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.

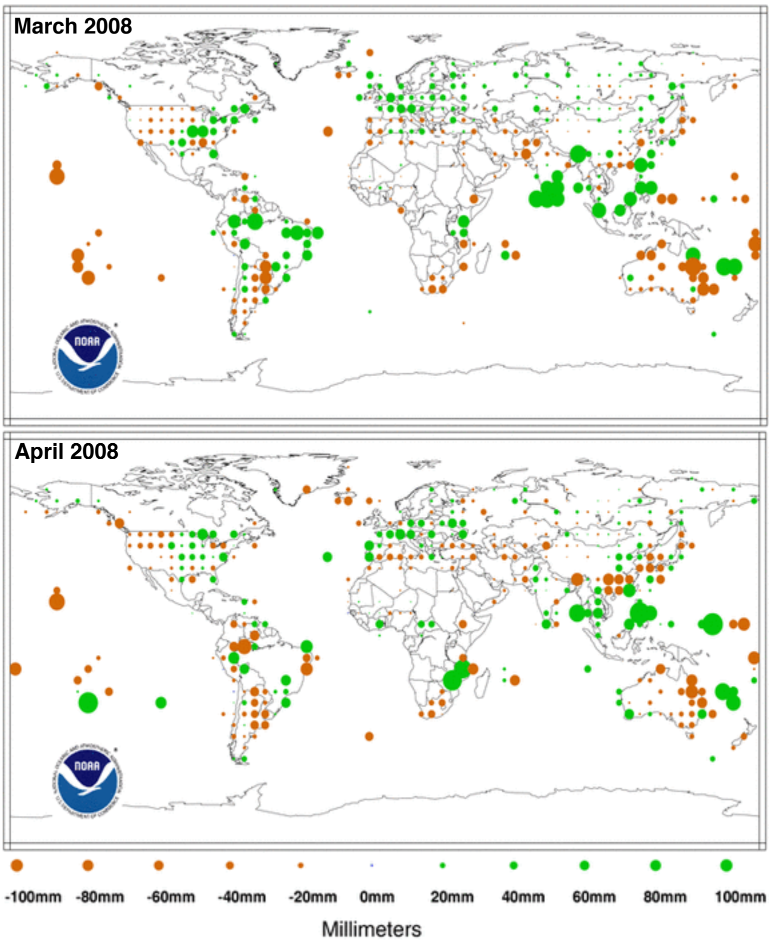
The global map of precipitation data obtained from the website: **http://www.ncdc.noaa.gov/temp-and-precip/global-maps/200803?products[]=map-prcp** for March and April 2008, which is shown below, also shows very small precipitation in the source region such as China and Mongolia as well as Siberia. These 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: Phtalate 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 $D_p > 7.0$ µm 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 µg m^{-3}) and OKI-2 (0.60 µg m^{-3}) than that in OKI-5 sample (0.15 µg 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 SO2 to an aqueous particle depends strongly on a pH value the particle as well. Have the authors determined the pH value of the particles in this range? If so, is it acidic, neutral or basic? This needs to be included in the discussion.

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 µm……………………………in 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 NH3 to form particle-phase NH4+ is not affected by the presence of SO42-, rather the pH value of the particle-phase. When the counter ions other than H+ are present in the particles, NH4+ is very unlikely to be present unless (NH4)2SO4 is thermodynamically favorable. What the authors meant here is most likely that acidic 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.

"NH_4^+ in the Okinawa aerosols shows a unimodal size distribution with a peak at 0.65-1.1 µm (Figure 5h), indicating that NH_4^+ is mainly formed by gas-to-particle conversion via the reaction with H_2SO_4 and HNO_3. Interestingly, the size distribution of NH_4^+ is similar to that of SO_4^{2-} and diacids such as oxalic acid (Figure 5g and 7a). We also found a strong correlation between SO_4^{2-} and NH_4^+ on the fine mode ($r = 0.99$)."

Please see lines 374-378 in the revised MS.

"NH_3 is an alkaline gas that neutralizes the acidic particles in the atmosphere. Kerminen et al. (1997a) proposed that particulate NH_4^+ is secondarily formed via heterogeneous reactions of gaseous NH_3 with acidic species (H_2SO_4 and HNO_3). The reaction of NH_3 with H_2SO_4 is favored over its reaction with HNO_3. The average NH_4^+/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 $(NH_4)_2SO_4$ 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 NH_4^+/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 NH_4^+/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.

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 C_2 and NH_4^+ ($r = 0.89$) in fine fraction suggested that C_2 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 C_2 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 C_2 diacid (Carlton et al. 2006, 2007; Legrand et al. 2007). The fine mode peak of C_2 at the size of 0.65-1.1 μm in Okinawa aerosols suggests a preferential production of C_2 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 C_2 diacid is similar to that of SO_4^{2-} (Figure 5g and 7a), suggesting a secondary formation of C_2 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 C_2 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 C2 diacid. Their good correlations do not necessarily indicate that C2 diacid is formed from C3-C5 diacids. It is also plausible that they all originate from the photooxidation of a mixture of VOCs during transport.
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 C_2 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.

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

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Abstract

Size-segregated aerosols (9-stages from <0.43 to >11.3 µm in diameter) were collected at Cape Hedo, Okinawa in spring 2008 and analyzed for water-soluble diacids (C_2-C_{12}), ω-oxoacids (ωC_2-ωC_9), pyruvic acid, benzoic acid and α-dicarbonyls (C_2-C_3) as well as water-soluble organic carbon (WSOC), organic carbon (OC) and major ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, and MSA^-). In all the size-segregated aerosols, oxalic acid (C_2) was found as the most abundant species followed by malonic and succinic acids whereas glyoxylic acid (ωC_2) was the dominant oxoacid and glyoxal (Gly) was more abundant than methylglyoxal. Diacids (C_2-C_5), ωC_2 and Gly as well as WSOC and OC peaked at 0.65-1.1 µm in fine mode whereas azelaic (C_9) and 9-oxononanoic (ωC_9) acids peaked at 3.3-4.7 µm in coarse mode. Sulfate and ammonium are enriched in fine mode whereas sodium and chloride are in coarse mode. Strong correlations of C_2-C_5 diacids, ωC_2 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. The coarse mode peaks of malonic and succinic acids were obtained in the samples with marine air masses, suggesting that they may be associated with the reaction on sea salt particles. Bimodal size distributions of longer-chain diacid (C_9) and oxoacid (ωC_9) with a major peak in the coarse mode suggest their production by photooxidation of biogenic unsaturated fatty acids via heterogeneous reactions on sea salt particles.

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

1 Introduction

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

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

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

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

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

2 Materials and method

2.1 Site description and aerosol collection

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

Size-segregated aerosol samples were collected at Cape Hedo Atmospheric and Aerosol Monitoring Station (CHAAMS) in March 18 to April 13, 2008. This period is characterized by the westerly wind in the lower troposphere, which is the principal process responsible for the transport of both fossil fuel combustion and biomass burning aerosols in East Asia to the western North Pacific. 9-Stage Andersen Middle Volume Impactor (Tokyo Dylec Company, Japan; 100 L min^{-1}) was used for the collection of size-segregated samples. The sampler was equipped with quartz fiber filters (QFF, 80 mm in diameter) that were pre-combusted at 450°C for 6 h in a furnace to eliminate the adsorbed organic compounds. A total of five sets (OKI-1 to OKI-5) of size-segregated aerosol samples were collected. Each sample set consists of nine filters for the sizes of <0.43, 0.43-0.65, 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 preheated 50 mL glass vial with a Teflon-lined screw cap and stored in a freezer at the station. The samples were stored in darkness at -20°C prior to analysis in Sapporo. One set of field blank was collected by placing a pre-combusted QFF for 30s without sucking air before installing real QFF into the sampler.

2.2 Analytical procedures

Diacids and related compounds were analyzed using the method reported in Kawamura and Ikushima (1993), and Kawamura (1993). Aliquot of the filters were extracted with organic-free ultrapure water (specific resistivity >18.2 MΩ-cm) under ultrasonication. The extracts were passed through glass column packed with quartz wool to remove insoluble particles and filter debris. The extracts were concentrated using a rotary evaporator under vacuum and derivatized to dibutyl esters and dibutoxy acetals with 14% BF_3 in *n*-butanol at 100°C. Acetonitrile and *n*-hexane were added into the derivatized sample and washed with organic-free pure water. The hexane layer was further concentrated using a rotary evaporator and dried to almost dryness by N_2 blowdown and dissolve in a known volume of *n*-hexane. A 2 μL aliquot of the sample was injected into a capillary GC (Hewlett-Packard HP6890) equipped with an FID detector. Authentic diacid dibutyl esters were used as external standards for the peak identification and quantification. Identifications of diacids and related compounds were confirmed by GC-mass spectrometry. Recoveries of authentic standards spiked to a pre-combusted QFF were 85% for oxalic acid (C_2) and more than 90% for malonic to adipic (C_3-C_6) acids. The detection limits of diacids and related compounds were ca. 0.002 ng m^{-3}. The analytical errors in duplicate analyses are within 10% for major species.

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

Organic and elemental carbon (OC and EC) was determined using a Sunset Lab carbon analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evolution protocol as described in detail by Wang et al. (2005a). A filter disc of 1.5 cm^2 was placed in a quartz tube inside the thermal desorption chamber of the analyzer and then stepwise heating was applied. Helium (He) gas is applied in the first ramp and is switched to mixture of He/O_2 in the second ramp. The evolved CO_2 during the oxidation at each temperature step was measured with non-dispersive infrared (NDIR) detector system. The detection limits of OC and EC were ca. 0.05 and 0.02 μgC m^{-3}, respectively. The analytical errors in the triplicate analysis of the filter sample were estimated to be 5% for OC and EC. EC was detected only in fine fractions. The concentration of total carbon (TC) was calculated by summing the concentrations of OC and EC in each size fraction.

For the determination of major ions, a punch of 20 mm diameter of each filter was extracted with organic-free ultrapure water under ultrasonication. These extracts were filtered through a disc filter (Millex-GV, Millipore; diameter of 0.22 μm) and injected to ion chromatograph (Compact IC 761; Metrohm, Switzerland) for measuring MSA^-, Cl^-, SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+} (Boreddy and Kawamura, 2015). Anions were separated on a SI-90 4E Shodex column (Showa Denko; Tokyo, Japan) using a mixture of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$ solution at a flow rate of 1.2 mL min^{-1} as an eluent and 40 mM H_2SO_4 for a suppressor. A Metrosep C2-150 Metrohm column was used for cation analysis using a mixture of 4 mM tartaric acid and 1 mM dipicolinic acid solution as an eluent at a flow rate of 1.0 mL min^{-1}. The injected loop volume was 200 μL. The detection limits for anions and cations were ca. 0.1 ng m^{-3}. The analytical error in duplicate analysis was about 10%.

Field blanks were extracted and analyzed like the real samples. However, blank levels were 0.1-5% of the concentrations of real samples. The reported concentrations of organic and inorganic species were corrected for the field blanks. All the chemicals including authentic standards were purchased from Wako Pure Chemical Co. (Japan), except for 14% BF_3/n-butanol (Sigma-Aldrich, USA).

2.3 Backward air mass trajectories and meteorology

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

Meteorological data including ambient temperature, relative humidity, wind speed and precipitation for each sample period were obtained from Japan Meteorological Agency (http://www/data/jma.go.jp). During our campaign, the temperature, relative humidity and wind 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 10.2 m s^{-1} (ave. 3.73±1.99 m s^{-1}), respectively. 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.

2.4 Estimation of liquid water content (LWC) of aerosol

LWC of aerosol was calculated for the size-segregated samples collected in Okinawa Island using the ISORROPIA II model (Fountoukis and Nenes, 2007). ISORROPIA II is a computationally efficient and rigorous thermodynamic equilibrium model that exhibits robust and rapid convergence under all aerosol types with high computational speed (Nenes et al., 1998). 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.

3 Results and discussion

3.1 Size-segregated aerosol chemical characteristics

We use 2.1 µm as a split diameter between the fine and coarse mode particles. Table 1 presents the concentrations of inorganic and carbonaceous species in the fine and coarse mode aerosols. Figure 3 shows the average concentrations of inorganic ions and organic matter (OM) in size-segregated aerosols. Abundances of OM in the atmosphere are generally estimated by multiplying the measured OC mass concentrations with the conversion factor of 1.6 for urban aerosols and 2.1 for aged aerosols (Turpin and Lim, 2001). CHAAMS is located in the outflow region of East Asian aerosols and local anthropogenic activities are insignificant. 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 (Takami et al., 2007; Takiguchi et al., 2008; Kunwar and Kawamura, 2014). Therefore, we used the conversion factor of 2.1, instead of 1.6 for calculation of OM.

Okinawa was strongly affected by continental air masses from Siberia and Mongolia as well as North China and Korea (Figure 2). It is difficult to specify the source regions of air masses for each sample set because the sampling duration was 3-5 days. Each sample contains mixed continental and oceanic air masses. The scavenging of aerosols by precipitation that could result in lower concentrations of aerosol particles in Okinawa might be insignificant during the sampling periods. 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.

Sulfate is the most abundant anion in fine fractions with a peak in 0.65-1.1 µm size whereas chloride is the dominant anion in coarse fractions with a maximum in >11.3 µm (Figure 3). The cation budget is largely controlled by ammonium in fine fractions whereas sodium is the most abundant cation in coarse fractions. The high abundance of SO_4^{2-} in fine particles suggests a significant contribution of anthropogenic sources including industrial emissions in East Asia via long-range transport of aerosols over the western North Pacific Rim. SO_4^{2-} is an anthropogenic tracer of industrial activities whereas NH_4^+ is the secondary product of NH_3 that is largely derived from the agricultural usage of nitrogen-based fertilizers (Pakkanen et al., 2001) and volatilization from soils and livestock waste in East Asia (Huang et al., 2006). The dominant presences of Na^+ and Cl^- in coarse fractions suggest a substantial contribution from sea salt. Na^+ and Cl^- are emitted from the ocean surface as relatively larger particles. Substantial amount of NO_3^- was detected in coarse mode, suggesting a formation of $Ca(NO_3)_2$ or $NaNO_3$ in coarse fractions through the reactive adsorption of gaseous HNO_3 onto pre-existing alkaline particles.

Diacids and related compounds detected in Okinawa are listed in Table 2 together with their concentrations in the fine and coarse modes. Their molecular distributions in size-segregated aerosols are shown in Figure 4. Oxalic acid (C_2) was found as the most abundant diacid followed by malonic (C_3) and succinic (C_4) acids in all size-segregated aerosols. The predominance of C_2 in size-segregated aerosols suggested that this diacid is produced by the photooxidation of VOCs and other organic precursors in gas and aqueous-phase (Warneck, 2003; Carlton et al., 2006) during long-range transport. The abundant presence of C_3 over C_4 diacid also indicates that this diacid was produced via atmospheric photooxidation of organic precursors during long-range transport to Okinawa (Kawamura and Sakaguchi, 1999; Kunwar and Kawamura, 2014). 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.

Phthalic (Ph) and adipic (C_6) acids are the next abundant diacids whereas ketomalonic acid (kC_3) is more abundant than C_6 diacid in the size ranges of 0.43-0.65 µm to 0.65-1.1 µm. Ph and C_6 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. Kawamura and Usukura (1993) reported that C_6 diacid is an oxidation product through the reaction of cyclohexene with ozone (O_3). The high abundances of Ph and C_6 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.

Azelaic acid (C_9) is always more abundant than the adjacent suberic (C_8) and decanedioic (C_{10}) acids in all the size-segregated aerosols. Kawamura and Gagosian (1987) proposed that C_9 is a photooxidation product of biogenic unsaturated fatty acids such as oleic acid ($C_{18:1}$) containing a double bond at C-9 position. Unsaturated fatty acids can be emitted from sea surface microlayers and from local vegetation in Okinawa (Kunwar and Kawamura, 2014). Moreover, air masses in spring are suggested to originate mostly from Russia and Mongolia as well as Korea based on seven-day backward trajectory analyses. Such continental air masses can also bring C_9 via atmospheric processing of biogenic unsaturated fatty acids during long-range transport. The abundant presence of C_9 indicates that atmospheric oxidation of biogenic unsaturated fatty acids also occurs in Okinawa aerosols during long-range transport. ω-Oxocarboxylic acids and α-dicarbonyls were detected in the Okinawa aerosols. Glyoxylic acid (ωC_2) was identified as the most abundant ω-oxoacid whereas glyoxal (Gly) was more abundant than methylglyoxal (MeGly) in all the sizes. ωC_2 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 C_2 diacid (Myriokefalitakis et al., 2011). The predominance of ωC_2 and Gly indicates their importance as key precursors of C_2 in Okinawa aerosols.

3.2 Inorganic species

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

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

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 μg m^{-3}) and OKI-2 (0.60 μg m^{-3}) than that in OKI-5 sample (0.15 μg 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. Such air mass origin again indicates a long-range transport of Asian dust from East Asia to the western North Pacific.

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

A unimodal size distribution of K^+ was observed in most sets of samples (OKI-1 to OKI-4) with a peak at 0.65-1.1 μm in diameter (Figure 5e). 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. The fine mode nss-K^+ accounted for 95% of the total K^+ in the OKI-2 sample set and 88% of that in the OKI-3 sample set when air masses are coming from Siberia and Mongolia as well as North China. The abundant presence of fine mode nss-K^+ in the OKI-2 and OKI-3 samples further indicates the long-range atmospheric transport of biomass burning aerosols from the Asian continent to the western North Pacific Rim. The coarse mode K^+ was strongly correlated with the coarse mode Cl^- ($r = 0.90$). This result suggests that the coarse mode K^+ in the sample sets OKI-1 and OKI-5 may be derived from sea salt particles.

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

$HNO_{3(g)} + NaCl_{(aq\ and\ s)} \rightarrow NaNO_{3(aq\ and\ s)} + HCl_{(g)}$ R-1

$2HNO_{3(g)} + CaCO_{3(s)} \rightarrow Ca(NO_3)_{2(s)} + H_2O + CO_{2(g)}$ R-2

As discussed earlier, the air masses originated from Siberia are transported over Mongolia and North China. Asian dust can be transported from the Asian continent to Okinawa. Therefore, it is possible that the gaseous HNO_3 might already have reacted with $CaCO_3$ (mineral dust particle) to from NO_3^- before arriving to Okinawa through R-2. 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. NO_3^- peaked at the same particle size of Ca^{2+}. Therefore, NO_3^- in Okinawa coarse mode aerosols is probably resulted from the pickup of HNO_3 gas by soil dust particles enriched with Ca^{2+} via heterogeneous reaction near the source regions. This process is further supported by a good correlation between NO_3^- and Ca^{2+} (0.98) in the coarse mode.

The particle size distributions of SO_4^{2-}, which is the major source of acid deposition (Pakkanen et al., 2001), have been the subject of numerous studies in the past few decades (Huang et al., 2006; Kouyoumdjian and Saliba, 2006). Condensation mode SO_4^{2-} arises from gas-phase oxidation of SO_2 followed by gas-to-particle conversion whereas fine mode SO_4^{2-} is formed through aqueous-phase oxidation of SO_2 in aerosols and cloud droplets (Seinfeld and Pandis, 1998). SO_4^{2-} on the coarse mode can be attributed to a combination of sulfate and heterogeneous reactions of SO_2 on soil dust or sea salt particles (Seinfeld and Pandis, 1998; Pakkanen et al., 2001). 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 particles 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.

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

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 the 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. This size distribution of MSA^- observed over Okinawa is consistent with previous studies from the China Sea by Gao et al. (1996), who suggested that MSA is produced through the oxidation of S-containing species in the marine atmosphere.

NH_4^+ in the Okinawa aerosols shows a unimodal size distribution with a peak at 0.65-1.1 µm (Figure 5h), indicating that NH_4^+ is mainly formed by gas-to-particle conversion via the reaction with H_2SO_4 and HNO_3. Interestingly, the size distribution of NH_4^+ is similar to that of SO_4^{2-} and diacids such as oxalic acid (Figure 5g and 7a). We also found a strong correlation between SO_4^{2-} and NH_4^+ on the fine mode ($r = 0.99$). Ion balance calculations are commonly used to evaluate the acid-base balance of aerosol particles. 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.

NH_3 is an alkaline gas that neutralizes the acidic particles in the atmosphere. Kerminen et al. (1997a) proposed that particulate NH_4^+ is secondarily formed via heterogeneous reactions of gaseous NH_3 with acidic species (H_2SO_4 and HNO_3). The reaction of NH_3 with H_2SO_4 is favored over its reaction with HNO_3. The average NH_4^+/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 $(NH_4)_2SO_4$ in fine mode. Interestingly, the average NH_4^+/SO_4^{2-} equivalent ratios in coarse mode particles ranged from 0.01 for the size bin >11.3 µm 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. Therefore, NO_3^- reacts with coarse particles that contain alkaline species (Ca^{2+}) in Okinawa aerosols.

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 neutralize by NH_3 in fine mode and exists in the form of NH_4HSO_4 in addition to $(NH_4)_2SO_4$. 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. We found that NH_4^+ showed a good correlation (r = 0.87) with LWC in the fine mode. This result implies that the abundant presence of NH_4^+ in fine mode also enhanced the LWC in fine mode of Okinawa aerosols. 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.

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

The mass-based size distribution of WSOC is characterized by a major peak at 0.65-1.1 µm in fine mode and by a small peak at 3.3-4.7 µm in coarse mode (Figure 8 and Table 1). 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. It is well recognized that biofuel combustion and biomass burning produce a large amount of WSOC (Mayol-Bracero et al., 2002). The WSOC concentrations showed high correlation with fine mode SO_4^{2-} (r = 0.96). Because production of SO_4^{2-} is strongly linked to photochemical activity, this result suggests an important secondary production of WSOC in fine mode particles during long-range atmospheric transport from East Asia. The WSOC concentrations also showed high correlation with K^+ (r =

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

Fine mode WSOC concentrations in OKI-1 to OKI-4 aerosol samples are 3-5 times higher (1.09 µg m^{-3} for OKI-4 to 1.61 µg m^{-3} for OKI-2) than that in the sample OKI-5 (0.31 µg m^{-3}). It is also noteworthy that fine mode fraction of WSOC in the samples OKI-1 to OKI-4 contributed 70-75% of total WSOC. We noted that the former 4 sample sets are more influenced by continental air masses than the last set (Figure 2). These results suggested that WSOC is more enriched in the samples with an influence of continental air masses from Siberia and Mongolia as well as North China and Korea. 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.

The mass-size distribution pattern of OC is similar to that of WSOC with a major peak in the 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 diameter (Figure 8). 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.

A significant portion of OC may be oxidized to WSOC during the atmospheric transport from East Asia to the western North Pacific. The mass ratio of WSOC/OC has been proposed as a measure of photochemical processing or aging of organics especially in long-range transported aerosols (Aggarwal and Kawamura, 2009). The WSOC/OC ratios varied from 0.51-0.76 with an 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 mode. The higher WSOC/OC ratio in fine mode suggests that organics are more significantly subjected to photochemical processing in fine mode aerosols during long-range transport from the Asian continent to Okinawa than coarse mode aerosols.

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).

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.

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

3.4 Dicarboxylic acids

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

The condensation mode of C_2 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 C_2 diacid (Carlton et al. 2006, 2007; Legrand et al. 2007). The fine mode peak of C_2 at the size of 0.65-1.1 μm in Okinawa aerosols suggests a preferential production of C_2 via the oxidation of precursors in the aerosol aqueous-phase during long-range atmospheric transport. We found that size distribution of C_2 diacid is similar to that of SO_4^{2-} (Figure

5g and 7a), suggesting a secondary formation of C_2 possibly in aerosol aqueous-phase. The good 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 a secondary photochemical product. 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.

Several sources are known to C_2 in atmospheric aerosols. They include primary sources and secondary formation via photooxidation of anthropogenic and biogenic precursors (Kawamura and Sakaguchi, 1999). C_2 is produced by the photooxidation of C_3 (Kawamura and Ikushima, 1993). C_2 and C_3 are formed by the photooxidation of C_4 whereas C_4 is produced by the photooxidation of glutaric acid (C_5) (Kawamura and Ikushima, 1993). The fine mode predominance of C_2 in Okinawa aerosols was probably associated with an enhanced aqueous oxidation of anthropogenic precursors emitted in East Asia during long-range transport. Lim et al. (2005) and Legrand et al. (2007) reported the formation of diacids in aqueous-phase. Here we investigate the impact of LWC of aerosols on the formation of diacids in Okinawa aerosols. 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. We found that the fine mode peak of C_2 is consistent with that of LWC in Okinawa samples (Figure 6b and 7a). 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.

The robust correlations of C_2 with C_3-C_5 diacids (r = 0.89-0.92) indicate that they have similar sources and origin or C_2 diacid might be produced via decay of longer-chain diacids during long-range transport. 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. 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). The gas-phase photooxidation of these VOCs produce Gly and MeGly, which are easily hydrated and partitioned into the aerosol phase with lifetime less than 3 h (Legrand et al., 2007; Kampf et al., 2012). The aqueous-phase oxidation of Gly and MeGly produces ωC_2, which can further oxidize in aqueous-phase to form C_2 diacid (Lim et al., 2005). It is noteworthy that ωC_2 and Gly are also enriched in fine mode in Okinawa aerosols. Their size distributions are discussed in more details in subsequent sections. Fine mode C_2 showed a significant positive correlation with ωC_2 ($r = 0.99$) and Gly (0.93) whereas weak correlation was found with MeGly (0.62). These results suggest that ωC_2 and Gly are important precursors of C_2 diacid and increased LWC in fine mode is favorable for aqueous phase oxidation of ωC_2 and Gly to result in C_2.

C_3 peaked at 0.65-1.1 µm in diameter (Figure 7b), being similar to C_2 diacid (Figure 7a), except for two sets of samples (OKI-1 and OKI-5) that showed peaks at 2.1-3.3 or 3.3-4.7 µm in the coarse mode. C_4 showed two peaks at the size bins of 0.65-1.1 and 2.1-3.3 µm in OKI-1 and OKI-5 samples (Figure 7c). The coarse mode peaks of this diacid in samples OKI-1 and OKI-5 may be associated with sea salt particles because the samples have an influence of marine air masses during the sampling period. Kawamura and Ikushima (1993) proposed that the ratio of malonic to succinic acid (C_3/C_4) is a tracer to indicate the extent of photochemical processing of longer chain diacids such as C_5 diacid. Because C_4 is oxidized to C_3, an increase in the C_3/C_4 ratio indicates an increased photochemical processing. The averaged C_3/C_4 ratio in sum of all the size fractions was found to be 1.5±0.1 in Okinawa aerosols. This result suggests that the extent of photochemical processing is much greater in Okinawa than Los Angeles (0.35) (Kawamura and Kaplan, 1987) but similar to that of urban Tokyo (1.5) (Kawamura and Ikushima, 1993), whereas it is lower than those of marine aerosols at Chichijima Island in the western North Pacific (2.0) (Mochida et al., 2003b) and the remote Pacific including tropics (3.9) (Kawamura and Sakaguchi, 1999). Figure 9a shows changes in the C_3/C_4 ratios as a function of particle size. The C_3/C_4 ratios exhibit higher values at 1.1-2.1 µm in fine mode and at 2.1-3.3 and 3.3-4.7 µm in coarse mode. This result suggests that C_3 production via C_4 decomposition occurs more efficiently at these size ranges by aqueous-phase processing.

It is noteworthy that emission sources can also control the size distributions of organic compounds. A bimodal size distribution of C_9 diacid was observed in Okinawa aerosols with a 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). C_9 is a tracer of biogenic sources. Kawamura and Gagosian (1987) reported that C_9 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 C_9 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 C_9 with Na^+ (r = 0.85) in coarse mode. This correlation is consistent with the idea that the precursors of C_9 are emitted from the ocean surface together with sea salt particles in coarse mode. Unsaturated fatty acids can also be directly emitted as fine particles from food cooking emission in China and long-range transported to the western North Pacific (Schauer et al., 1996; Wang et al., 2011). The minor peak of C_9 in fine mode can be explained by the oxidation of fine-mode unsaturated fatty acids derived from food cooking or gaseous unsaturated fatty acids.

A unimodal size distribution was obtained for Ph with a fine mode peak at 0.65-1.1 µm, except for one sample set (OKI-5) that showed a bimodal distribution with almost equal peaks at 0.65-1.1 and 2.1-3.3 µm (Figure 7g). This aromatic diacid is a tracer of anthropogenic sources. 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 SO_4^{2-}, NH_4^+ and K^+. The comparable coarse mode peak in the OKI-5 sample set suggests an adsorption of gaseous Ph onto coarse particles. Terephthalic acid (tPh), which is a tracer of plastic burning (Kawamura and Pavuluri, 2011), showed a unimodal distribution peaking at the size bin of 0.65-1.1 µm (Figure 7h). tPh is mostly emitted from the burning of plastic wastes such as plastic bags and bottles, and then deposited on pre-existing fine particles.

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

It is important to understand whether anthropogenic or biogenic organic precursors are oxidized to increase the atmospheric level of shorter-chain (C_2-C_5) diacids and related compounds (ωC_2 and Gly) in fine mode of Okinawa aerosols. The strong correlation of C_2-C_5 diacids with Ph (r = 0.83-0.90) was found in fine mode. This result suggests that anthropogenic precursors are more important sources of C_2-C_5 diacids than biogenic precursors in fine mode. The weak correlations of C_2-C_5 diacids with C_9 (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 C_2-C_5 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 ωC_2 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.

3.5 ω-Oxocarboxylic acids and pyruvic acid

ω-Oxocarboxylic acids (ωC_2-ωC_9) are secondarily produced in the atmosphere and also directly emitted from fossil fuel combustion and biomass burning. They are further oxidized into diacids via the oxidation of aldehyde group of the compounds (Kawamura et al., 1996; Warneck, 2003). The size distribution of glyoxylic acid (ωC_2) shows a unimodal pattern with a peak at 0.65-1.1 µm (Figure 7i). Mochida et al. (2007) reported a strong bimodal pattern of oxoacids with a peak in the coarse aerosol mode off the coast of East Asia. They suggested that the coarse mode was likely due to either uptake of oxoacids or their heterogeneous reactions on sea salt particles. The fine mode maxima of oxoacids indicate that they are secondarily produced in the atmosphere by the photochemical oxidation of gaseous precursors during long-range transport to Okinawa. Interestingly, we found that size distribution of C_2 diacid is similar to that of ωC_2 oxoacid (Figure 7a and i). Those similarities suggest that both C_2 and ωC_2 are simultaneously produced via gas and aqueous-phase oxidation of their precursors. The diacids may be produced by the oxidation of corresponding ω-oxoacids in aerosols during long-range transport.

The important precursor of ωC_2 in atmospheric aerosols is Gly and MeGly (Lim et al., 2005; Myriokefalitakis et al., 2011). We found that ωC_2 is strongly correlated with Gly (r = 0.92) and moderately correlated with MeGly (0.55) in the fine mode. The former result suggests that Gly is a key precursor of ωC_2 in Okinawa aerosols. The significant positive correlation of ωC_2 with LWC (0.95) in fine mode suggests the formation of ωC_2 via oxidation of Gly in the aerosol aqueous-phase. The strong correlation of fine mode ωC_2 with SO_4^{2-} (0.96) further confirms secondary formation of ωC_2 from the precursors originated from anthropogenic and biogenic sources during long-range transport to Okinawa. Although the enhanced ωC_2 concentrations in fine mode might be a result of aqueous oxidation, ωC_2 may be rather controlled by biomass burning activity. This is supported by the significant positive correlation of ωC_2 with K^+ ($r = 0.90$) in the fine mode.

A bimodal size distribution was observed for 9-oxononanoic acid (ωC_9) (Figure 7k). We found 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 distribution of ωC_9 is similar to that of C_9 diacid. ωC_9 is another counterpart of photooxidation product of biogenic unsaturated fatty acids such as oleic ($C_{18:1}$) acid having a double bond at C-9 position (Kawamura and Gagosian, 1987). 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.

Pyruvic acid (Pyr) showed a bimodal size distribution with a major peak on coarse mode at the 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 peak of Pyr on coarse mode may suggest that pyruvic acid is possibly produced by the heterogeneous photooxidation of isoprene emitted from the ocean surface probably on sea salt particles. Several studies suggested that Pyr is produced via the aqueous-phase photooxidation of MeGly that is a gas-phase oxidation product of isoprene emitted from the ocean surface (Lim et al., 2005; Carlton et al., 2006).

3.6 α-Dicarbonyls

Gly and MeGly are gas-phase oxidation products of numerous VOCs such as benzene, toluene and xylene (Volkamer et al., 2001) as well as ethylene and isoprene (Zimmermann and Poppe, 1996) and terpenes (Lim et al., 2005). Gly may be associated with pollution sources whereas MeGly may be involved with biogenic sources. Gly peaked at 0.65-1.1 µm in the fine mode in the Okinawa samples. The fine mode peak of Gly is similar to those of K^+ and SO_4^{2-} (Figure 5e and g), suggesting their similar sources and formation pathways in the aerosols. Although gas-phase oxidation of isoprene has been reported as the largest global source of Gly (Zimmermann and Poppe, 1996), oxidation of anthropogenic aromatic hydrocarbons from fossil fuel combustion and biomass burning is also suggested as alternative source of Gly in the atmosphere (Jung et al., 2010). The peak of Gly at 0.65-1.1 µm may be associated with the combustion sources and the subsequent gas-phase oxidation of the precursors during long-range transport to Okinawa. A good correlation of Gly with K^+ or NH_4^+ ($r = 0.86$) in fine mode further suggests that biomass burning is a major source of fine mode Gly in Okinawa aerosols.

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

3.7 Benzoic acid

The size distribution of benzoic acid is presented in Figure 7o. Two sample sets (OKI-1 and OKI-2) showed unimodal size distribution of benzoic acid with a peak at 0.65-1.1 or 1.1-2.1 µm in the fine mode. Benzoic acid is directly emitted from the automobile emissions (Kawamura et al., 1985) and secondarily produced by photochemical oxidation of automobile-derived aromatic compounds (Ho et al., 2006). Although benzoic acid is semi-volatile and mainly found in gas-phase (Kawamura et al., 2000; Fraser et al., 1998), it can be observed in particulate phase via gas-to-particle conversion by forming salts such as ammonium benzoate or potassium benzoate. Duan et al. (2008) reported high level of ambient toluene (11 μg m^{-3}) in China during an ozone episode in 2006 and suggested that photooxidation of toluene is one of major sources of benzoic acid in the atmosphere.

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

4 Summary and conclusions

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

SO_4^{2-}, NH_4^+, and diacids up to 5-carbon atoms as well as glyoxylic acid (ωC_2) and glyoxal (Gly) showed good correlations with peaks in fine mode (0.65-1.1 μm). WSOC and OC also peaked on fine mode with an additional minor peak on coarse mode. Similar size distributions and strong correlations of diacids (C_2-C_5), ωC_2 and Gly with SO_4^{2-} in fine mode suggest their secondary formation possibly in the aerosol aqueous-phase. They may have also been directly emitted from biomass burning as suggested by strong correlations with K^+ in fine mode. The strong correlations of fine mode SO_4^{2-} and NH_4^+ with LWC imply that abundant presences of SO_4^{2-} and NH_4^+ in fine mode promote to enhance the LWC in fine mode of Okinawa aerosols, which is favorable for the aqueous oxidation of precursor compounds to result in C_2 (r is 0.91 for LWC and C_2). The robust correlations of C_2 with C_3-C_5 diacids as well as ωC_2 and Gly indicate that they are the key precursors of C_2 diacid in Okinawa aerosols.

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

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Table 1. Concentrations (μg 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

[a] Fine mode represents aerosol size of $D_p < 2.1$ μm.

[b] Coarse mode represents aerosol size of $D_p > 2.1$ μm.

[c] Standard deviation.

[d] Minimum.

[e] Maximum.

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	$HOOC-CH=CH-COOH$ - *cis*	0.81	0.25	0.41	1.05	0.73	0.23	0.37	0.95
Fumaric	F	$HOOC-CH=CH-COOH$ - *trans*	0.31	0.09	0.20	0.42	0.21	0.08	0.12	0.30
Methylmaleic	mM	$HOOC-C(CH_3)=CH-COOH$ - *cis*	0.34	0.27	0.11	0.76	0.57	0.48	0.11	1.37
Unsaturated aromatic diacids										
Phthalic	Ph	$HOOC-(C_6H_4)-COOH$ - *o-isomer*	6.29	2.85	1.99	9.3	2.79	0.81	1.85	3.9
Isophthalic	iPh	$HOOC-(C_6H_4)-COOH$ - *m-isomer*	0.46	0.07	0.35	0.55	0.17	0.06	0.09	0.22
Terephthalic	tPh	$HOOC-(C_6H_4)-COOH$ - *p-isomer*	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	$HOOC-CH_2-CH_2-HC(O)(CH_2)_2-COOH$	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	ωC_2	$OHC-COOH$	14.1	5.92	4.77	20.2	4.81	2.00	2.23	7.20
3-Oxopropanoic	ωC_3	$OHC-CH_2-COOH$	0.08	0.05	0.00	0.12	0.05	0.04	0.02	0.12
4-Oxobutanoic	ωC_4	$OHC-(CH_2)_2-COOH$	2.23	1.12	0.86	3.56	0.68	0.35	0.41	1.22
9-Oxononanoic	ωC_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_5C_6-COOH	16.5	11.0	4.57	28.3	1.98	1.01	0.70	3.38

[a] Fine mode represents aerosol size of $D_p < 2.1$ µm.
[b] Coarse mode represents aerosol size of $D_p > 2.1$ µm.
[c] Standard deviation.
[d] Minimum.
[e] Maximum.

Table 3. Pearson correlation coefficients[a] (*r*) matrix among the selected measured chemical species/components in the fine and coarse mode aerosols in Okinawa Island in the Western North Pacific Rim.

	Fine mode[b]																					
	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	MSA^-	Cl^-	NO_3^-	SO_4^{2-}	WSOC	OC	C_2	C_3	C_4	C_5	C_9	Ph	ωC_2	Pyr	Gly	MeGly	LWC
Na^+	1.00																					
NH_4^+	-0.25	1.00																				
K^+	-0.32	0.99	1.00																			
Mg^{2+}	0.98	-0.16	-0.23	1.00																		
Ca^{2+}	-0.21	0.62	0.33	-0.15	1.00																	
MSA^-	-0.32	0.92	0.92	-0.17	0.53	1.00																
Cl^-	0.65	-0.85	-0.85	0.58	-0.33	-0.78	1.00															
NO_3^-	0.65	-0.56	-0.55	0.68	0.22	-0.36	0.76	1.00														
SO_4^{2-}	-0.10	0.99	0.98	-0.02	0.59	0.89	-0.78	-0.49	1.00													
WSOC	0.10	0.91	0.93	0.16	0.30	0.79	-0.57	-0.27	0.96	1.00												
OC	0.12	0.91	0.95	0.16	0.25	0.80	-0.57	-0.32	0.93	0.99	1.00											
C_2	0.12	0.89	0.85	-0.13	0.22	0.80	-0.53	-0.30	0.92	0.99	0.98	1.00										
C_3	-0.05	0.90	0.89	-0.05	0.20	0.66	-0.68	-0.53	0.90	0.93	0.96	0.89	1.00									
C_4	-0.12	0.96	0.95	-0.09	0.15	0.76	-0.75	-0.55	0.96	0.95	0.96	0.92	0.99	1.00								
C_5	-0.12	0.99	0.96	-0.05	0.33	0.87	-0.80	-0.53	0.99	0.93	0.93	0.91	0.95	0.97	1.00							
C_9	0.64	0.01	0.02	0.61	0.42	-0.16	0.46	0.47	0.10	0.20	0.39	0.38	0.33	0.23	0.09	1.00						
Ph	0.41	0.78	0.73	0.46	0.42	0.63	-0.40	-0.16	0.87	0.92	0.93	0.90	0.83	0.83	0.86	0.23	1.00					
ωC_2	0.11	0.92	0.90	0.19	0.19	0.82	-0.57	-0.25	0.96	0.99	0.99	0.99	0.90	0.93	0.95	0.36	0.93	1.00				
Pyr	0.01	0.93	0.88	0.12	0.39	0.88	-0.73	-0.33	0.96	0.88	0.87	0.85	0.80	0.86	0.96	0.03	0.38	0.91	1.00			
Gly	0.01	0.86	0.86	0.15	0.09	0.92	-0.52	-0.07	0.86	0.89	0.82	0.93	0.70	0.78	0.85	0.21	0.85	0.92	0.85	1.00		
MeGly	0.15	0.35	0.39	0.26	0.13	0.52	0.06	0.50	0.36	0.53	0.35	0.62	0.25	0.31	0.31	0.48	0.36	0.55	0.29	0.75	1.00	
LWC	0.16	0.87	0.83	0.30	0.53	0.88	-0.53	-0.13	0.92	0.90	0.87	0.92	0.82	0.83	0.89	0.18	0.90	0.95	0.95	0.95	0.55	1.00

	Coarse mode[c]																					
	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	MSA^-	Cl^-	NO_3^-	SO_4^{2-}	WSOC	OC	C_2	C_3	C_4	C_5	C_9	Ph	ωC_2	Pyr	Gly	MeGly	LWC
Na^+	1.00																					
NH_4^+	0.60	1.00																				
K^+	0.96	0.77	1.00																			
Mg^{2+}	0.98	0.63	0.33	1.00																		
Ca^{2+}	-0.12	0.03	-0.06	-0.29	1.00																	
MSA^-	-0.15	-0.66	-0.03	-0.25	-0.02	1.00																
Cl^-	0.98	0.59	0.90	0.98	-0.27	-0.22	1.00															
NO_3^-	-0.30	-0.23	-0.15	-0.39	0.98	0.28	-0.55	1.00														
SO_4^{2-}	0.33	0.32	0.56	0.28	0.63	0.25	0.16	0.67	1.00													
WSOC	-0.18	-0.26	0.06	-0.20	0.23	0.55	-0.36	0.92	0.72	1.00												
OC	-0.11	-0.10	0.13	-0.10	0.21	0.36	-0.28	0.92	0.72	0.97	1.00											
C_2	-0.05	0.26	0.30	0.15	0.63	0.09	-0.08	0.88	0.76	0.93	0.82	1.00										
C_3	0.32	0.33	0.53	0.31	0.68	0.18	0.15	0.75	0.92	0.88	0.82	0.93	1.00									
C_4	0.33	0.39	0.60	0.35	0.53	0.16	0.33	0.32	0.88	0.31	0.55	0.36	0.63	1.00								
C_5	0.05	0.05	0.22	-0.06	0.62	0.32	-0.05	0.43	0.75	0.28	0.38	0.22	0.45	0.91	1.00							
C_9	0.85	0.20	0.25	0.91	-0.16	-0.59	0.85	-0.31	0.18	-0.08	-0.25	0.25	0.30	0.19	-0.23	1.00						
Ph	-0.52	-0.54	-0.29	-0.54	0.73	0.59	-0.66	0.93	0.54	0.56	0.33	0.63	0.58	0.21	0.40	-0.58	1.00					
ωC_2	0.23	0.37	0.85	0.68	0.12	0.42	0.59	0.23	0.73	0.53	0.52	0.53	0.76	0.60	0.32	0.23	0.21	1.00				
Pyr	-0.09	-0.01	0.13	-0.08	0.81	0.23	-0.26	0.93	0.73	0.99	0.93	0.96	0.90	0.33	0.28	-0.01	0.22	0.49	1.00			
Gly	0.26	0.26	0.78	0.57	0.05	0.52	0.58	0.06	0.69	0.28	0.33	0.22	0.55	0.76	0.57	0.24	0.12	0.89	0.21	1.00		
MeGly	0.55	0.69	0.67	0.58	0.48	-0.20	0.48	0.18	0.77	0.16	0.13	0.25	0.58	0.93	0.75	0.46	-0.05	0.49	0.22	0.59	1.00	
LWC	0.61	0.03	0.53	0.56	-0.70	0.48	0.63	-0.51	-0.10	-0.19	-0.13	-0.29	-0.08	-0.03	-0.22	0.23	-0.31	0.57	-0.28	0.63	-0.13	1.00

See Table 1 and 2 for abbreviation.

[a] Correlation is significant at 0.05 level for the values where *r* is > 0.80.

[b] Fine mode represents aerosol size of $D_p < 2.1$ µm.

[c] Coarse mode represents aerosol size of $D_p > 2.1$ µm.

Figure Captions

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

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.

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

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

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

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

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

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

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

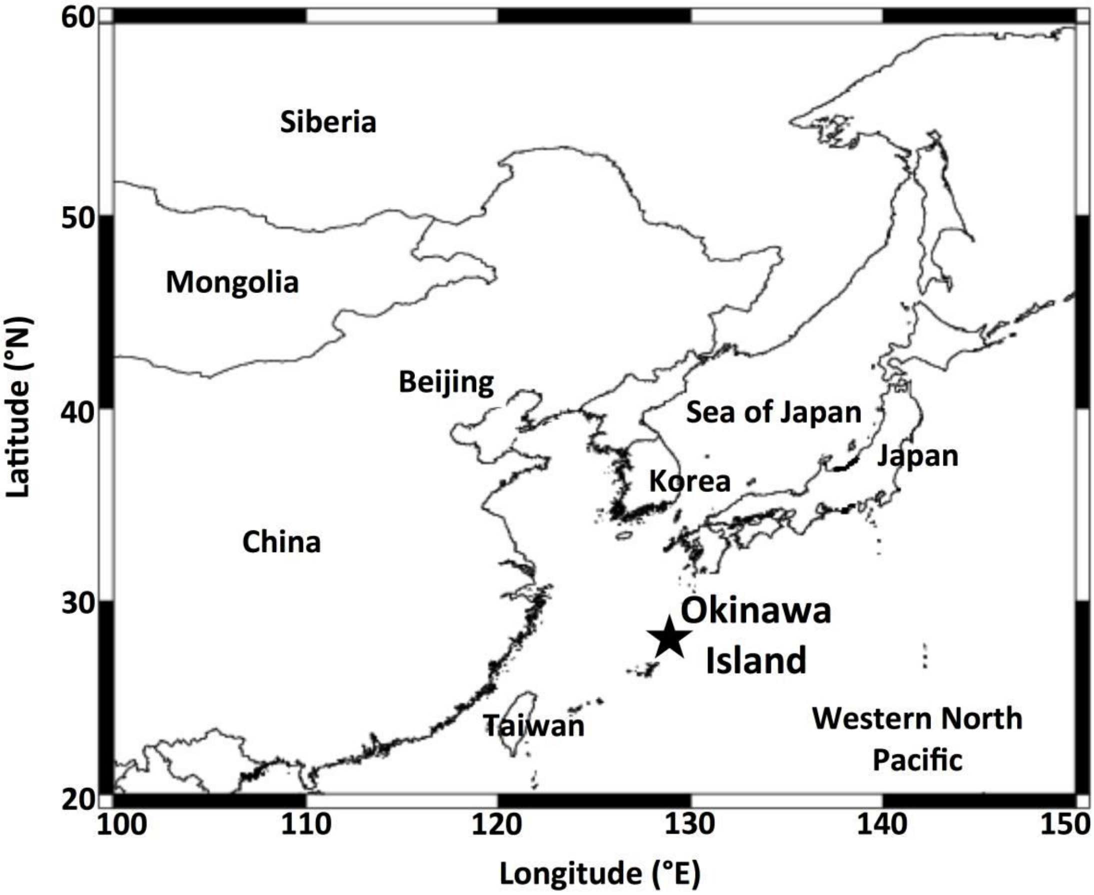
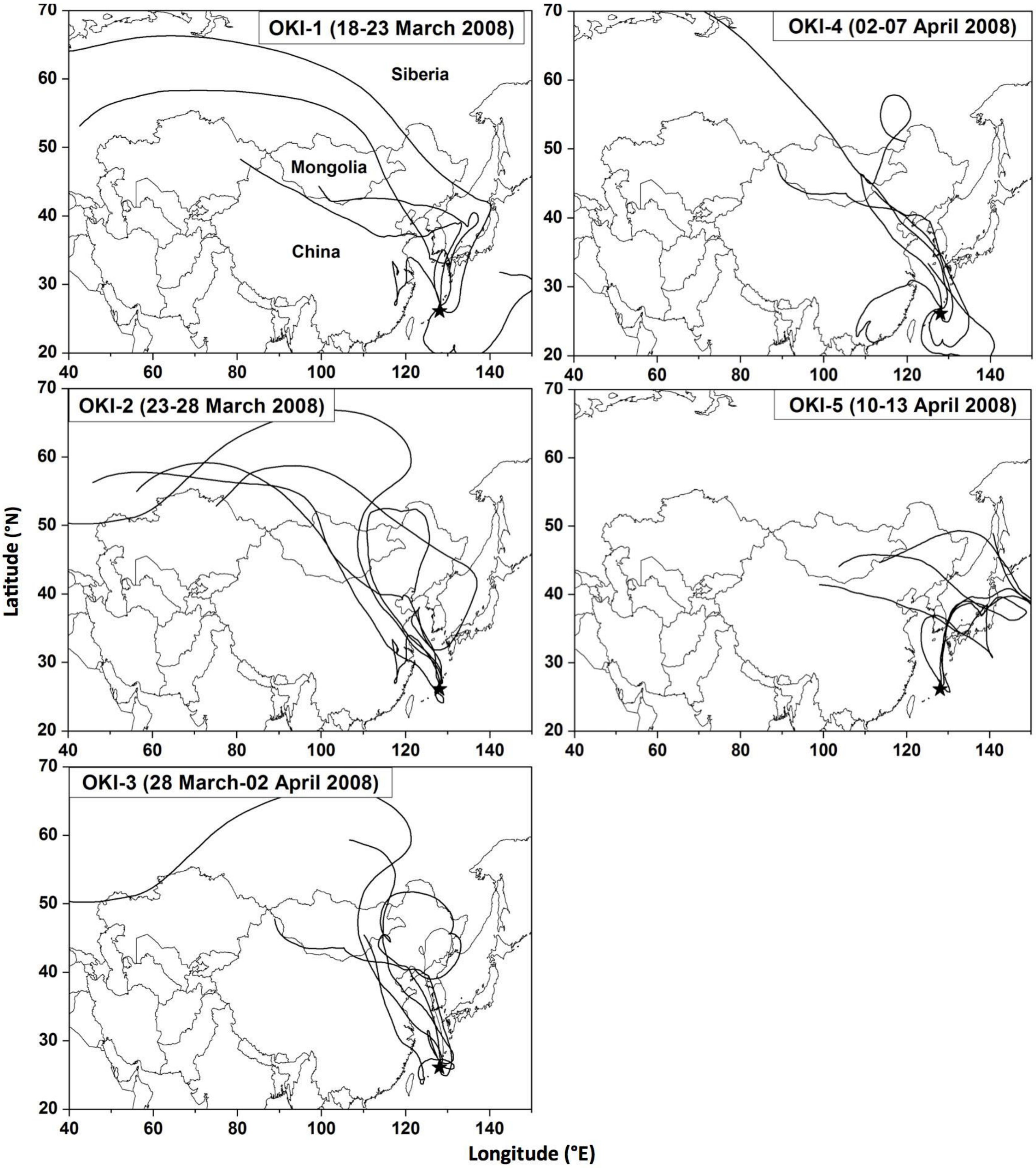


Figure 1. A map of East Asia with the location of Okinawa Island (26.87°N and 128.25°E) and major megacities.



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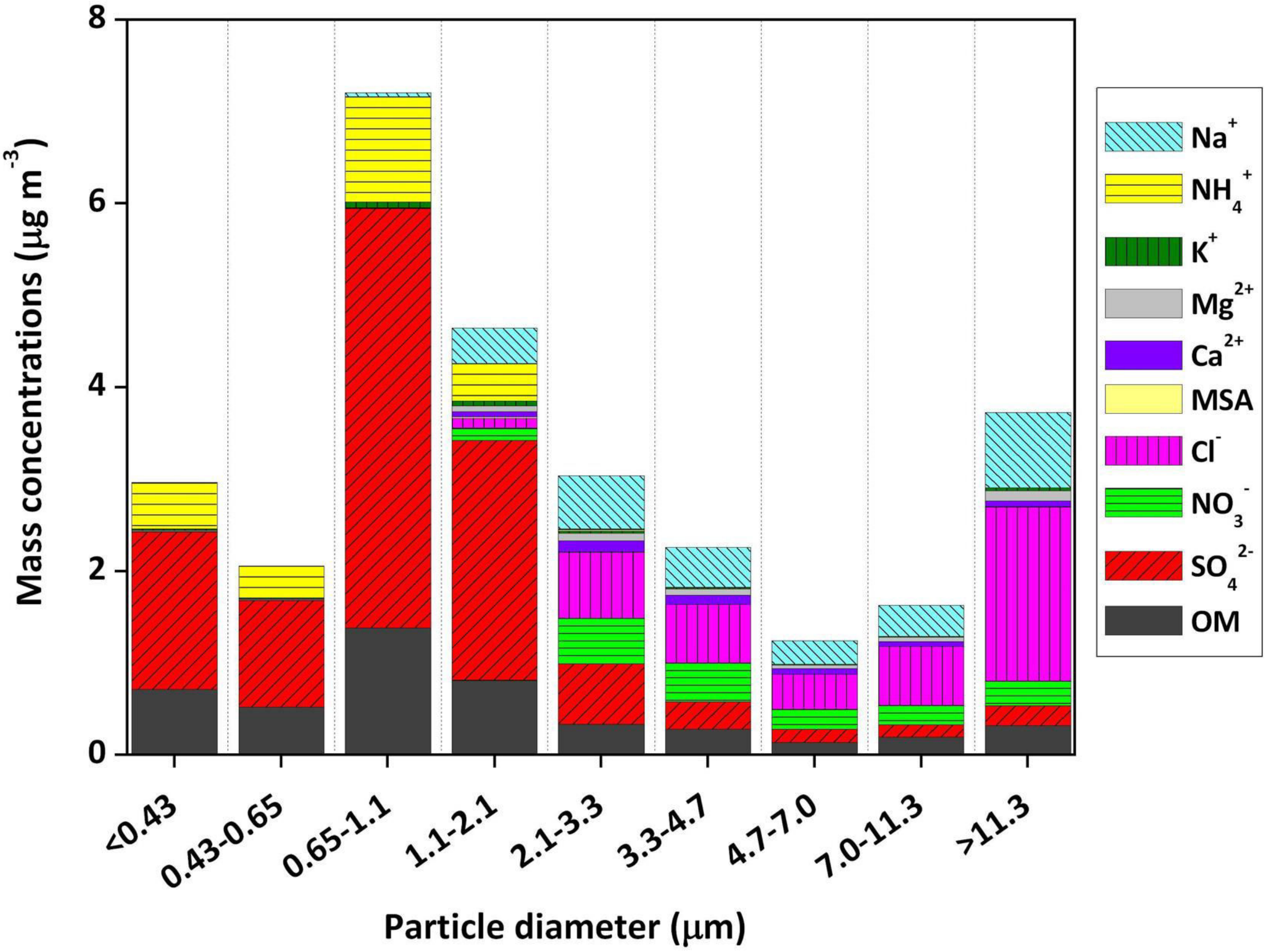

Figure 3. Average size-segregated chemical composition of spring aerosols collected at Okinawa Island.

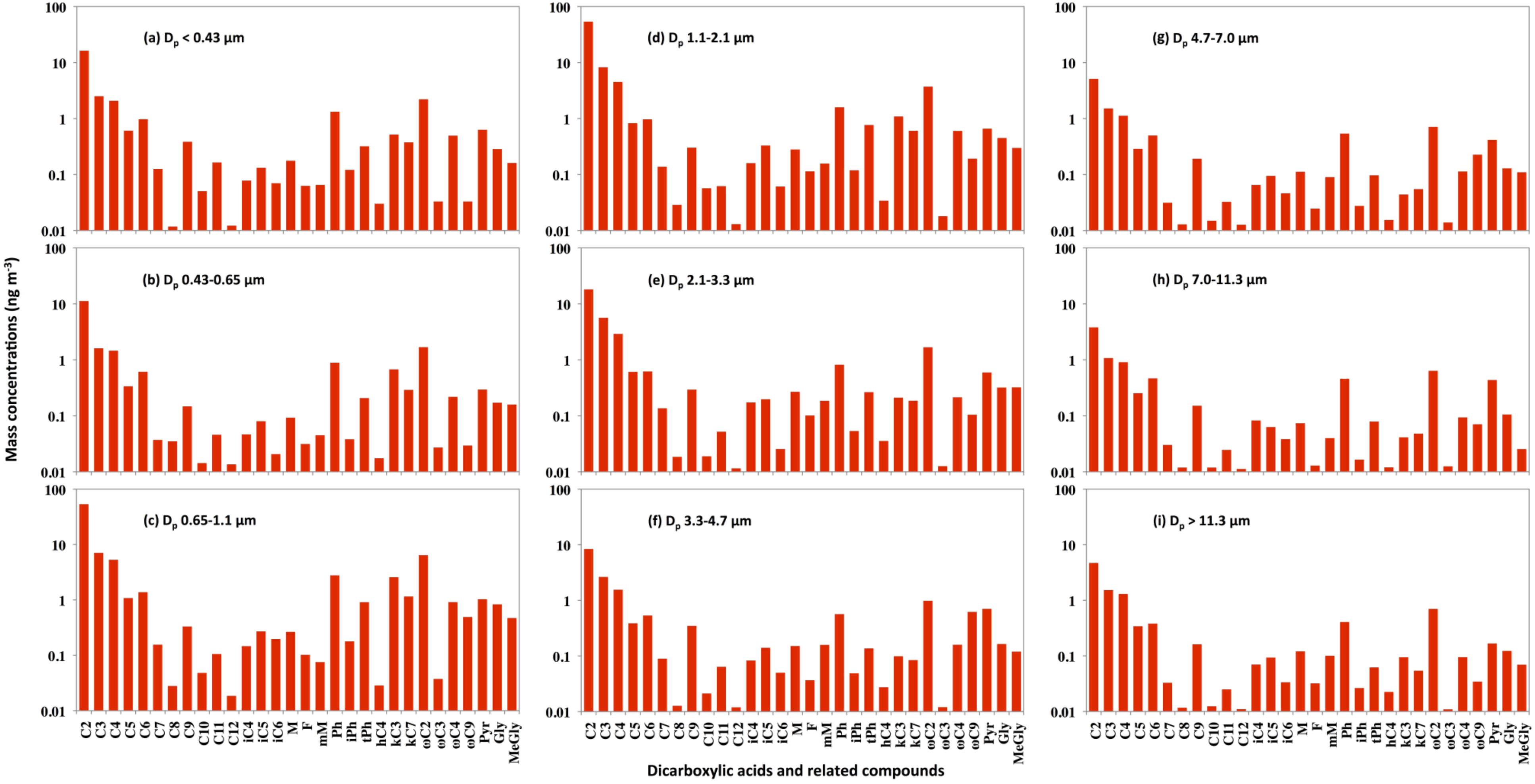

Figure 4. Average molecular distributions of water-soluble dicarboxylic acids and related compounds in size-segregated aerosols collected at Okinawa Island.

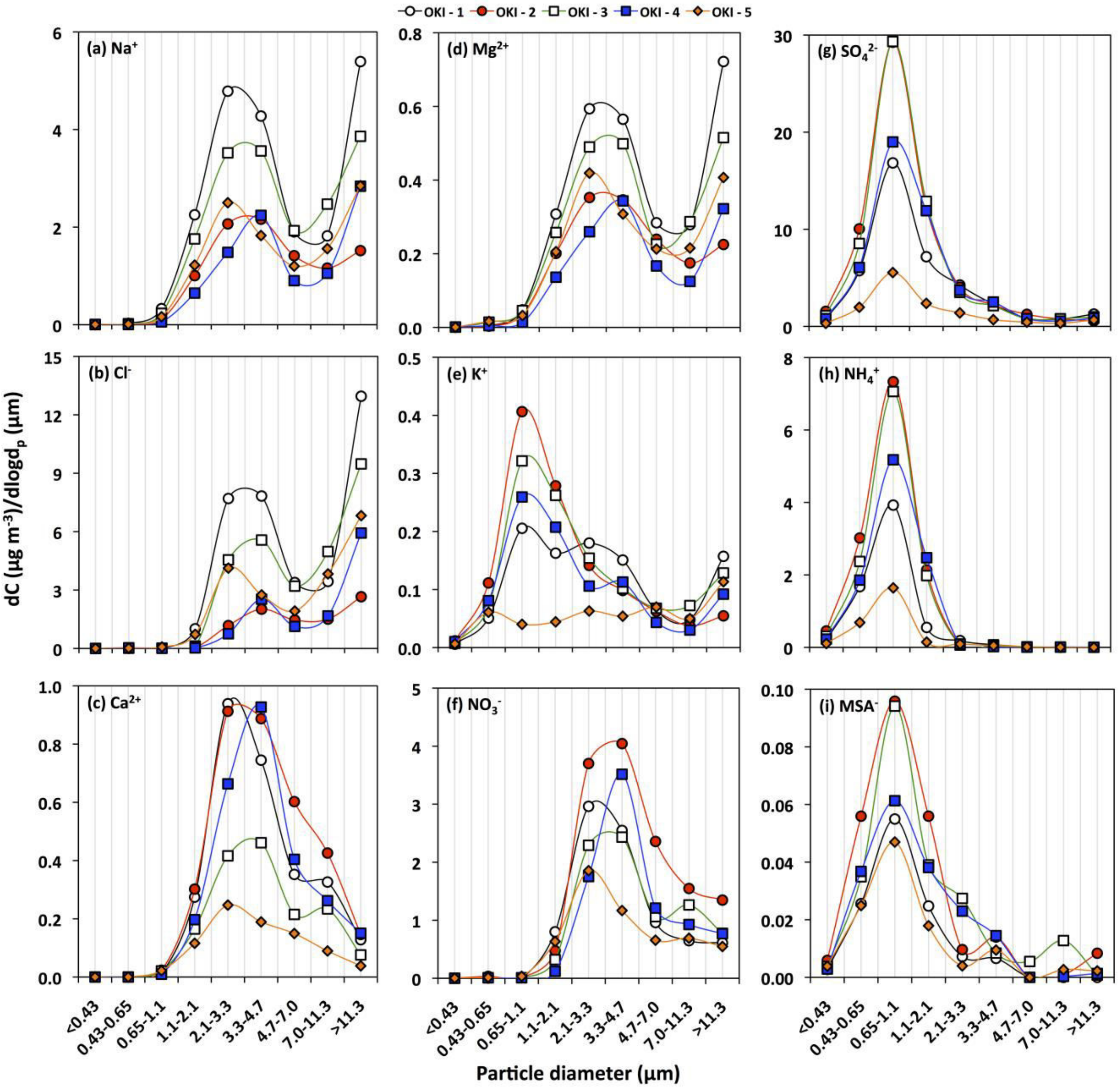

Figure 5. Size distributions of water-soluble inorganic ions in the aerosol samples collected at Okinawa Island.

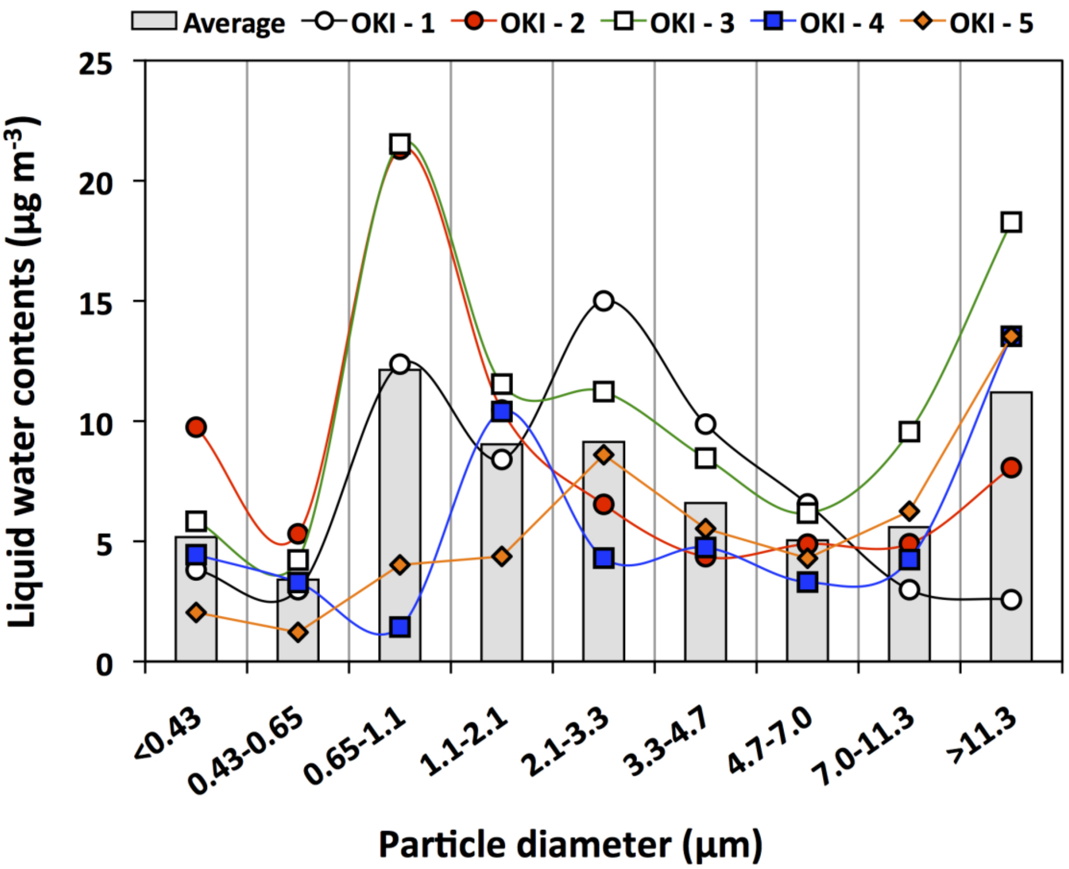

Figure 6. Aerosol liquid water contents for each sample in size-segregated aerosols and mean liquid water contents of size-segregated aerosols at Okinawa Island.

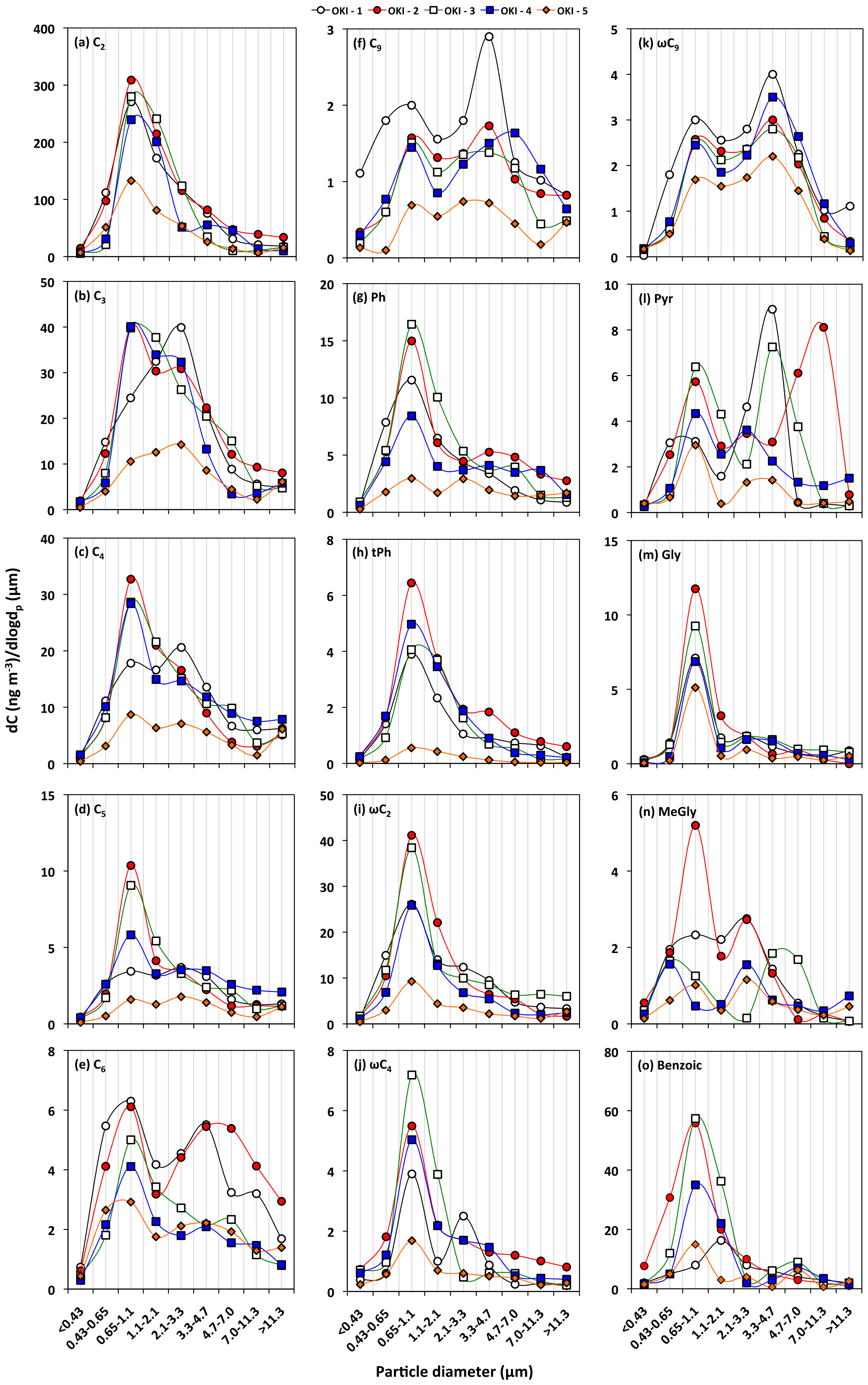

Figure 7. Size distributions of selected water-soluble dicarboxylic acids and related compounds in the aerosol samples collected at Okinawa Island.

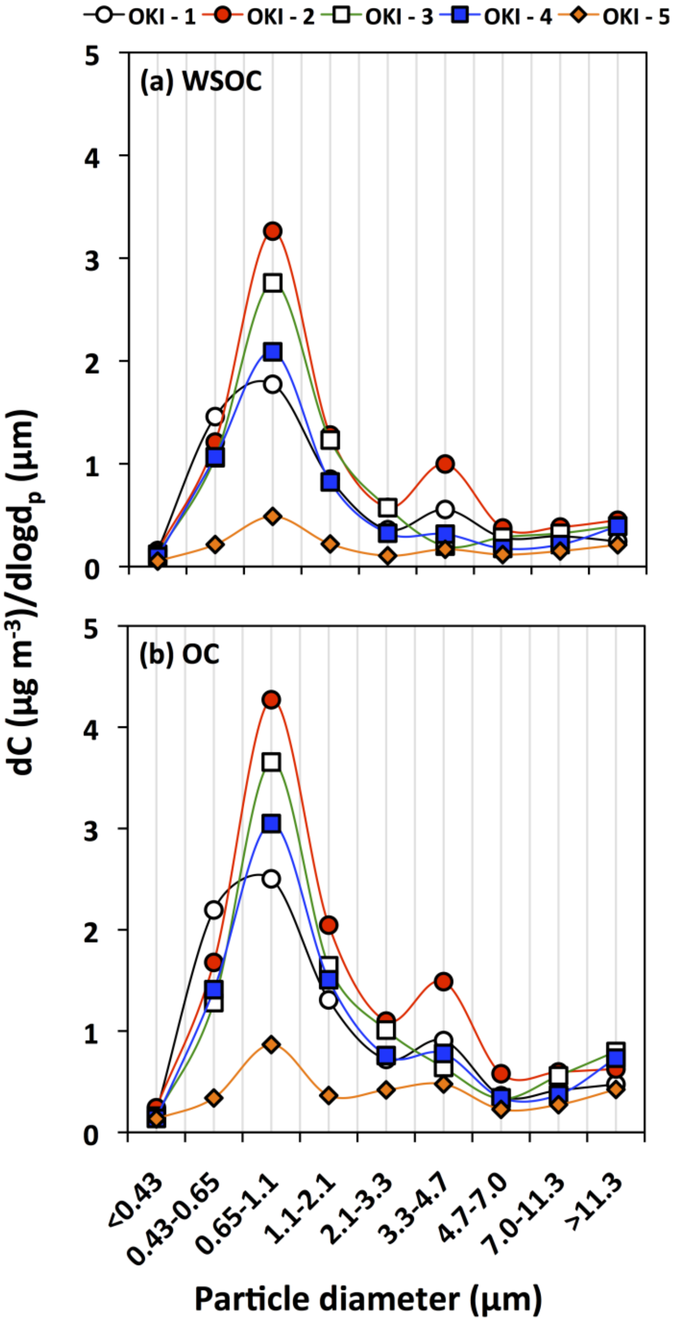

Figure 8. Size distributions of water-soluble organic carbon (WSOC) and organic carbon (OC) in the aerosol samples collected at Okinawa Island.

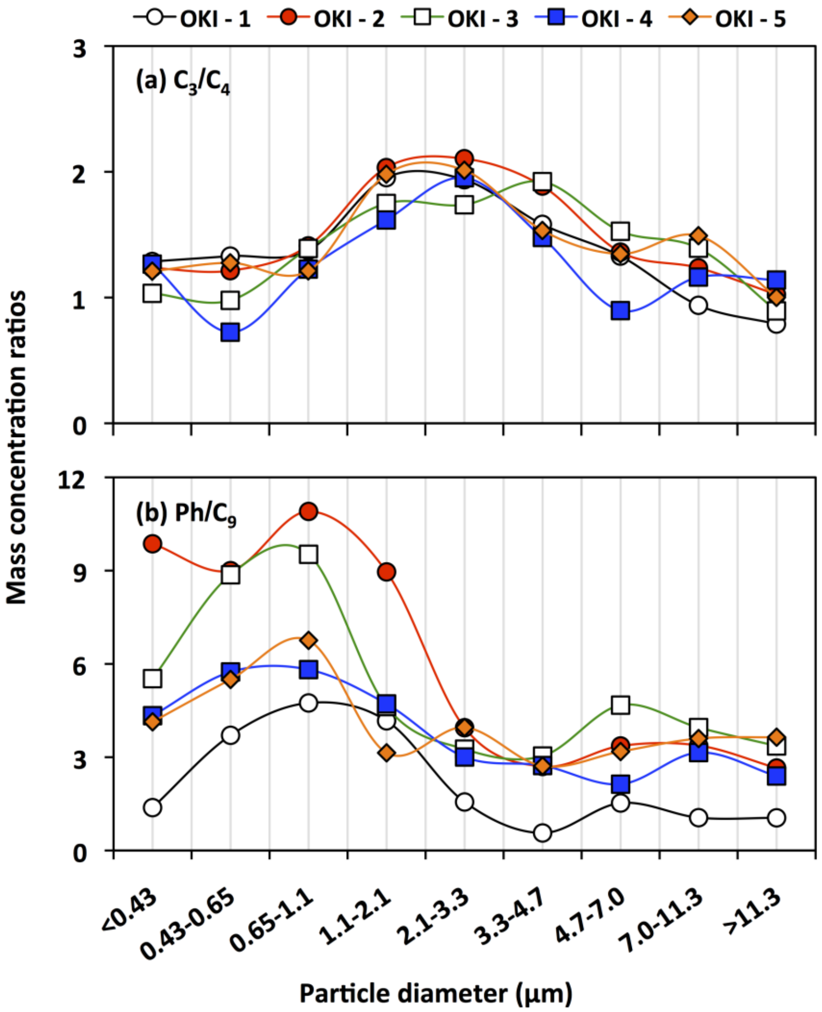

Figure 9. Mass concentration ratio of malonic to succinic acid and phthalic to azelaic acid in size-segregated aerosols collected at Okinawa Island.