₄ showed two peaks at the size bins of 0.65-1.1 and 2.1-3.3 μ m in OKI-1 and OKI-5
 542 samples (Figure 7c). The coarse mode peaks of this diacid in samples OKI-1 and OKI-5 may be
 543 associated with sea salt particles because the samples have an influence of marine air masses during
 544 the sampling period. Kawamura and Ikushima (1993) proposed that the ratio of malonic to succinic
 545 acid (C₃/C₄) is a tracer to indicate the extent of photochemical processing of longer chain diacids
 546 such as C₅ diacid. Because C₄ is oxidized to C₃, an increase in the C₃/C₄ ratio indicates an increased
 547 photochemical processing. The averaged C₃/C₄ ratio in sum of all the size fractions was found to be
 548 1.5 ± 0.1 in Okinawa aerosols. This result suggests that the extent of photochemical processing is
 549 much greater in Okinawa than Los Angeles (0.35) (Kawamura and Kaplan, 1987) but similar to that
 550 of urban Tokyo (1.5) (Kawamura and Ikushima, 1993), whereas it is lower than those of marine
 551 aerosols at Chichijima Island in the western North Pacific (2.0) (Mochida et al., 2003b) and the
 552 remote Pacific including tropics (3.9) (Kawamura and Sakaguchi, 1999). Figure 9a shows changes
 553 in the C₃/C₄ ratios as a function of particle size. The C₃/C₄ ratios exhibit higher values at 1.1-2.1 μ m
 554 in fine mode and at 2.1-3.3 and 3.3-4.7 μ m in coarse mode. This result suggests that C₃ production
 555 via C₄ decomposition occurs more efficiently at these size ranges by aqueous-phase processing.

556 It is noteworthy that emission sources can also control the size distributions of organic
557 compounds. A bimodal size distribution of C₉ diacid was observed in Okinawa aerosols with a
558 major peak on coarse mode at 3.3-4.7 μm and minor peak on fine mode at 0.65-1.1 μm (Figure 7f).
559 C₉ is a tracer of biogenic sources. Kawamura and Gagosian (1987) reported that C₉ is derived from
560 the photooxidation of unsaturated fatty acids such as oleic (C_{18:1}) and linoleic (C_{18:2}) acids that are
561 produced from the sea surface microlayers to the marine atmosphere with sea salt particles. These
562 unsaturated fatty acids, which are coated in sea salt particles, predominantly reside in the coarse
563 size range (Mochida et al., 2007; Aggarwal et al., 2010). The major peak of C₉ on coarse mode is
564 due to the heterogeneous particle-phase oxidation of unsaturated fatty acids on the sea salt surface.
565 We found significant correlation of C₉ with Na⁺ ($r = 0.85$) in coarse mode. This correlation is
566 consistent with the idea that the precursors of C₉ are emitted from the ocean surface together with
567 sea salt particles in coarse mode. Unsaturated fatty acids can also be directly emitted as fine
568 particles from food cooking emission in China and long-range transported to the western North
569 Pacific (Schauer et al., 1996; Wang et al., 2011). The minor peak of C₉ in fine mode can be
570 explained by the oxidation of fine-mode unsaturated fatty acids derived from food cooking or
571 gaseous unsaturated fatty acids.

572 A unimodal size distribution was obtained for Ph with a fine mode peak at 0.65-1.1 μm, except
573 for one sample set (OKI-5) that showed a bimodal distribution with almost equal peaks at 0.65-1.1
574 and 2.1-3.3 μm (Figure 7g). This aromatic diacid is a tracer of anthropogenic sources. Ph is directly
575 emitted from combustion sources and secondarily produced in the atmosphere by the
576 photooxidation of polycyclic aromatic hydrocarbons such as naphthalene (NAP) and o-xylene
577 derived from incomplete combustion of fossil fuel (Kawamura and Kaplan, 1987). NAP is largely
578 exists in gas-phase and has been suggested to be a major precursor of Ph in the atmosphere
579 (Schauer et al., 1996). The major peak of Ph on fine mode might be due to the preferential
580 production of Ph via gas-phase photooxidation of NAP followed by subsequent condensation onto
581 pre-existing fine mode particles during long-range transport. The high levels of NAP were found in
582 gas-phase and aerosols in source regions in East Asia (Liu et al., 2007; Tao et al., 2007), which
583 indicated NAP as a potential precursor of Ph diacid in Okinawa aerosols. The high levels of

584 precursors (NAP) in the source regions might favor the significant secondary production of Ph
585 during long-range transport in the western North Pacific. Moreover, the enrichment of Ph in fine
586 mode further suggests that preferential origin of this diacid is related to combustion sources either
587 by primary emission and/or secondary production from the precursor compounds, which is
588 consistent with other anthropogenic constituents such as SO_4^{2-} , NH_4^+ and K^+ . The comparable
589 coarse mode peak in the OKI-5 sample set suggests an adsorption of gaseous Ph onto coarse
590 particles. Terephthalic acid (tPh), which is a tracer of plastic burning (Kawamura and Pavuluri,
591 2011), showed a unimodal distribution peaking at the size bin of 0.65-1.1 μm (Figure 7h). tPh is
592 mostly emitted from the burning of plastic wastes such as plastic bags and bottles, and then
593 deposited on pre-existing fine particles.

594 Ph diacid originates from various anthropogenic sources whereas C_9 diacid is produced by the
595 oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987; Kawamura and
596 Ikushima, 1993). Therefore, Ph/ C_9 ratio is mostly used as marker to know the source strength of
597 anthropogenic and biogenic sources of diacids. The higher Ph/ C_9 ratio shows more influence of
598 anthropogenic sources whereas lower ratio shows more influence of biogenic sources. Figure 9b
599 shows the changes in the ratios of Ph/ C_9 as a function of particle sizes. The higher Ph/ C_9 ratios were
600 obtained on the fine mode particles than coarse mode particles. The results suggest that fine
601 aerosols are significantly influenced by anthropogenic sources whereas the coarse aerosols are more
602 influenced by biogenic sources. The significant contribution of Ph on the fine mode demonstrates
603 that this aromatic diacid is mainly produced by the photooxidation of aromatic hydrocarbons such
604 as naphthalene emitted from fossil fuel combustion in gas-phase followed by condensation of the
605 product onto pre-existing fine particles during long-range transport in the atmosphere.

606 It is important to understand whether anthropogenic or biogenic organic precursors are oxidized
607 to increase the atmospheric level of shorter-chain ($\text{C}_2\text{-C}_5$) diacids and related compounds (ωC_2 and
608 Gly) in fine mode of Okinawa aerosols. The strong correlation of $\text{C}_2\text{-C}_5$ diacids with Ph ($r = 0.83\text{-}$
609 0.90) was found in fine mode. This result suggests that anthropogenic precursors are more
610 important sources of $\text{C}_2\text{-C}_5$ diacids than biogenic precursors in fine mode. The weak correlations of
611 $\text{C}_2\text{-C}_5$ diacids with C_9 ($r = 0.09\text{-}0.38$) further suggest that biogenic precursors such as unsaturated

612 fatty acids are not a major source of shorter-chain diacids in fine mode. The higher influences of
613 anthropogenic VOCs than biogenic VOCs can also be evidenced by a lack of correlation ($r = 0.25-$
614 0.36) between C_2-C_5 diacids and MeGly in fine mode. Myriokefalitakis et al. (2011) proposed that
615 about 80% of MeGly is formed in the atmosphere by the oxidation of biogenic VOCs such as
616 isoprene. Strong correlations of ωC_2 and Gly with Ph ($r = 0.90$ and 0.85) also suggest that
617 anthropogenic precursors are their major sources in fine mode of Okinawa aerosols.

618 3.5 ω -Oxocarboxylic acids and pyruvic acid

619 ω -Oxocarboxylic acids ($\omega C_2-\omega C_9$) are secondarily produced in the atmosphere and also directly
620 emitted from fossil fuel combustion and biomass burning. They are further oxidized into diacids via
621 the oxidation of aldehyde group of the compounds (Kawamura et al., 1996; Warneck, 2003). The
622 size distribution of glyoxylic acid (ωC_2) shows a unimodal pattern with a peak at $0.65-1.1 \mu m$
623 (Figure 7i). Mochida et al. (2007) reported a strong bimodal pattern of oxoacids with a peak in the
624 coarse aerosol mode off the coast of East Asia. They suggested that the coarse mode was likely due
625 to either uptake of oxoacids or their heterogeneous reactions on sea salt particles. The fine mode
626 maxima of oxoacids indicate that they are secondarily produced in the atmosphere by the
627 photochemical oxidation of gaseous precursors during long-range transport to Okinawa.
628 Interestingly, we found that size distribution of C_2 diacid is similar to that of ωC_2 oxoacid (Figure
629 7a and i). Those similarities suggest that both C_2 and ωC_2 are simultaneously produced via gas and
630 aqueous-phase oxidation of their precursors. The diacids may be produced by the oxidation of
631 corresponding ω -oxoacids in aerosols during long-range transport.

632 The important precursor of ωC_2 in atmospheric aerosols is Gly and MeGly (Lim et al., 2005;
633 Myriokefalitakis et al., 2011). We found that ωC_2 is strongly correlated with Gly ($r = 0.92$) and
634 moderately correlated with MeGly (0.55) in the fine mode. The former result suggests that Gly is a
635 key precursor of ωC_2 in Okinawa aerosols. The significant positive correlation of ωC_2 with LWC
636 (0.95) in fine mode suggests the formation of ωC_2 via oxidation of Gly in the aerosol aqueous-
637 phase. The strong correlation of fine mode ωC_2 with SO_4^{2-} (0.96) further confirms secondary
638 formation of ωC_2 from the precursors originated from anthropogenic and biogenic sources during

639 long-range transport to Okinawa. Although the enhanced ωC_2 concentrations in fine mode might be
640 a result of aqueous oxidation, ωC_2 may be rather controlled by biomass burning activity. This is
641 supported by the significant positive correlation of ωC_2 with K^+ ($r = 0.90$) in the fine mode.

642 A bimodal size distribution was observed for 9-oxononanoic acid (ωC_9) (Figure 7k). We found
643 that the peak at 3.3-4.7 μm in coarse mode is larger than that at 0.65-1.1 μm in fine mode. The size
644 distribution of ωC_9 is similar to that of C_9 diacid. ωC_9 is another counterpart of photooxidation
645 product of biogenic unsaturated fatty acids such as oleic ($\text{C}_{18:1}$) acid having a double bond at C-9
646 position (Kawamura and Gagosian, 1987). Although air masses during the sampling period are
647 mostly originated from Siberia, Mongolia, Korea and North China (Figure 2), where unsaturated
648 fatty acids of higher plant origin are abundantly supplied to this marine receptor site, sea surface
649 microlayers in the surroundings of Okinawa can also emit unsaturated fatty acids abundantly. The
650 positive correlation of ωC_9 with Na^+ ($r = 0.83$) can also be seen in coarse mode. This suggests that
651 the major peak of ωC_9 on the coarse mode may be due to the heterogeneous oxidation of
652 unsaturated fatty acids of marine phytoplankton origin on the surface of sea salt particles. This
653 result further suggests enhanced input of biogenic organic precursors derived from the ocean on the
654 coarse size range in Okinawa aerosols.

655 Pyruvic acid (Pyr) showed a bimodal size distribution with a major peak on coarse mode at the
656 size of 3.3-4.7 or 7.0-11.3 μm and a minor peak on fine mode at the size of 0.65-1.1 μm . The larger
657 peak of Pyr on coarse mode may suggest that pyruvic acid is possibly produced by the
658 heterogeneous photooxidation of isoprene emitted from the ocean surface probably on sea salt
659 particles. Several studies suggested that Pyr is produced via the aqueous-phase photooxidation of
660 MeGly that is a gas-phase oxidation product of isoprene emitted from the ocean surface (Lim et al.,
661 2005; Carlton et al., 2006).

662 3.6 α -Dicarbonyls

663 Gly and MeGly are gas-phase oxidation products of numerous VOCs such as benzene, toluene and
664 xylene (Volkamer et al., 2001) as well as ethylene and isoprene (Zimmermann and Poppe, 1996)
665 and terpenes (Lim et al., 2005). Gly may be associated with pollution sources whereas MeGly may

666 be involved with biogenic sources. Gly peaked at 0.65-1.1 μm in the fine mode in the Okinawa
667 samples. The fine mode peak of Gly is similar to those of K^+ and SO_4^{2-} (Figure 5e and g),
668 suggesting their similar sources and formation pathways in the aerosols. Although gas-phase
669 oxidation of isoprene has been reported as the largest global source of Gly (Zimmermann and
670 Poppe, 1996), oxidation of anthropogenic aromatic hydrocarbons from fossil fuel combustion and
671 biomass burning is also suggested as alternative source of Gly in the atmosphere (Jung et al., 2010).
672 The peak of Gly at 0.65-1.1 μm may be associated with the combustion sources and the subsequent
673 gas-phase oxidation of the precursors during long-range transport to Okinawa. A good correlation
674 of Gly with K^+ or NH_4^+ ($r = 0.86$) in fine mode further suggests that biomass burning is a major
675 source of fine mode Gly in Okinawa aerosols.

676 In contrast, we found a bimodal size distribution of MeGly with two peaks on the fine and coarse
677 modes. Biogenic VOCs such as isoprene emitted from the ocean surface are subjected to oxidation
678 leading to the formation of MeGly in the atmosphere through aqueous-phase chemistry (Carlton et
679 al., 2006; Ervens et al., 2008). The peak of MeGly on coarse mode suggests that MeGly might be
680 produced by the aqueous-phase oxidation of isoprene emitted from the ocean surface on sea salt
681 particles. MeGly could act as a precursor of secondary organic aerosols (SOA) in the atmosphere
682 (Kroll et al., 2005; Liggiio et al., 2005). Gly and MeGly are largely present in gaseous phase and
683 only small portion is in ambient aerosols (Kawamura et al., 2013), although hydrated Gly and
684 MeGly likely exist in aerosols. However, aerosol phase α -dicarbonyls are important in terms of
685 heterogeneous oxidation to result in oxalic acid, which is the most abundant organic species in
686 aerosols. The oxidation of α -dicarbonyls in aerosol phase should promote their transfer from gas to
687 particle phase, affecting the gas/aerosol partitioning of Gly and MeGly, which may have a
688 significant effect on the chemical and physical properties of aerosols.

689 **3.7 Benzoic acid**

690 The size distribution of benzoic acid is presented in Figure 70. Two sample sets (OKI-1 and OKI-2)
691 showed unimodal size distribution of benzoic acid with a peak at 0.65-1.1 or 1.1-2.1 μm in the fine
692 mode. Benzoic acid is directly emitted from the automobile emissions (Kawamura et al., 1985) and

693 secondarily produced by photochemical oxidation of automobile-derived aromatic compounds (Ho
694 et al., 2006). Although benzoic acid is semi-volatile and mainly found in gas-phase (Kawamura et
695 al., 2000; Fraser et al., 1998), it can be observed in particulate phase via gas-to-particle conversion
696 by forming salts such as ammonium benzoate or potassium benzoate. Duan et al. (2008) reported
697 high level of ambient toluene ($11 \mu\text{g m}^{-3}$) in China during an ozone episode in 2006 and suggested
698 that photooxidation of toluene is one of major sources of benzoic acid in the atmosphere.

699 The major peak of benzoic acid at small size bin of 0.65-1.1 or 1.1-2.1 μm suggest that a
700 significant portion of this compound in the Okinawa aerosols is likely produced by gas-to-particle
701 conversion via the reaction with NH_3 and alkaline metals and the subsequent deposition onto pre-
702 existing fine particles during long-range transport. We observed an additional small peak of benzoic
703 acid at 4.7-7.0 μm on the coarse mode for the sample sets of OKI-3 to OKI-5. Because benzoic acid
704 mainly exists in gas-phase in the atmosphere due to the relatively high volatility (Fraser et al., 1998),
705 the small peak on the coarse mode indicates a potential adsorption of gaseous benzoic acid onto
706 larger particles that may contain alkaline Na, K and Ca, or uptake by sea spray water droplets
707 emitted from sea surface.

708 **4 Summary and conclusions**

709 Nine-stage aerosol particles from <0.43 to $>11.3 \mu\text{m}$ in diameter, collected in spring 2008 at Cape
710 Hedo, Okinawa in the western North Pacific Rim, were analyzed for water-soluble diacids and
711 related compounds as well as major ions. The molecular distributions of diacids were characterized
712 by the predominance of oxalic acid (C_2) followed by malonic (C_3) and succinic (C_4) acids in all
713 stages, suggesting that they are most likely produced by the photooxidation of VOCs and particulate
714 organic precursors in the source region and/or during long-range atmospheric transport. The
715 abundant presence of SO_4^{2-} as well as phthalic and adipic acids in Okinawa suggested the
716 significant contributions of anthropogenic sources including industrial emissions in East Asia via
717 long-range atmospheric transport.

718 SO_4^{2-} , NH_4^+ , and diacids up to 5-carbon atoms as well as glyoxylic acid (ωC_2) and glyoxal (Gly)
719 showed good correlations with peaks in fine mode (0.65-1.1 μm). WSOC and OC also peaked on

720 fine mode with an additional minor peak on coarse mode. Similar size distributions and strong
721 correlations of diacids (C_2 - C_5), ωC_2 and Gly with SO_4^{2-} in fine mode suggest their secondary
722 formation possibly in the aerosol aqueous-phase. They may have also been directly emitted from
723 biomass burning as suggested by strong correlations with K^+ in fine mode. The strong correlations
724 of fine mode SO_4^{2-} and NH_4^+ with LWC imply that abundant presences of SO_4^{2-} and NH_4^+ in fine
725 mode promote to enhance the LWC in fine mode of Okinawa aerosols, which is favorable for the
726 aqueous oxidation of precursor compounds to result in C_2 (r is 0.91 for LWC and C_2). The robust
727 correlations of C_2 with C_3 - C_5 diacids as well as ωC_2 and Gly indicate that they are the key
728 precursors of C_2 diacid in Okinawa aerosols.

729 We observed an enrichment of C_3 and C_4 diacids on coarse mode particles in the aerosols with
730 marine air mass origin, indicating that their formation is associated with the heterogeneous
731 reactions on sea salt particles. Longer-chain diacid (C_9) and ω -oxoacid (ωC_9) showed bimodal size
732 distribution with a major peak on coarse mode, suggesting that they are produced by photooxidation
733 of unsaturated fatty acids mainly derived from phytoplankton via heterogeneous reactions on sea
734 spray particles. We observed that WSOC and OC in fine particles are photochemically more
735 processed in the atmosphere than in coarse particles during long-range transport. This study
736 demonstrates that anthropogenic and biomass burning aerosols emitted from East Asia have
737 significant influence on the molecular compositions of water-soluble organic aerosols in the
738 western North Pacific Rim.

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751 **References**

- 752 **Ansari, A. S. and Pandis, S. N.: Prediction of multicomponent inorganic atmospheric aerosol**
 753 **behavior, Atmos. Environ., 33, 745-757, 1999.**
- 754 **Ansari, A. S. and Pandis, S. N.: Water absorption by secondary organic aerosol and its effect on**
 755 **inorganic aerosol behavior, Environ. Sci. Technol., 34, 71-77, 2000.**
- 756 Agarwal, S., Aggarwal, S. G., Okuzawa, K., and Kawamura, K.: Size distributions of dicarboxylic
 757 acids, ketoacids, alpha-dicarbonyls, sugars, WSOC, OC, EC and inorganic ions in
 758 atmospheric particles over Northern Japan: implication for long-range transport of Siberian
 759 biomass burning and East Asian polluted aerosols, Atmos. Chem. Phys., 10, 5839-5858,
 760 2010.
- 761 Aggarwal, S. G. and Kawamura, K.: Carbonaceous and inorganic composition in long-range
 762 transported aerosols over northern Japan: implications for aging of water-soluble organic
 763 fraction, Atmos. Environ., 43, 2532-2540, 2009.
- 764 Andreas, E.L.: A new sea spray generation function for wind speeds up to 32 m s^{-1} , J. Phys.
 765 Oceanogr., 28, 2175-2184, 1998.
- 766 Bian, Q., Huang, X. H. H., and Yu, J. Z.: One-year observations of size distribution characteristics
 767 of major aerosol constituents at a coastal site in Hong Kong - Part 1: Inorganic ions and
 768 oxalate, Atmos. Chem. Phys., 14, 9013-9027, 2014.
- 769 Boreddy, S. K. R. and Kawamura K.: A 12-year observation of water-soluble inorganic ions in TSP
 770 aerosols collected at a remote marine location in the western North Pacific: An outflow region
 771 of Asian dust, Atmos. Chem. Phys., 15, 6437-6453, 2015.
- 772 Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H. J., and Ervens, B.:
 773 Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous
 774 photooxidation experiments, Atmos. Environ., 41, 7588-7602, 2007.
- 775 Carlton, A. G., Turpin, B. J., Lim, H. J., Altieri, K. E., and Seitzinger, S.: Link between isoprene
 776 and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic
 777 acids in clouds, Geophys. Res. Lett., 33, L06822, doi:10.1029/2005GL025374, 2006.
- 778 Davidson, C. I., Phalen, R. F., and Solomon, P. A.: Airborne particulate matter and human health: A
 779 review, Aerosol. Sci. Tech., 39, 737-749, 2005.
- 780 Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajec-
 781 tory) Model, available at: <http://www.arl.noaa.gov/HYSPLIT.php> (last access: 5 January
 782 2015), NOAA Air Resources Laboratory, College Park, MD.
- 783 Duan, J. C., Tan, J. H., Yang, L., Wu, S., and Hao, J. M.: Concentration, sources and ozone
 784 formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing,
 785 Atmos. Res., 88, 25-35, 2008.
- 786 **Engelhart, G. J., Hildebrandt, L., Kostenidou, E., Mihalopoulos, N., Donahue, N. M., and Pandis, S.**
 787 **N.: Water content of aged aerosol, Atmos. Chem. Phys., 11, 911-920, 2011.**
- 788 Engling, G., Lee, J. J., Sie, H. J., Wu, Y. C., and Yet-Pole, I.: Anhydrosugar characteristics in
 789 biomass smoke aerosol-case study of environmental influence on particle-size of rice straw
 790 burning aerosol, J. Aerosol Sci., 56, 2-14, 2013.

- 791 Ervens, B., Carlton, A. G., Turpin, B. J., Altieri, K. E., Kreidenweis, S. M., and Feingold, G.:
792 Secondary organic aerosol yields from cloud-processing of isoprene oxidation products,
793 *Geophys. Res. Lett.*, 35, L02816, doi:10.1029/2007gl031828, 2008.
- 794 Ervens, B., Cubison, M., Andrews, E., Feingold, G., Ogren, J. A., Jimenez, J. L., DeCarlo, P., and
795 Nenes, A.: Prediction of cloud condensation nucleus number concentration using
796 measurements of aerosol size distributions and composition and light scattering enhancement
797 due to humidity, *J. Geophys. Res.*, 112, D10S32, doi:10.1029/2006jd007426, 2007.
- 798 Ervens, B. and Volkamer, R.: Glyoxal processing by aerosol multiphase chemistry: towards a
799 kinetic modeling framework of secondary organic aerosol formation in aqueous particles,
800 *Atmos. Chem. Phys.*, 10, 8219-8244, 2010.
- 801 Falkovich, A. H., Graber, E. R., Schkolnik, G., Rudich, Y., Maenhaut, W., and Artaxo, P.: Low
802 molecular weight organic acids in aerosol particles from Rondonia, Brazil, during the
803 biomass-burning, transition and wet periods, *Atmos. Chem. Phys.*, 5, 781-797, 2005.
- 804 Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic
805 equilibrium model for K^+ - Ca^{2+} - Mg^{2+} - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosols, *Atmos. Chem.*
806 *Phys.*, 7, 4639-4659, 2007.
- 807 Fraser, M. P., Cass, G. R., and Simoneit, B. R. T.: Gas-phase and particle-phase organic compounds
808 emitted from motor vehicle traffic in a Los Angeles roadway tunnel, *Environ. Sci. Technol.*,
809 32, 2051-2060, 1998.
- 810 Gao, Y., Arimoto, R., Duce, R. A., Chen, L. Q., Zhou, M. Y., and Gu, D. Y.: Atmospheric non-sea-
811 salt sulfate, nitrate and methanesulfonate over the China Sea, *J. Geophys. Res.*, 101, 12601-
812 12611, 1996.
- 813 Gao, X., Xue, L., Wang, X., Wang, T., Yuan, T., Gao, R., Zhou, Y., Nie, W., Zhang, Q., and Wang,
814 W.: Aerosol ionic components at Mt. Heng in central southern China: abundances, size
815 distribution, and impacts of long-range transport, *Sci. Total Environ.*, 433, 498-506, 2012.
- 816 Geng, H., Park, Y., Hwang, H., Kang, S., and Ro, C. U.: Elevated nitrogen-containing particles
817 observed in Asian dust aerosol samples collected at the marine boundary layer of the Bohai
818 Sea and the Yellow Sea, *Atmos. Chem. Phys.*, 9, 6933-6947, 2009.
- 819 Geng, C. and Mu, Y.: Carbonyl sulfide and dimethyl sulfide exchange between trees and the
820 atmosphere, *Atmos. Environ.*, 40, 1373-1383, 2006.
- 821 Hagler, G. S. W., Bergin, M. H., Smith, E. A., and Dibb, J. E.: A summer time series of particulate
822 carbon in the air and snow at Summit, Greenland, *J. Geophys. Res.*, 112, D21309,
823 doi:10.1029/2007JD008993, 2007.
- 824 Hanisch, F. and Crowley, J.N.: Heterogeneous reactivity of gaseous nitric acid on Al_2O_3 , $CaCO_3$,
825 and atmospheric dust samples: A Knudsen cell study, *J. Phys.Chem. (A)*, 105, 3096-3106,
826 2001a.
- 827 Hanisch, F. and Crowley, J.N.: The heterogeneous reactivity of gaseous nitric acid on authentic
828 mineral dust samples, and on individual mineral and clay mineral components, *Phys. Chem.*
829 *Chem. Phys.*, 3, 2474-2482, 2001b.

- 830 Ho, K. F., Lee, S. C., Cao, J. J., Kawamura, K., Watanabe, T., Cheng, Y., and Chow, J. C.:
831 Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong
832 Kong, *Atmos. Environ.*, 40, 3030-3040, 2006.
- 833 Huang, X. F., Yu, J. Z., He, L. Y., and Yuan, Z. B.: Water-soluble organic carbon and oxalate in
834 aerosols at a coastal urban site in China: Size distribution characteristics, sources, and
835 formation mechanisms, *J. Geophys. Res.*, 111, D22212, doi:10.1029/2006JD007408, 2006.
- 836 **Jacobson, M. Z.: Atmospheric Pollution: History, Science, and Regulation. Cambridge University**
837 **Press, United Kingdom, 2002.**
- 838 Jacobson, M. C., Hansson, H. C., Noone, K. J., and Charlson, R. J.: Organic atmospheric aerosols:
839 Review and state of science, *Rev. Geophys.*, 38, 267-294, 2000.
- 840 **Jafferson, A., Tanner, D. J., Eisele, F. L., Davis, D. D., Chen, G., Creawford, J., Huey, J. W.,**
841 **Torres, A. L., and Berresheim, H.: OH photochemistry and methane sulfonic acid formation**
842 **in the coastal Antarctic boundary layer, *J. Geophys. Res.*, 103, 1647-1656, 1998.**
- 843 Jung, J. S., Tsatsral, B., Kim, Y. J., and Kawamura, K.: Organic and inorganic aerosol compositions
844 in Ulaanbaatar, Mongolia, during the cold winter of 2007 to 2008: Dicarboxylic acids,
845 ketocarboxylic acids, and alpha-dicarbonyls, *J. Geophys. Res.*, 115, D22203,
846 doi:10.1029/2010JD014339, 2010.
- 847 Kampf, C. J., Corrigan, A. L., Johnson, A. M., Song, W., Keronen, P., Konigstedt, R., Williams, J.,
848 Russel, L. M., Petaja, T., Fischer, H., and Hoffmann, T.: First measurements of reactive alpha-
849 dicarbonyl concentrations on PM_{2.5} aerosols over the Boreal forest in Finland during
850 HUMPPA-COPEC 2010 - source apportionment and links to aerosol aging, *Atmos. Chem.*
851 *Phys.*, 12, 6145-6155, 2012.
- 852 Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Van
853 Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski,
854 Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K.,
855 Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a
856 review, *Atmos. Chem. Phys.*, 5, 1053-1123, 2005.
- 857 Kaufman, Y. J. and Fraser, R. S.: The effect of smoke particles on clouds and climate forcing,
858 *Science*, 277, 1636-1639, 1997.
- 859 Kawamura, K. and Gagosian, R. B.: Implications of ω-oxocarboxylic acids in the remote marine
860 atmosphere for photo-oxidation of unsaturated fatty acids, *Nature*, 325, 330-332, 1987.
- 861 Kawamura, K. and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the
862 urban atmosphere, *Environ. Sci. Technol.*, 27, 2227-2235, 1993.
- 863 Kawamura, K. and Kaplan, I. R.: Motor Exhaust Emissions as a Primary Source for Dicarboxylic-
864 Acids in Los-Angeles Ambient Air, *Environ. Sci. Technol.*, 21, 105-110, 1987.
- 865 Kawamura, K. and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids in
866 marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.*, 104, 3501-3509,
867 1999.
- 868 Kawamura, K. and Usukura, K.: Distributions of low molecular weight dicarboxylic acids in the
869 North Pacific aerosol samples, *J. Oceanogr.*, 49, 271-283, 1993.

- 870 Kawamura, K., Imai, Y., and Barrie, L. A.: Photochemical production and loss of organic acids in
871 high Arctic aerosols during long-range transport and polar sunrise ozone depletion events,
872 *Atmos. Environ.*, 39, 599-614, 2005.
- 873 Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of dicarboxylic
874 acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, *Atmos.*
875 *Environ.*, 30, 1709-1722, 1996.
- 876 Kawamura, K., Narukawa, M., Li, S. M., and Barrie, L. A.: Size distributions of dicarboxylic acids
877 and inorganic ions in atmospheric aerosols collected during polar sunrise in the Canadian high
878 Arctic, *J. Geophys. Res.*, 112, D10307, doi:10.1029/2006JD008244, 2007.
- 879 Kawamura, K., Ng, L., and Kaplan, I. R., Determination of organic acids (C₁-C₁₀) in the
880 atmosphere, motor-exhausts and engine oils, *Environ. Sci. Technol.*, 19, 1082-1086, 1985.
- 881 Kawamura, K., Okuzawa, K., Aggarwal, S. G., Irie, H., Kanaya, Y., and Wang, Z.: Determination
882 of gaseous and particulate carbonyls (glycolaldehyde, hydroxyacetone, glyoxal,
883 methylglyoxal, nonanal and decanal) in the atmosphere at Mt. Tai, *Atmos. Chem. Phys.*, 13,
884 5369-5380, 2013.
- 885 Kawamura, K. and Pavuluri, C.M.: New Directions: Need for better understanding of plastic waste
886 burning as inferred from high abundance of terephthalic acid in South Asian aerosols, *Atmos.*
887 *Environ.*, 44, 5320-5321, 2011.
- 888 Kawamura, K., Steinberg, S., and Kaplan, I. R.: Homologous series of C₁-C₁₀ monocarboxylic acids
889 and C₁-C₆ carbonyls in Los Angeles air and motor vehicle exhausts, *Atmos. Environ.*, 34,
890 4175-4191, 2000.
- 891 Kawamura, K.: Identification of C₂-C₁₀ ω-oxocarboxylic acids, pyruvic acid, and C₂-C₃ α-
892 dicarbonyls in wet precipitation and aerosol samples by capillary GC and GC/MS, *Anal.*
893 *Chem.*, 65, 3505-3511, 1993.
- 894 Kerminen, V. -M., Pakkanen, T. A., and Hillamo, R. E.: Interactions between inorganic trace gases
895 and supermicrometer particles at a coastal site, *Atmos. Environ.*, 31, 2753-2765, 1997a.
- 896 Kerminen, V. -M., Aurela, M., Hillamo, R. E., and Virkkula, A.: Formation of particulate MSA:
897 deductions from size distribution measurements in the Finnish Arctic, *Tellus*, 49b, 159-171,
898 1997b.
- 899 Kerminen, V. -M., Teinila, K., Hillamo, R., and Makela, T.: Size-segregated chemistry of
900 particulate dicarboxylic acids in the Arctic atmosphere, *Atmos. Environ.*, 33, 2089-2100,
901 1999.
- 902 Kleeman, M. J. and Cass, G. R.: Effect of emissions control strategies on the size and composition
903 distribution of urban particulate air pollution, *Environ. Sci. Technol.*, 33, 177-189, 1999.
- 904 Kouyoumdjian, H. and Saliba, N. A.: Mass concentration and ion composition of coarse and fine
905 particles in an urban area in Beirut: effect of calcium carbonate on the absorption of nitric and
906 sulfuric acids and the depletion of chloride, *Atmos. Chem. Phys.*, 6, 1865-1877, 2006.
- 907 Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.:
908 Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl
909 compounds, *J. Geophys. Res.*, 110, D23207, doi:10.1029/2005jd006004, 2005.

- 910 Kumar, A., Sarin, M. M., and Sudheer, A. K.: Mineral and anthropogenic aerosols in Arabian Sea-
911 atmospheric boundary layer: Sources and spatial variability, *Atmos. Environ.*, 42, 5169-5181,
912 2008.
- 913 Kundu S., Kawamura, K., Andreae, T. W., Hoffer, A., and Andreae, M. O.: Molecular distributions
914 of dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls in biomass burning aerosols:
915 implications for photochemical production and degradation in smoke layers, *Atmos. Chem.*
916 *Phys.*, 10, 2209-2225, 2010.
- 917 Kunwar, B. and Kawamura, K.: Seasonal distribution and sources of low molecular weight
918 dicarboxylic acids, ω -oxocarboxylic acids, pyruvic acid, α -dicarbonyls and fatty acids in
919 ambient aerosols from subtropical Okinawa in the western Pacific Rim, *Environ. Chem.*, 11,
920 673-689, 2014.
- 921 Legrand, M., Preunkert, S., Oliveira, T., Pio, C. A., Hammer, S., Gelencser, A., Kasper-Giebl, A.,
922 and Laj, P.: Origin of C₂-C₅ dicarboxylic acids in the European atmosphere inferred from
923 year-round aerosol study conducted at a west-east transect, *J. Geophys. Res.*, 112, D23S07,
924 doi:10.1029/2006JD008019, 2007.
- 925 Liggió, J. L., Li, S. M., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, *J.*
926 *Geophys. Res.*, 110, D10304, doi:10.1029/2004JD005113, 2005.
- 927 Lim, H. J., Carlton, A. G., and Turpin, B. J.: Isoprene forms secondary organic aerosol through
928 cloud processing: Model simulations, *Environ. Sci. Technol.*, 39, 4441-4446, 2005.
- 929 Lim, Y. B., Tan, Y., Perri, M. J., Seitzinger, S. P., and Turpin, B. J.: Aqueous chemistry and its role
930 in secondary organic aerosol (SOA) formation, *Atmos. Chem. Phys.*, 10, 10521-10539, 2010.
- 931 Liu, S. Z., Tao, S., Liu, W. X., Liu, Y. N., Dou, H., Zhao, J. Y., Wang, L. G., Wang, J. F., Tian, Z.
932 F., and Gao, Y.: Atmospheric polycyclic aromatic hydrocarbons in north China: A winter-
933 time study, *Environ. Sci. Technol.*, 41, 8256-8261, 2007.
- 934 Mayol-Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari, S., Facchini,
935 M. C., Fuzzi, S., and Artaxo, P.: Water-soluble organic compounds in biomass burning
936 aerosols over Amazonia - 2. Apportionment of the chemical composition and importance of
937 the polyacidic fraction, *J. Geophys. Res.*, 107, 8091, doi:10.1029/2001jd000522, 2002.
- 938 Meinardi, S., Simpson, I. J., Blake, N. J., Blake, D. R., and Rowland, E. S.: Dimethyl disulfide
939 (DMDS) and dimethyl sulfide (DMS) emissions from biomass burning in Australia, *Geophys.*
940 *Res. Lett.*, 30, 1454, doi:10.1029/2003GL016967, 2003.
- 941 Mkoma, S. L., Kawamura, K., and Fu, P. Q.: Contributions of biomass/biofuel burning to organic
942 aerosols and particulate matter in Tanzania, East Africa, based on analyses of ionic species,
943 organic and elemental carbon, levoglucosan and mannosan, *Atmos. Chem. Phys.*, 13, 10325-
944 10338, 2013.
- 945 Miyazaki, Y., Kawamura, K., and Sawano, M.: Size distributions and chemical characterization of
946 water-soluble organic aerosols over the western North Pacific in summer, *J. Geophys. Res.*,
947 115, D23210, doi:10.1029/2010JD014439, 2010.
- 948 Miyazaki, Y., Kawamura, K., Jung, J., Furutani, H., and Uematsu, M.: Latitudinal distributions of
949 organic nitrogen and organic carbon in marine aerosols over the western North Pacific,
950 *Atmos. Chem. Phys.*, 11, 3037-3049, 2011.

- 951 Mochida, M., Kawamura, K., Umemoto, N., Kobayashi, M., Matsunaga, S., Lim, H. J., Turpin, B.
952 J., Bates, T. S., and Simoneit, B. R. T.: Spatial distributions of oxygenated organic
953 compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the
954 western Pacific and off the coast of East Asia: Continental outflow of organic aerosols during
955 the ACE-Asia campaign, *J. Geophys. Res.*, 108, 8638, doi:10.1029/2002JD003249, 2003a.
- 956 Mochida, M., Umemoto, N., Kawamura, K., and Uematsu, M.: Bimodal size distribution of C₂-C₄
957 dicarboxylic acids in the marine aerosols, *Geophys. Res. Lett.*, 30, 1672, doi:
958 10.1029/2003GL017451, 2003b.
- 959 Mochida, M., Umemoto, N., Kawamura, K., Lim, H. J., and Turpin, B. J.: Bimodal size
960 distributions of various organic acids and fatty acids in the marine atmosphere: Influence of
961 anthropogenic aerosols, Asian dusts, and sea spray off the coast of East Asia, *J. Geophys.*
962 *Res.*, 112, D15209, doi:10.1029/2006JD007773, 2007.
- 963 Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers,
964 A., and Kanakidou, M.: In-cloud oxalae formation in the regional troposphere: a 3-D
965 modelling study, *Atmos. Chem. Phys.*, 11, 5761-5782, 2011.
- 966 Nenes, A., Pandis, S. N., and Pilinis, C.: ISORROPIA: A new thermodynamic equilibrium model
967 for multiphase multicomponent inorganic aerosols, *Aquat. Geochem.*, 4, 123-152, 1998.
- 968 Pakkanen, T. A., Loukkola, K., Korhonen, C. H., Aurela, M., Makela, T., Hillamo, R. E., Aarnio,
969 P., Koskentalo, T., Kousa, A., and Maenhaut, W.: Sources and chemical composition of
970 atmospheric fine and coarse particles in the Helsinki area, *Atmos. Environ.*, 35, 5381-5391,
971 2001.
- 972 Pavuluri, C. M., Kawamura, K., Mihalopoulos, N., and Swaminathan, T.: Laboratory
973 photochemical processing of aqueous aerosols: formaion and degradation of dicarboxylic
974 acids, oxocarboxylic acids, and alpha-dicarbonyls, *Atmos. Chem. Phys.*, 15, 7999-8012, 2015.
- 975 Pope, C. A. and Dockery, D. W.: Health effects of fine particulate air pollution: Lines that connect,
976 *J. Air Waste Manage.*, 56, 709-742, 2006.
- 977 Pradeep Kumar, P., Broekhuizen, K., and Abbatt, J. P. D.: Organic acids as cloud condensation
978 nuclei: Laboratory studies of highly soluble and insoluble species, *Atmos. Chem. Phys.*, 3,
979 509-520, 2003.
- 980 Quinn, P. K., Covert, D. S., Bates, T. S., Kapustin, V. N., Ramseybell, D. C., and McInnes, L. M.:
981 Dimethylsulfide cloud condensation nuclei climate system - relevant size-resolved
982 measurements of the chemical and physical-properties of atmospheric aerosol-particles, *J.*
983 *Geophys. Res.*, 98, 10411-10427, 1993.
- 984 Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D.: Atmosphere - Aerosols, climate,
985 and the hydrological cycle, *Science*, 294, 2119-2124, 2001.
- 986 Schauer, J. J., Rogge, W. F., Hildemann, L. M., Mazurek, M. A., and Cass, G. R.: Source
987 apportionment of airborne particualte matter using organic compounds as tracers, *Atmos.*
988 *Environ.*, 30, 3837-3855, 1996.
- 989 Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: From air pollution to climate
990 change, 2nd edition, J. Wiley, New York, 2006.

- 991 Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics, John Wiley & Sons, New
992 York, 1998.
- 993 Seinfeld, J. H. and Pankow, J. F.: Organic atmospheric particulate material, *Annu. Rev. Phys.*
994 *Chem.*, 54, 121-140, 2003.
- 995 Sempéré, R. and Kawamura, K.: Trans-hemispheric contribution of C₂-C₁₀ α,ω -dicarboxylic acids,
996 and related polar compounds to water-soluble organic carbon in the western Pacific aerosols
997 in relation to photochemical oxidation reactions, *Glob. Biogeochem. Cycle*, 17, 1069,
998 doi:10.1029/2002GB001980, 2003.
- 999 Shimada, K., Shimida, M., Takami, A., Hasegawa, S., Akihiro, F., Arakaki, T., Izumi, W., and
1000 Hatakeyama, S.: Mode and place of origin of carbonaceous aerosols transported from East
1001 Asia to Cape Hedo, Okinawa, Japan, *Aerosol Air. Qual. Res.*, 15, 799-813, 2015.
- 1002 Simoneit, B. R. T., Medeiros, P. M., and Didyk, B. M.: Combustion products of plastics as
1003 indicators for refuse burning in the atmosphere, *Environ. Sci. Technol.*, 39, 6961-6970, 2005.
- 1004 Speer, R. E., Edney, E. O., and Kleindienst, T. E.: Impact of organic compounds on the
1005 concentrations of liquid water in ambient PM_{2.5}, *J. Aerosol Sci.*, 34, 63-77, 2003.
- 1006 Takami, A., Miyoshi, T., Shimono, A., Kaneyasu, N., Kato, S., Kajii, Y., and Hatakeyama, S.:
1007 Transport of anthropogenic aerosols from Asia and subsequent chemical transformation, *J.*
1008 *Geophys. Res.*, 112, D22S31, doi 10.1029/2006jd008120, 2007.
- 1009 Takiguchi, Y., Takami, A., Sadanaga, Y., Lun, X. X., Shimizu, A., Matsui, I., Sugimoto, N., Wang,
1010 W., Bandow, H., and Hatakeyama, S.: Transport and transformation of total reactive nitrogen
1011 over the East China Sea, *J. Geophys. Res.*, 113, D10306, doi:10.1029/2007jd009462, 2008.
- 1012 Tao, J., Zhang, L., Engling, G., Zhang, R., Yang, T., Cao, J., Zhu, C., Wang, Q., and Luo, L.:
1013 Chemical composition of PM_{2.5} in an urban environment in Chengdu, China: Importance of
1014 springtime dust storms and biomass burning, *Atmos. Res.*, 122, 270-283, 2013.
- 1015 Tao, S., Wang, Y., Wu, S. M., Liu, S. Z., Dou, H., Liu, Y. N., Lang, C., Hu, F., and Xing, B. S.:
1016 Vertical distribution of polycyclic aromatic hydrocarbons in atmospheric boundary layer of
1017 Beijing in winter, *Atmos. Environ.*, 41, 9594-9602, 2007.
- 1018 Tsai, Y. I. and Chen, C. L.: Characterization of Asian dust storm and non-Asian dust storm PM_{2.5}
1019 aerosol in southern Taiwan, *Atmos. Environ.*, 40, 4734-4750, 2006.
- 1020 Turpin, B. J. and Lim, H. J.: Species contributions to PM_{2.5} mass concentrations: Revisiting
1021 common assumptions for estimating organic mass, *Aerosol. Sci. Tech.*, 35, 602-610, 2001.
- 1022 Volkamer, R., Platt, U., and Wirtz, K.: Primary and secondary glyoxal formation from aromatics:
1023 Experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene, and p-
1024 xylene, *J. Phys. Chem. A*, 105, 7865-7874, 2001.
- 1025 Wang, G. H., Kawamura, K., Xie, M. J., Hu, S. Y., Li, J. J., Zhou, B. H., Cao, J. J., and An, Z. S.:
1026 Selected water-soluble organic compounds found in size-resolved aerosols collected from
1027 urban, mountain and marine atmospheres over East Asia, *Tellus*, 63, 371-381, 2011.
- 1028 Wang, G. H., Zhao, B. H., Cheng, C. L., Cao, J. J., Li, J. J., Meng, J. J., Tao, J., Zhang, R. J., and
1029 Fu, P. Q.: Impact of Gobi desert dust on aerosol chemistry of Xi'an, inland China during

- 1030 spring 2009: differences in composition and size distribution between the urban ground
1031 surface and the mountain atmosphere, *Atmos. Chem. Phys.*, 13, 819-835, 2013.
- 1032 Wang, H., Kawamura, K., and Shooter, D.: Carbonaceous and ionic components in wintertime
1033 atmospheric aerosols from two New Zealand cities: Implication for solid fuel combustion,
1034 *Atmos. Environ.*, 39, 5865-5875, 2005a.
- 1035 Wang, Y., Zhuang, G. S., Sun, Y., and An, Z. S.: Water-soluble part of the aerosol in the dust storm
1036 season - evidence of the mixing between mineral and pollution aerosols, *Atmos. Environ.*, 39,
1037 7020-7029, 2005b.
- 1038 Warneck, P.: In-cloud chemistry opens pathway to the formation of oxalic acid in the marine
1039 atmosphere, *Atmos. Environ.*, 37, 2423-2427, 2003.
- 1040 Yamasoe, M. A., Artaxo, P., Miguel, A. H., and Allen, A. G.: Chemical composition of aerosol
1041 particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species
1042 and trace elements, *Atmos. Environ.*, 34, 1641-1653, 2000.
- 1043 Zimmermann, J. and Poppe, D.: A supplement for the RADM2 chemical mechanism: The
1044 photooxidation of isoprene, *Atmos. Environ.*, 30, 1255-1269, 1996.

Table 1. Concentrations ($\mu\text{g m}^{-3}$) of carbonaceous species and major inorganic ions in the fine and coarse mode aerosols in Okinawa Island in the Western North Pacific.

Inorganic ions	Fine mode ^a				Coarse mode ^b			
	Mean	S.D. ^c	Min. ^d	Max. ^e	Mean	S.D.	Min.	Max.
Water-soluble inorganic ions								
Cations								
Na ⁺	0.44	0.20	0.21	0.72	2.42	0.89	1.60	3.65
NH ₄ ⁺	2.40	1.18	0.74	3.69	0.03	0.01	0.03	0.05
K ⁺	0.14	0.06	0.04	0.21	0.09	0.02	0.07	0.12
Mg ²⁺	0.07	0.02	0.04	0.10	0.34	0.11	0.24	0.49
Ca ²⁺	0.06	0.02	0.04	0.09	0.41	0.19	0.15	0.60
Total cations	3.12	1.22	1.28	4.37	3.29	1.02	2.55	4.82
Anions								
MSA ⁻	0.04	0.01	0.03	0.06	0.01	0.00	0.00	0.01
Cl ⁻	0.12	0.13	0.02	0.29	4.27	2.25	1.77	7.25
NO ₃ ⁻	0.14	0.08	0.04	0.23	1.61	0.54	0.94	2.41
SO ₄ ²⁻	10.1	4.85	2.88	14.9	1.46	0.44	0.69	1.81
Total anions	10.4	4.73	3.33	15.1	7.35	2.20	5.69	10.6
Total water-soluble ions								
Total water-soluble ions	13.5	5.95	4.61	19.5	10.6	3.22	8.33	15.4
Carbonaceous components								
WSOC	1.12	0.49	0.31	1.61	0.33	0.13	0.15	0.52
OC	1.62	0.59	0.62	2.12	0.60	0.17	0.36	0.82
OM	3.43	1.31	1.30	4.87	1.25	0.36	0.75	1.73
EC	0.05	0.03	0.00	0.09	-	-	-	-
TC	1.67	0.65	0.62	2.41	0.60	0.17	0.36	0.82

^aFine mode represents aerosol size of $D_p < 2.1 \mu\text{m}$.^bCoarse mode represents aerosol size of $D_p > 2.1 \mu\text{m}$.^cStandard deviation.^dMinimum.^eMaximum.

Table 2. Concentrations (ng m⁻³) of water-soluble dicarboxylic acids and related polar compounds in the fine and coarse mode aerosols in Okinawa Island in the Western North Pacific.

Compounds	Abbreviation	Chemical formula	Fine mode ^a				Coarse mode ^b			
			Mean	S.D. ^c	Min. ^d	Max. ^e	Mean	S.D.	Min.	Max.
Dicarboxylic acids										
Saturated normal-chain diacids										
Oxalic	C ₂	HOOC-COOH	135	37.4	76.0	176	40.2	14.7	22.1	60.0
Malonic	C ₃	HOOC-CH ₂ -COOH	19.5	6.84	7.56	23.6	12.4	3.52	6.87	15.5
Succinic	C ₄	HOOC-(CH ₂) ₂ -COOH	13.4	4.98	5.08	17.5	8.02	2.21	4.66	10.1
Glutaric	C ₅	HOOC-(CH ₂) ₃ -COOH	3.30	1.54	1.00	4.75	1.89	0.57	1.07	2.66
Adipic	C ₆	HOOC-(CH ₂) ₄ -COOH	3.49	1.09	2.47	4.98	2.50	1.24	1.45	4.23
Pimelic	C ₇	HOOC-(CH ₂) ₅ -COOH	0.46	0.24	0.04	0.63	0.32	0.11	0.20	0.44
Suberic	C ₈	HOOC-(CH ₂) ₆ -COOH	0.07	0.07	0.00	0.16	0.04	0.02	0.02	0.07
Azelaic	C ₉	HOOC-(CH ₂) ₇ -COOH	1.20	0.72	0.51	2.41	1.15	0.60	0.49	2.10
Decanedioic	C ₁₀	HOOC-(CH ₂) ₈ -COOH	0.17	0.11	0.01	0.30	0.08	0.07	0.03	0.19
Undecanedioic	C ₁₁	HOOC-(CH ₂) ₉ -COOH	0.47	0.33	0.13	0.76	0.25	0.10	0.14	0.38
Dodecanedioic	C ₁₂	HOOC-(CH ₂) ₁₀ -COOH	0.07	0.03	0.03	0.09	0.05	0.02	0.02	0.07
Branched-chain diacids										
Methylmalonic	iC ₄	HOOC-CH(CH ₃)-COOH	0.43	0.23	0.09	0.71	0.47	0.37	0.09	0.99
Methylsuccinic	iC ₅	HOOC-CH(CH ₃)-COOH	0.81	0.27	0.37	1.00	0.59	0.13	0.45	0.80
2-Methylglutaric	iC ₆	HOOC-CH(CH ₃)-(CH ₂) ₂ -COOH	0.35	0.24	0.05	0.70	0.19	0.20	0.04	0.53
Unsaturated aliphatic diacids										
Maleic	M	HOOC-CH=CH-COOH - <i>cis</i>	0.81	0.25	0.41	1.05	0.73	0.23	0.37	0.95
Fumaric	F	HOOC-CH=CH-COOH - <i>trans</i>	0.31	0.09	0.20	0.42	0.21	0.08	0.12	0.30
Methylmaleic	mM	HOOC-C(CH ₃)=CH-COOH - <i>cis</i>	0.34	0.27	0.11	0.76	0.57	0.48	0.11	1.37
Unsaturated aromatic diacids										
Phthalic	Ph	HOOC-(C ₆ H ₄)-COOH - <i>o-isomer</i>	6.29	2.85	1.99	9.3	2.79	0.81	1.85	3.9
Isophthalic	iPh	HOOC-(C ₆ H ₄)-COOH - <i>m-isomer</i>	0.46	0.07	0.35	0.55	0.17	0.06	0.09	0.22
Terephthalic	tPh	HOOC-(C ₆ H ₄)-COOH - <i>p-isomer</i>	2.21	1.15	0.32	3.30	0.64	0.38	0.09	1.17
Multifunctional diacids										
Malic	hC ₄	HOOC-CH(OH)-CH ₂ -COOH	0.14	0.05	0.11	0.21	0.14	0.06	0.07	0.20
Ketomalonic	kC ₃	HOOC-C(O)-COOH	4.92	3.79	0.46	9.28	0.49	0.17	0.32	0.77
4-Ketopimelic	kC ₇	HOOC-CH ₂ -CH ₂ -HC(O)(CH ₃) ₂ -COOH	2.57	0.83	1.26	3.20	0.43	0.16	0.26	0.69
Total diacids			196	58.1	98.3	253	74.1	24.3	41.4	105
ω -Oxocarboxylic acids										
Glyoxylic	ω C ₂	OHC-COOH	14.1	5.92	4.77	20.2	4.81	2.00	2.23	7.20
3-Oxopropanoic	ω C ₃	OHC-CH ₂ -COOH	0.08	0.05	0.00	0.12	0.05	0.04	0.02	0.12
4-Oxobutanoic	ω C ₄	OHC-(CH ₂) ₂ -COOH	2.23	1.12	0.86	3.56	0.68	0.35	0.41	1.22
9-Oxononanoic	ω C ₉	OHC-(CH ₂) ₇ -COOH	0.74	0.20	0.54	1.07	1.06	0.34	0.57	1.41
Total oxoacids			17.1	7.04	6.27	25.0	6.60	2.33	3.26	9.52
Ketoacid										
Pyruvic	Pyr	CH ₃ -C(O)-COOH	2.61	0.76	1.67	3.48	2.32	1.20	0.76	4.09
α -Dicarbonyls										
Glyoxal	Gly	OHC-CHO	2.74	1.12	1.45	4.40	0.84	0.26	0.50	1.17
Methylglyoxal	MeGly	CH ₃ -C(O)-CHO	1.09	0.98	0.25	2.53	0.65	0.16	0.45	0.87
Total α -dicarbonyls			2.83	1.59	1.03	4.68	1.49	0.37	0.96	1.86
Aromatic monoacid										
Benzoic acid		H ₅ C ₆ -COOH	16.5	11.0	4.57	28.3	1.98	1.01	0.70	3.38

^aFine mode represents aerosol size of D_p < 2.1 μ m.^bCoarse mode represents aerosol size of D_p > 2.1 μ m.^cStandard deviation.^dMinimum.^eMaximum.

1045 **Figure Captions**

1046 **Figure 1.** A map of East Asia with the location of Okinawa Island (26.87°N and 128.25°E) and
1047 major megacities in Asia.

1048 **Figure 2.** NOAA HYSPLIT seven-day backward air mass trajectories at 500 m a.g.l. for the aerosol
1049 samples (OKI-1 to OKI-5) at Okinawa Island. The dates given in each panel in figure are the
1050 starting and ending date of collection of aerosol samples in Okinawa Island.

1051 **Figure 3.** Average size-segregated chemical composition of spring aerosols collected at Okinawa
1052 Island.

1053 **Figure 4.** Average molecular distributions of water-soluble dicarboxylic acids and related
1054 compounds in size-segregated aerosols collected at Okinawa Island.

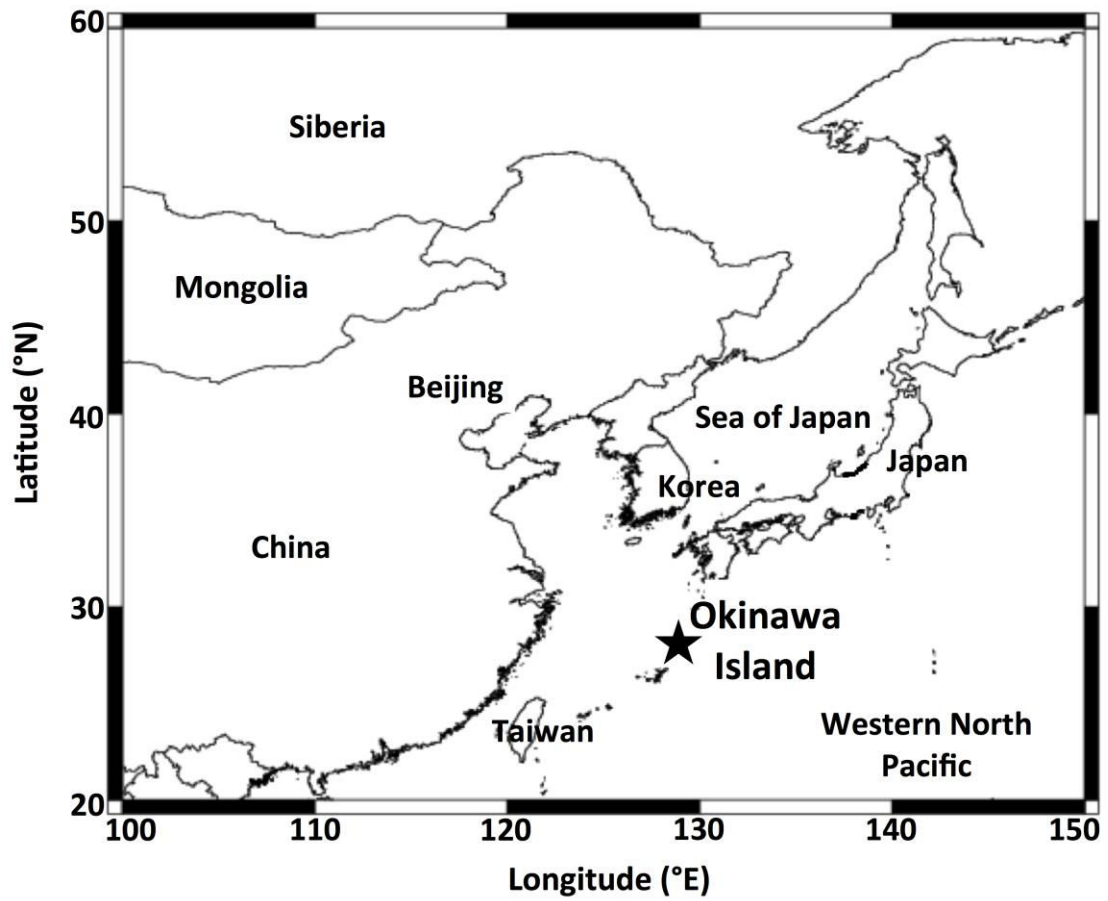
1055 **Figure 5.** Size distributions of water-soluble inorganic ions in the aerosol samples collected at
1056 Okinawa Island.

1057 **Figure 6.** Aerosol liquid water contents for each sample in size-segregated aerosols and mean liquid
1058 water contents of size-segregated aerosols at Okinawa Island.

1059 **Figure 7.** Size distributions of selected water-soluble dicarboxylic acids and related compounds in
1060 the aerosol samples collected at Okinawa Island.

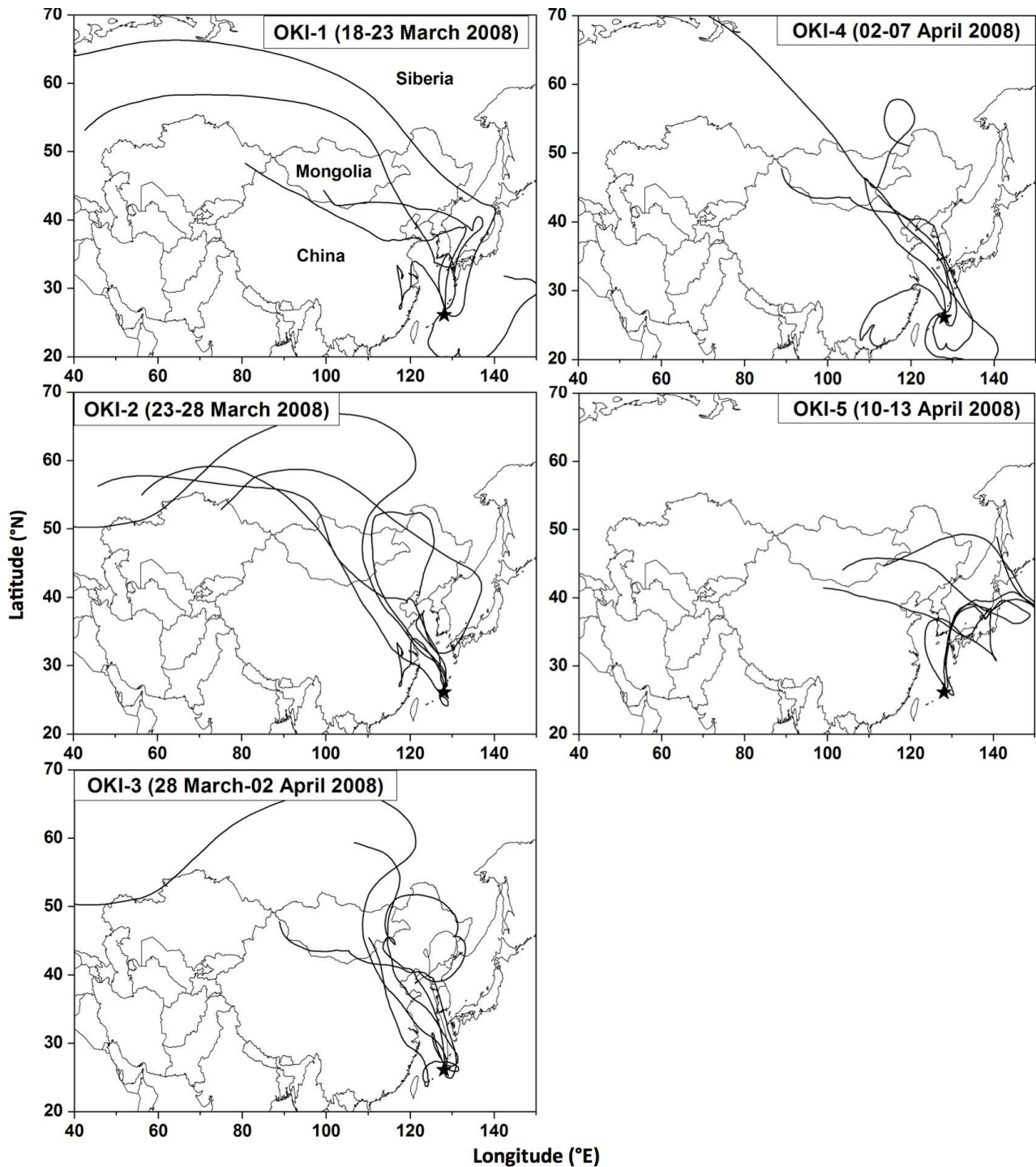
1061 **Figure 8.** Size distributions of water-soluble organic carbon (WSOC) and organic carbon (OC) in
1062 the aerosol samples collected at Okinawa Island.

1063 **Figure 9.** Mass concentration ratio of malonic to succinic acid and phthalic to azelaic acid in size-
1064 segregated aerosols collected at Okinawa Island.



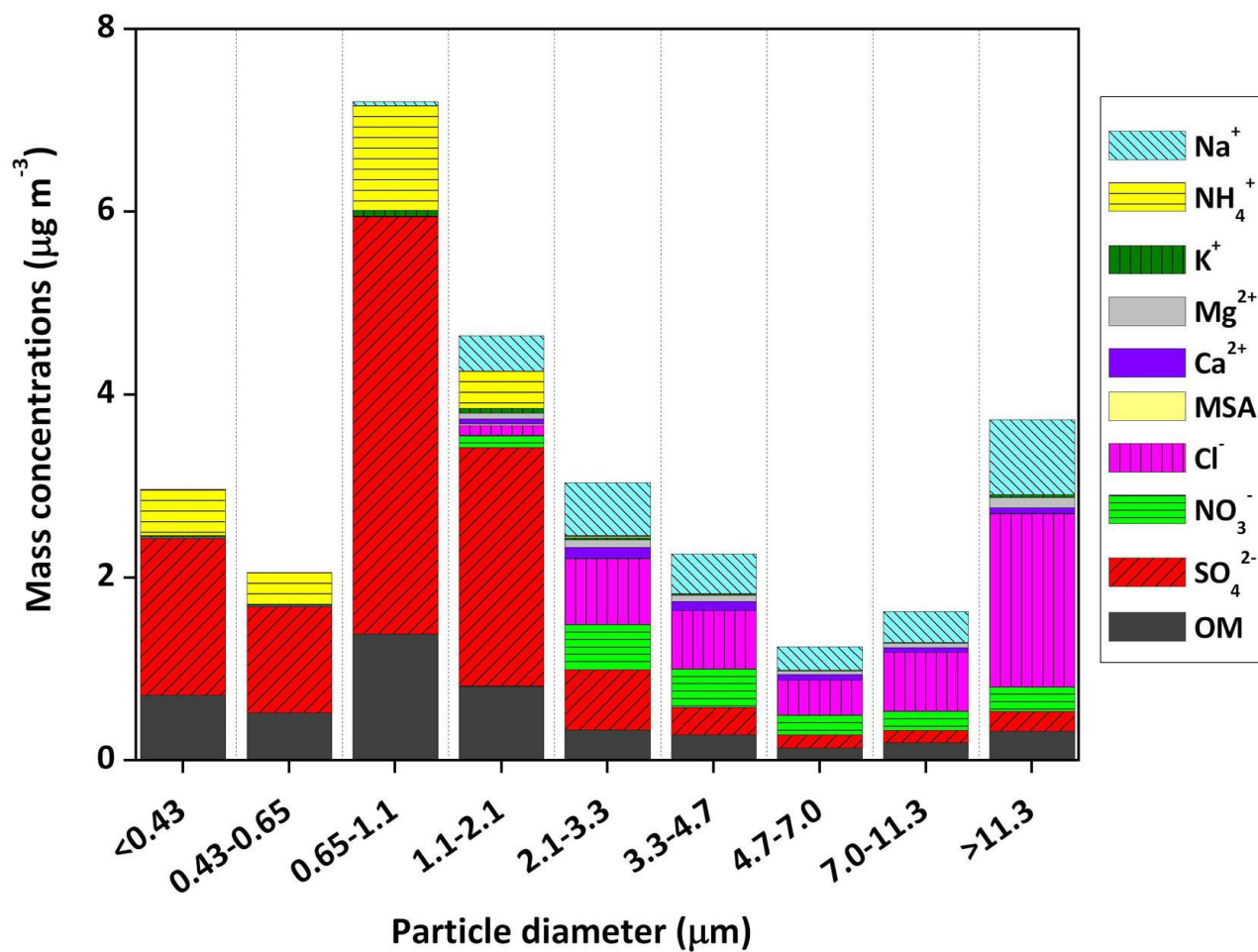
1065

1066 **Figure 1.** A map of East Asia with the location of Okinawa Island (26.87°N and 128.25°E) and
1067 major megacities.



1068

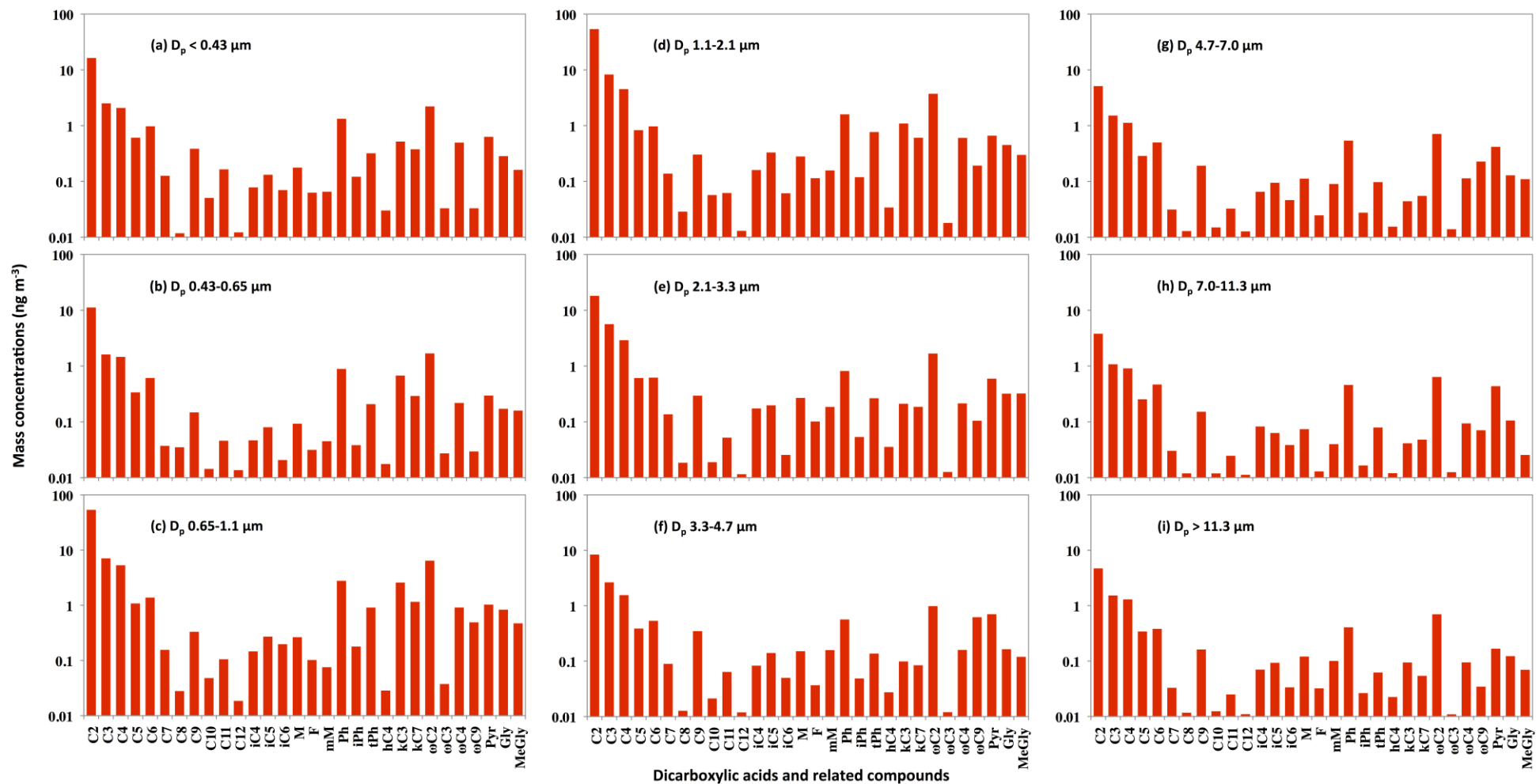
1069 **Figure 2.** NOAA HYSPLIT seven-day backward air mass trajectories at 500 m a.g.l. for the aerosol
 1070 samples (OKI-1 to OKI-5) at Okinawa Island. The dates given in each panel in figure are the
 1071 starting and ending date of collection of aerosol samples in Okinawa Island.



1072

1073 **Figure 3.** Average size-segregated chemical composition of spring aerosols collected at Okinawa

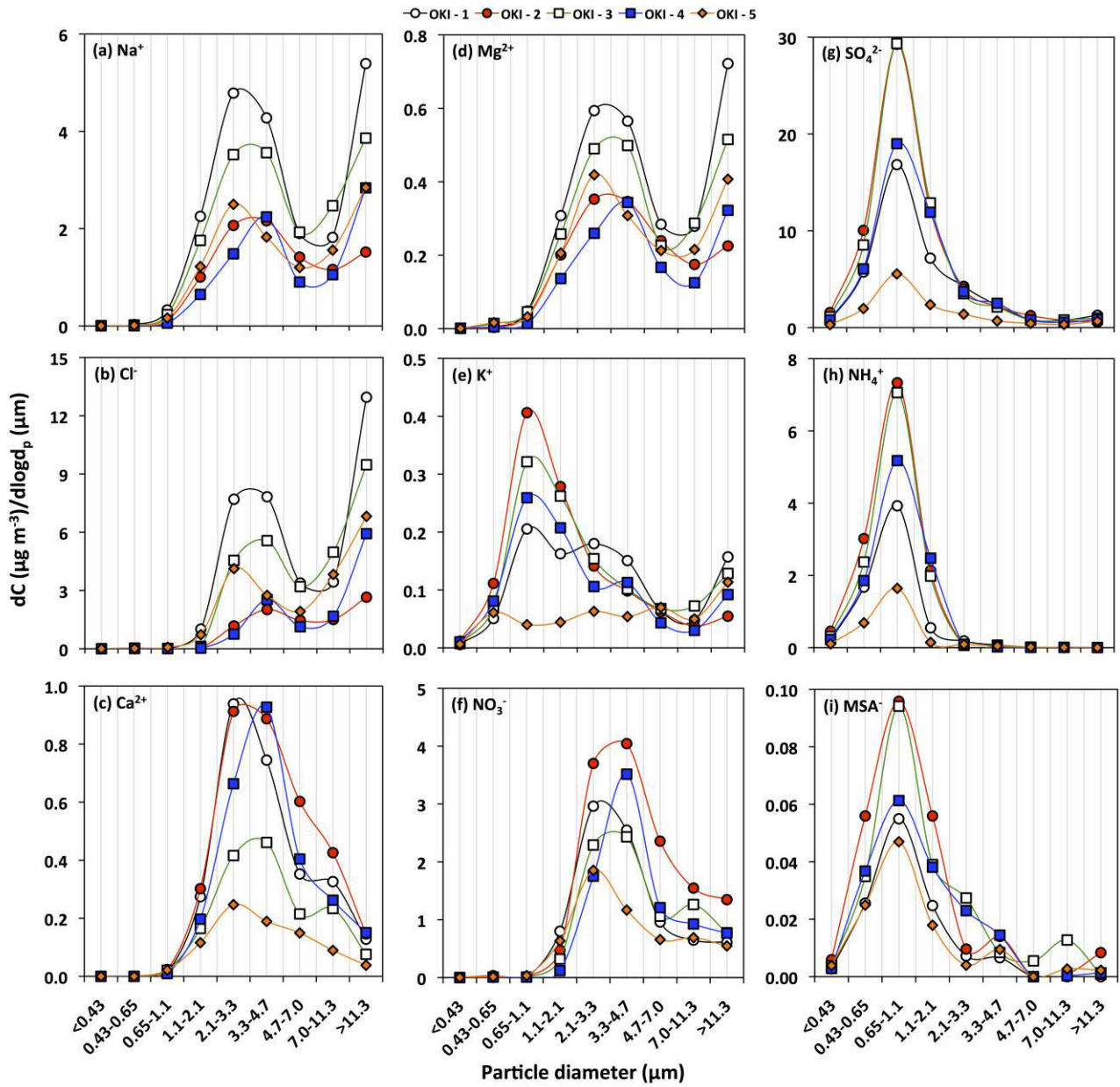
1074 Island.



1075

1076 **Figure 4.** Average molecular distributions of water-soluble dicarboxylic acids and related compounds in size-segregated aerosols collected at Okinawa

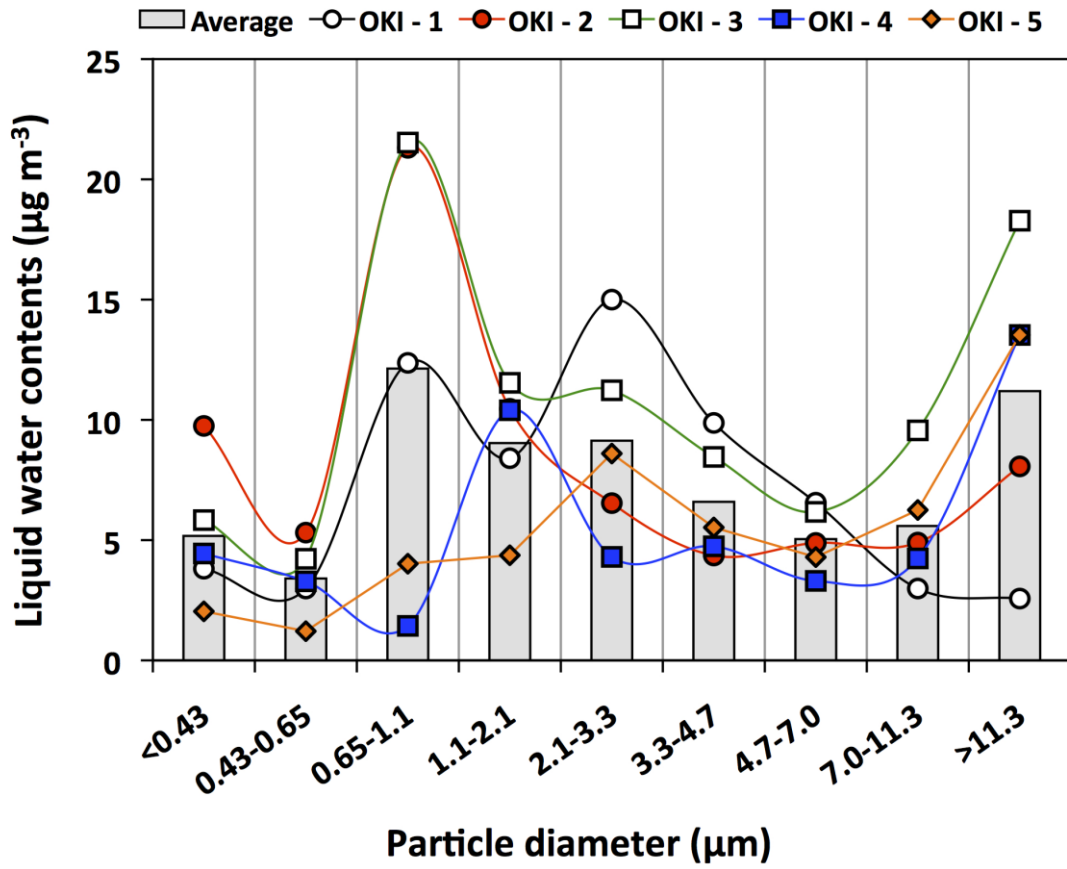
1077 Island.



1078

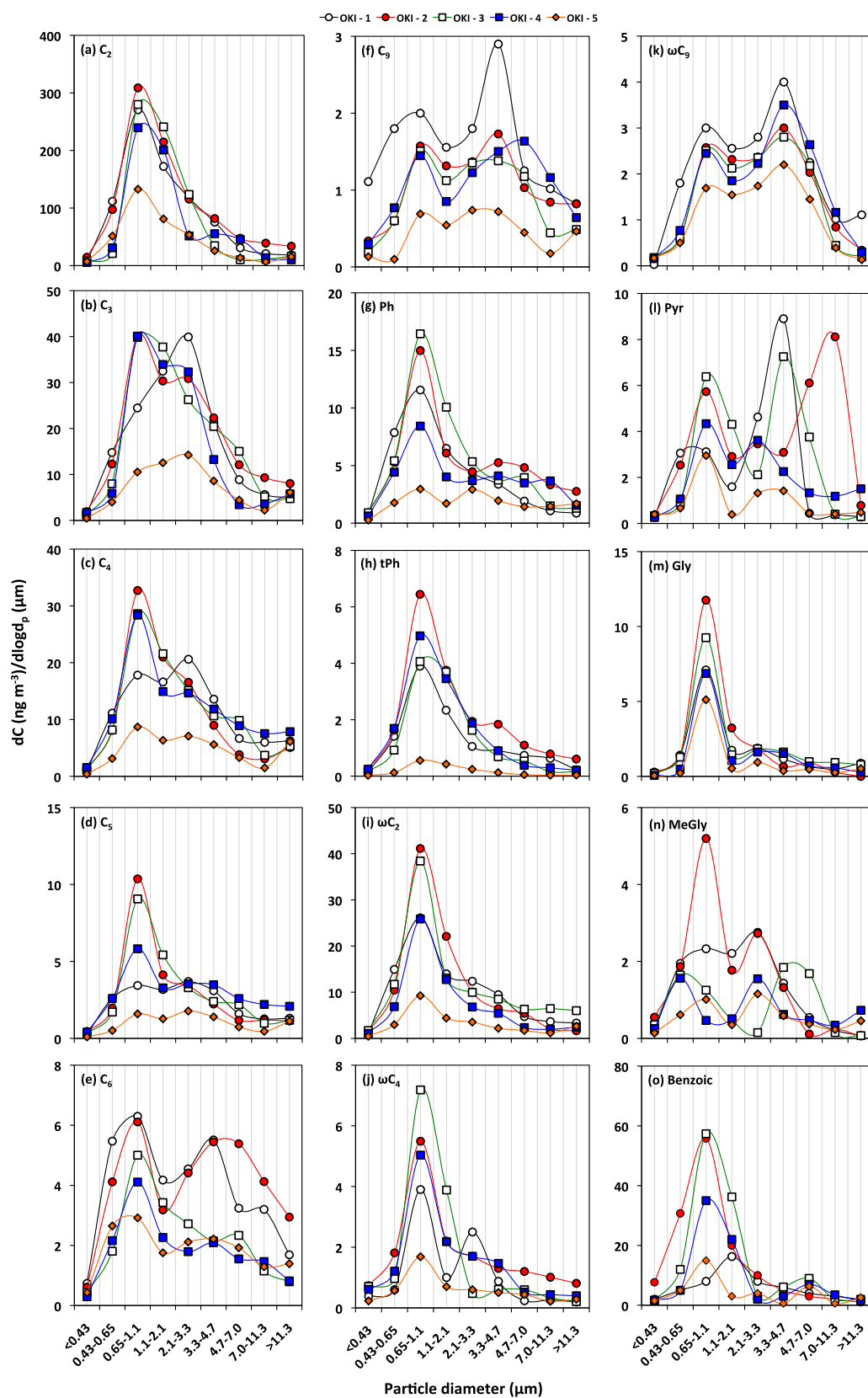
1079 **Figure 5.** Size distributions of water-soluble inorganic ions in the aerosol samples collected at

1080 Okinawa Island.



1081

1082 **Figure 6.** Aerosol liquid water contents for each sample in size-segregated aerosols and mean liquid
 1083 water contents of size-segregated aerosols at Okinawa Island.

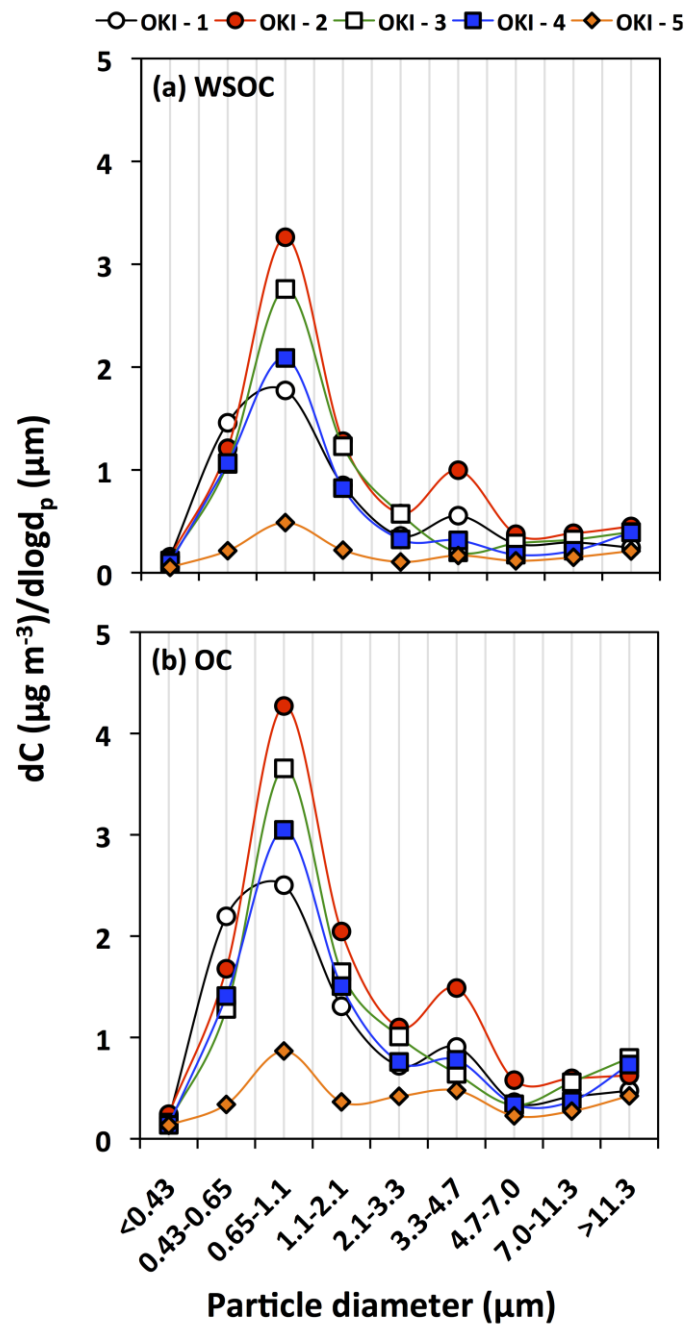


1084

1085 **Figure 7.** Size distributions of selected water-soluble dicarboxylic acids and related compounds in

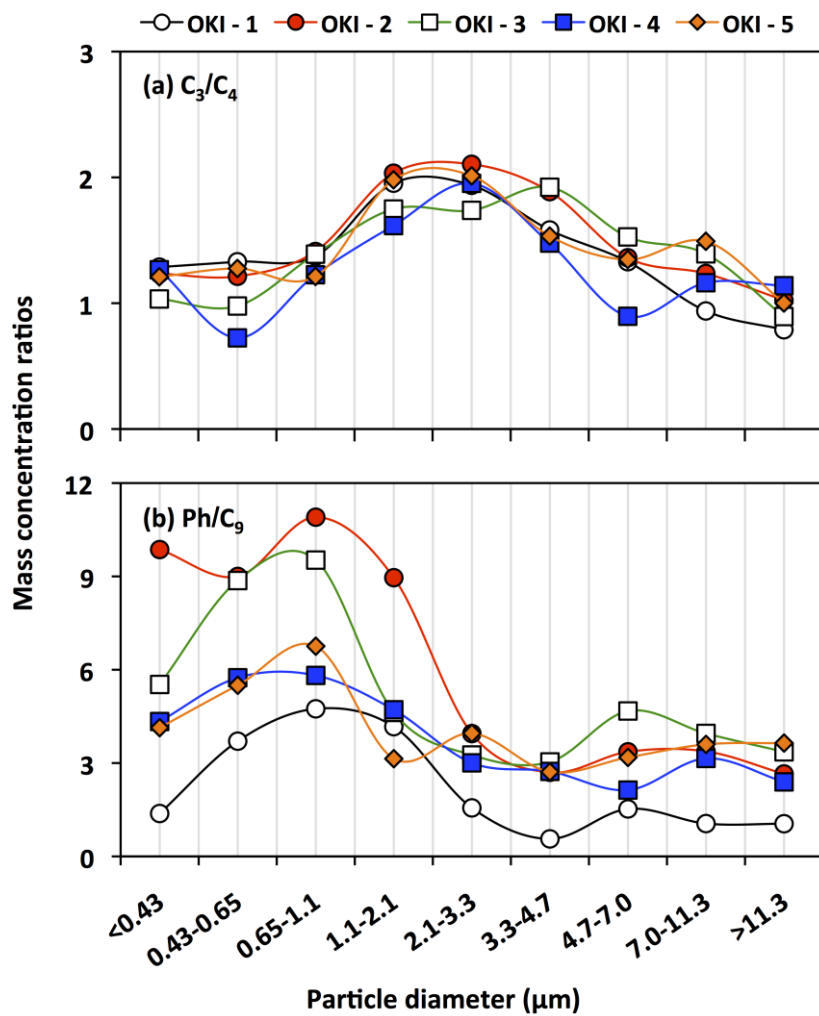
1086 the aerosol samples collected at Okinawa Island.

1087



1088

1089 **Figure 8.** Size distributions of water-soluble organic carbon (WSOC) and organic carbon (OC) in
 1090 the aerosol samples collected at Okinawa Island.



1091

1092 **Figure 9.** Mass concentration ratio of malonic to succinic acid and phthalic to azelaic acid in size-
 1093 segregated aerosols collected at Okinawa Island.