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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 (nine stages from < 0.43to >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 $(\omega C_2-\omega C_9)$, pyruvic acid, benzoic acid, and α -dicarbonyls (C₂-C₃) as well as water-soluble organic carbon (WSOC), organic carbon (OC), and major ions (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, SO₄²⁻, and MSA^{-}). In all the size-segregated aerosols, oxalic acid (C₂) was found to be 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 (C₂–C₅), ω C₂, and Gly as well as WSOC and OC peaked at fine mode (0.65-1.1 µm) whereas azelaic (C₉) and 9-oxononanoic (ω C₉) acids peaked at coarse mode (3.3-4.7 µm). Sulfate and ammonium were enriched in fine mode, whereas sodium and chloride were 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 also have been directly emitted from biomass burning in fine mode as supported by strong correlations with potassium (r = 0.85-0.96), which is a tracer of biomass burning. Bimodal size distributions of longer-chain diacid (C_9) and oxoacid (ωC_9) with a major peak in the coarse mode suggest that they were emitted from the sea surface microlayers

and/or produced by heterogeneous oxidation of biogenic unsaturated fatty acids on sea salt particles.

1 Introduction

Tropospheric aerosol is an important environmental issue because it dramatically reduces the visibility (Jacobson et al., 2000; Kanakidou et al., 2005), affects the radiative forcing of climate (Seinfeld and Pandis, 1998), and causes 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 with diameters of $0.1-1.0 \,\mu\text{m}$ 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 evidence for the sources and formation pathways of 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; Kawamura and Bikkina, 2016). 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 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. Rapid industrialization in East Asia is expected to have an important impact on global atmospheric chemistry over the next decades (Wang et al., 2013; Tao et al., 2013; Bian et al., 2014). Large amounts of coal and biomass burning in East Asia add more anthropogenic aerosols which alter 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 have previously been 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 the western North Pacific Rim.

We collected size-segregated aerosol samples with nine size ranges in spring 2008 in Cape Hedo, Okinawa, in the western North Pacific Rim. 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 ($\omega C_2 - \omega C_9$), pyruvic acid (C₃), and α -dicarbonyls (C₂-C₃) to better understand the sources and processing of water-soluble organic compounds at this marine receptor site. 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 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 Fig. 1. Okinawa is located in the outflow region of con-



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

tinental aerosols and on the pathways to the Pacific. Cape Hedo has been used as a supersite of the 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 Atmosphere and Aerosol Monitoring Station (CHAAMS) from 18 March to 13 April 2008. This period was characterized by 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; $100 \,\mathrm{L\,min^{-1}}$) was used for the collection of size-segregated samples. The sampler was equipped with quartz fiber filters (QFFs, 80 mm in diameter) that were precombusted at 450 °C for 6h 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 $>11.3 \,\mu\text{m}$. 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 blanks was collected by placing a precombusted QFF into the sampler for 30 s without sucking air before installing the real QFF.

2.2 Analytical procedures

Diacids and related compounds were determined by the method of Kawamura and Ikushima (1993), and Kawamura (1993). Aliquot of the filters was extracted with organic-free ultrapure water (specific resistivity >18.2 M Ω cm) under ultrasonication. The extracts were passed through a 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 % BF₃ in *n*-butanol at 100 °C. Acetonitrile and *n*-hexane were added into the derivatized sample and washed with organicfree pure water. The hexane layer was further concentrated using a rotary evaporator under vacuum and dried to almost dryness by N₂ blowdown and dissolved in 100 µL of *n*-hexane. $2 \mu L$ of the sample was injected into a capillary gas chromatograph (GC) (Hewlett-Packard HP6890) equipped with a flame ionization 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 precombusted 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 $0.22 \,\mu$ m). 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 by H. Wang et al. (2005). 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 was applied in the first ramp and was 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 a non-dispersive infrared detector system. The detection limits of OC and EC were ca. 0.05 and $0.02 \,\mu gC \,m^{-3}$, 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 ul-

trapure water under ultrasonication. These extracts were filtered through a disc filter (Millex-GV, Millipore; diameter of $0.22 \,\mu$ m) and injected into an ion chromatograph (Compact IC 761; Metrohm, Switzerland) for measuring MSA⁻, Cl⁻, SO₄²⁻, NO₃⁻, Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺ (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 Na₂CO₃ and 1.7 mM NaHCO₃ solution at a flow rate of 1.2 mL min⁻¹ as an eluent and 40 mM H₂SO₄ 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 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% BF₃/*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 7-day trajectories at 500 m above the ground level for the samples collected on Okinawa are shown in Fig. 2. Typical air mass trajectories corresponding to 09:00 UTC for the samples collected on Okinawa are shown in Fig. S1 in the Supplement.

Meteorological data including ambient temperature, relative humidity, and wind speed for each sample period were obtained from Japan Meteorological Agency (http://www.jma.go.jp). During our campaign, ambient temperature, relative humidity, and wind speed ranged from 11.9 to 26.6 °C (ave. 20.0 ± 2.6 °C), 43.0 to 91.0 % (ave. 70.0 ± 12.0 %), and 0.10 to 10.2 m s⁻¹ (ave. 3.73 ± 1.99 m s⁻¹), respectively. The 7-day trajectories along with the meteorological data, including precipitation and downward solar radiation flux, are shown in Fig. S2.

2.4 Estimation of liquid water content (LWC) of aerosol

LWC of aerosol was calculated for the size-segregated samples collected on 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



Figure 2. Seven-day backward air mass trajectories (NOAA HYSPLIT) at 500 m a.g.l. (09:00 UTC) for the aerosol samples (OKI-1 to OKI-5) collected on Okinawa Island. The dates given in each panel are the starting and ending times of the collection of aerosol samples on Okinawa Island. The color scale shows the altitude of the air parcel.

(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 a "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 $2.1 \,\mu\text{m}$ 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 coarsemode aerosols. Abundances of organic matter (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 Okinawa undergo the atmospheric oxidation during the long-range transport, the fraction of oxygenated organic species is often high (Takami et al., 2007; Irei et al., 2014; Kunwar and Kawamura, 2014). Therefore, we used the conversion factor of 2.1, instead of 1.6 for the calculation of OM.

OM was more enriched in fine-size fractions than in the coarse-size fractions (Table 1). The elevated level of OM in fine fractions on Okinawa suggests a substantial contribu-

Table 1. Concentrations (μ g m⁻³) of major inorganic ions and carbonaceous species in the fine- and coarse-mode aerosols on Okinawa Island in the western North Pacific.

Inorganic ions	Fine m	ode ^a			Coarse mode ^b									
	Mean	SD ^c	Min. ^d	Max. ^e	Mean	SD	Min.	Max.						
	Water-s	soluble i	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 w	ater-sol	uble 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 $D_p < 2.1 \,\mu\text{m}$. ^b Coarse mode represents aerosol size of $D_p > 2.1 \,\mu\text{m}$. ^c Standard deviation. ^d Minimum. ^e Maximum.

tion of organic aerosols primarily from combustion sources, and secondarily from photochemical processes during longrange atmospheric transport. The OM in fine-mode aerosol on Okinawa may consist of oxygenated organic compounds such as diacids, ω -oxoacids, and α -dicarbonyls. Okinawa was strongly affected by long-range transport of continental air masses from Siberia and Mongolia as well as North China and Korea (Fig. 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. Precipitation may have an insignificant effect on the transport of pollutants from the source region to Okinawa because air masses did not experience serious precipitation events during transport (Fig. S2a).

Sulfate is the most abundant anion in fine mode, whereas chloride is the dominant anion in coarse mode. The cation budget is largely controlled by ammonium in fine mode, whereas sodium is the most abundant cation in coarse mode. The high abundance of SO_4^{2-} in fine particles suggests a sig-

nificant 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 NH₃ 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 mode suggest a substantial contribution from sea salt. Na⁺ and Cl⁻ are emitted from the ocean surface as relatively larger particles. A substantial amount of NO₃⁻ was detected in coarse mode, suggesting a formation of Ca(NO₃)₂ or NaNO₃ in coarse fractions through the reactive adsorption of gaseous HNO₃ onto preexisting alkaline particles.

The molecular distributions of detected diacids and related compounds in size-segregated aerosols are shown in Fig. 3. Table 2 presents the summarized concentrations of those compounds in fine and coarse modes. Oxalic acid (C_2) was

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Compounds	Abbreviation	Chemical formula	Fine mode ^a					Coarse mode ^b					
			Mean	SD ^c	Min. ^d	Max. ^e	Mean	SD	Min.	Max.			
		Dicarboxylic	acids										
	Saturated i	normal-chain diacids											
Oxalic	C ₂	НООС-СООН	135	37.4	76.0	176	40.2	14.7	22.1	60.0			
Malonic	C ₃	HOOC-CH2-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	C5	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			
	Branch	ed-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			
	Unsaturat	ed aliphatic diacids											
Maleic	М	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			
-	Unsaturat	ed aromatic diacids											
DI-4111	DI		(20	2.95	1.00	0.2	2 70	0.91	1.95	2.0			
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			
Torophthalia	1Pn tPh	$HOOC_{6}H_{4}$)- $COOH_{7}m$ isomer	0.46	0.07	0.35	0.55	0.17	0.06	0.09	0.22			
Terephtnanc	tPli	$HOOC-(C_6H_4)-COOH - p-isomer$	2.21	1.15	0.52	5.50	0.04	0.58	0.09	1.17			
	Multif	unctional diacids											
Malic	hC ₄	HOOC-CH(OH)-CH2-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 dia		196	58.1	98.3	253	74.1	24.3	41.4	105				
		ω	Oxocarbo	oxylic a	cids								
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-CH2-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			
						acid							
Pyruvic	Pyr	СН3-С(О)-СООН	2.61	0.76	1.67	3.48	2.32	1.20	0.76	4.09			
			α-Dica	bonyls									
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-dica	arbonyls	2.83	1.59	1.03	4.68	1.49	0.37	0.96	1.86				
		Α	romatic	monoac	id								
Benzoic acid		16.5	11.0	4.57	28.3	1.98	1.01	0.70	3.38				

Table 2. Summarized concentrations (ng m $^{-3}$) of water-soluble dicarboxylic acids and related polar compounds in the fine- and coarse-modeaerosols from Okinawa Island in the western North Pacific Rim.

^a Fine mode represents aerosol size of $D_p > 2.1 \,\mu$ m. ^b Coarse mode represents aerosol size of $D_p > 2.1 \,\mu$ m. ^c Standard deviation. ^d Minimum. ^e Maximum.



Figure 3. Average molecular distributions of water-soluble dicarboxylic acids and related compounds in size-segregated aerosols collected on Okinawa Island.

found to be 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 is due to the fact that it can be secondarily produced by the photooxidation of anthropogenic and biogenic organic precursors in gas and aqueous phase (Kawamura and Sakaguchi, 1999; Warneck, 2003; Carlton et al., 2006). C_2 can also be produced primarily from fossil fuel combustion (Kawamura and Kaplan, 1987) and biomass burning (Kundu et al., 2010) in East Asia and is long-range-transported to Okinawa.

Phthalic (Ph) and adipic (C_6) acids are the next abundant diacids, whereas ketomalonic acid (kC₃) is more abundant than C₆ diacid in the size ranges of 0.43-0.65 to 0.65-1.1 µm (Fig. 3). Ph and C₆ diacids originate from various anthropogenic sources and thus they can be used as anthropogenic tracers. Ph primarily originates from coal burning and vehicular emissions, whereas photooxidation of aromatic hydrocarbons such as naphthalene and o-xylene derived from incomplete combustion of fossil fuel form Ph via secondary processes (Kawamura and Kaplan, 1987). Moreover, 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 longrange 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 C₆ diacid is an oxidation product through the reaction of cyclohexene

with ozone (O₃). The high abundances of Ph and C₆ diacids on Okinawa suggest a significant influence of anthropogenic sources in East Asia via long-range transport of aerosols over the western North Pacific Rim.

Azelaic acid (C₉) is more abundant than adjacent suberic (C_8) and decanedioic (C_{10}) acids in all the sizesegregated aerosols (Fig. 3 and Table 2). 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 on Okinawa (Kunwar and Kawamura, 2014). Moreover, Okinawa was affected by long-range transport of air masses from Siberia and Mongolia as well as North China and Korea (Fig. 2). Such continental air masses can also deliver C₉ via atmospheric processing of unsaturated fatty acids during long-range transport. The abundant presence of C₉ indicates that atmospheric oxidation of unsaturated fatty acids also occurs in Okinawa aerosols during longrange 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 products of several anthropogenic and biogenic VOCs and are primarily generated by fossil fuel combustion and biomass burning (Zimmermann and Poppe, 1996; Volkamer et al., 2001), and are further oxidized to C2 diacid (Myriokefalitakis et al.,

Table 3. Pearson correlation coefficients^a (r) matrix among the selected chemical species/components measured in the fine- and coarse-mode aerosols from 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	C3	C_4	C5	C9	Ph	ωC_2	ωC9	Gly	Benzoic	LWC
Na ⁺	1.00																					
NH_4^+	-0.25	1.00																				
K+	-0.32	0.99	1.00	1.00																		
Mg2+	0.98	-0.16	-0.23	1.00	1.00																	
Ca ²⁺	-0.21	0.62	0.33	-0.15	1.00	1.00																
CI	0.52	-0.85	-0.85	0.58	-0.33	-0.78	1.00															
NO ₂	0.65	-0.56	-0.55	0.68	0.22	-0.36	0.76	1.00														
so 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											
C2	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	4.00								
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	1.00							
C5	-0.12	0.99	0.96	-0.05	0.55	0.87	-0.80	-0.55	0.99	0.95	0.95	0.91	0.95	0.97	0.00	1.00						
Ph	0.41	0.78	0.73	0.46	0.42	0.63	-0.40	-0.16	0.10	0.20	0.93	0.90	0.83	0.83	0.86	0.23	1.00					
ωC2	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				
ωC9	0.23	0.22	0.12	0.18	-0.56	-0.01	-0.32	-0.53	0.29	0.13	0.22	0.05	0.31	0.26	0.32	0.80	0.02	0.16	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	-0.11	1.00		
Benzoic	-0.13	0.99	0.99	-0.05	-0.23	0.90	-0.27	0.46	0.99	0.96	0.99	0.93	0.91	0.96	0.99	0.12	0.85	0.96	0.21	0.90	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	0.19	0.95	0.91	1.00
										C	oarse mod	e ^c										
	Na ⁺	NH_4^+	K ⁺	Mg ²⁺	Ca ²⁺	MSA ⁻	Cl-	NO_3^-	SO_4^{2-}	WSOC	OC	C2	C3	C ₄	C5	C ₉	Ph	ωC_2	ωC9	Gly	Benzoic	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	1.00																	
Ca ²⁺	-0.12	0.03	-0.06	-0.29	1.00	1.00																
CI-	-0.15	-0.66	0.05	-0.25	-0.02	_0.22	1.00															
NO.	-0.30	-0.23	-0.15	-0.39	0.98	0.22	-0.55	1.00														
SO2-	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											
C2	-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								
C5	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	1.00						
C9 Ph	-0.52	-0.54	-0.29	-0.54	-0.16	-0.59	-0.65	-0.51	0.18	-0.08	-0.25	0.25	0.50	0.19	-0.23	-0.58	1.00					
ωCa	0.23	0.37	0.85	0.68	0.12	0.42	0.59	0.23	0.73	0.53	0.53	0.53	0.76	0.60	0.32	0.23	0.21	1.00				
ωC ₉	0.83	0.53	0.82	0.87	-0.33	0.03	0.80	-0.22	0.21	0.07	0.16	0.28	0.38	0.08	-0.31	0.93	-0.28	0.33	1.00			
Chu	0.04	0.26	0.78	0.57	0.05	0.52	0.59	0.06	0.00	0.29	0.22	0.22	0.55	0.76	0.57	0.24	0.12	0.80	0.12	1.00		
Giy	0.26	0.20	0.78	0.57	0.05	0.52	0.56	0.00	0.69	0.20	0.55	0.22	0.55	0.70	0.57	0.24	0.12	0.09	0.15	1.00		
Benzoic	-0.26 -0.40	-0.60	-0.57	-0.36	-0.70	0.32	-0.29	-0.43	-0.89	-0.28	-0.35	-0.57	-0.73	-0.91	-0.77	-0.37	0.12	-0.48	-0.07	-0.51	1.00	

See Tables 1 and 2 for abbreviations. ^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.

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 Fig. 4. 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 (Fig. 4a 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 falls 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 are produced the size of 5–20 µm. Their coarse-mode peaks at 2.1–3.3 µm or 3.3–4.7 and > 11.3 µm in

Okinawa aerosols were 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 coarsemode Na⁺ and Cl⁻ (r = 0.98), suggesting their similar origin and sources.

A high concentration of Ca²⁺ in coarse-mode particles demonstrates its contribution 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 a remote marine site is also proposed as an important source of Ca²⁺ (Y. Wang et al., 2005). Ca²⁺ showed unimodal distribution with a peak at either 2.1–3.3 or 3.3– 4.7 µm (Fig. 4c). The coarse-mode Ca²⁺ is mostly derived from crustal CaCO₃, which heterogeneously reacts with acidic gases (HNO₃ and SO₂) (Kerminen et al., 1997a). This formation mechanism is further supported by a strong correlation of coarse-mode Ca²⁺ with NO₃⁻ (r = 0.98). There is no correlation between Ca²⁺ and Na⁺ or Cl⁻ (r = -0.12 or -0.27), revealing that sea salt contribution of Ca²⁺ is neg-



Figure 4. Size distributions of water-soluble inorganic ions in the aerosol samples collected on Okinawa Island.

ligible in Okinawa aerosols. This result suggests that longrange transport of soil dust is an important contributor of Ca^{2+} in the marine aerosols from the western North Pacific Rim.

There are natural limestone caves formed by elevated coral reefs on Okinawa Island. Although local limestone dust may also be resuspended in the atmosphere by wind (Shimada et al., 2015), the local dust contribution to the ambient level of Ca^{2+} on Okinawa may be small. This interpretation can be supported by the fact that Ca^{2+} peaked 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 upper coarse size range when the contribution of locally produced soil particles is significant (Bian et al., 2014). 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 the OKI-5 sample (0.15 µg m⁻³). Backward trajectories also indicated that the

air masses which originated from Mongolia and Siberia were transported to Okinawa during the collection of OKI-1 and OKI-2 samples, whereas the OKI-5 sample has an influence of marine air masses. Such air mass origin again indicates the 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 $0.1-0.5 \,\mu$ m in diameter (Kaufman and Fraser, 1997; Kleeman and Cass, 1999). A unimodal size distribution of K⁺ was observed in most sample sets (OKI-1 to OKI-4), with a peak at 0.65–1.1 μ m in diameter (Fig. 4e). The peak of K⁺ at 0.65–1.1 μ m suggests that biomass burning particles emitted in East Asia might have undergone growth to a relatively large size by

absorbing water vapor from the atmosphere during longrange transport to Okinawa. 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 total K⁺ in the OKI-2 sample set and 88 % of that in the OKI-3 sample set when air masses come 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 a long-range atmospheric transport of biomass burning aerosols from the Asian continent to the western North Pacific Rim.

NO_x is a precursor of NO₃⁻, which can be converted to HNO₃ and then react with NH₃ to form NH₄NO₃. A unimodal size distribution of NO₃⁻ was observed with a peak at 2.1–3.3 or 3.3–4.7 µm in diameter (Fig. 4f). It should also be noted that the NO₃⁻ concentration in coarse mode is much higher than that in fine mode (Table 1). This result suggests that either dust or sea salt particles are the source of coarse-mode NO₃⁻ on Okinawa. Coarse-mode NO₃⁻ is produced by heterogeneous reaction of gaseous NO₂ or HNO₃ with alkaline metals such as Na⁺ and Ca²⁺ as shown in Reactions (R1) and (R2) (Kouyoumdjian and Saliba, 2006; Seinfeld and Pandis, 2006).

 $\begin{aligned} HNO_{3(g)} + NaCl_{(aq and s)} &\rightarrow NaNO_{3(aq and s)} + HCl_{(g)} \quad (R1) \\ 2HNO_{3(g)} + CaCO_{3(s)} &\rightarrow Ca(NO_3)_{2(s)} + H_2O + CO_{2(g)} \quad (R2) \end{aligned}$

As discussed earlier, the air masses which 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 HNO₃ might already have reacted with CaCO₃ (mineral dust particle) to form 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 coarse-mode NO_3^- . Although this correlation is not significant (p = 0.51), the negative correlation may indicate some reactive loss of NO₃⁻ from sea salt particles in coarse mode on Okinawa. NO_3^- peaked at the same particle size of Ca^{2+} . Therefore, NO₃⁻ in Okinawa coarse-mode aerosols probably resulted from the uptake of HNO3 gas by soil dust particles enriched with Ca²⁺ via heterogeneous reactions near the source regions. This process is further supported by a good correlation between NO₃⁻ and Ca²⁺ (r = 0.98) in coarse mode.

The particle size distributions of SO_4^{2-} , which is a 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 SO₂ followed by gas-to-particle conversion, whereas fine-mode SO_4^{2-} is formed through aqueous-phase oxidation of SO₂ in aerosols and cloud droplets (Seinfeld and Pandis, 1998). SO_4^{2-} on coarse mode can be attributed to a combination of sulfate and heterogeneous reactions of SO₂ 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 (Fig. 4g). Gao et al. (2012) suggested that an in-cloud process produces SO_4^{2-} as larger particles by aqueous-phase oxidation of SO_2 in cloud droplets. Therefore, the peak of SO_4^{2-} at 0.65–1.1 µm on Okinawa may be involved with aqueous-phase oxidation of SO_2 in aerosols.

Size distribution of methanesulfonate (MSA⁻) is similar to that of SO_4^{2-} (Fig. 4i) on 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 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 an enhanced emission of DMS from biomass burning followed by the subsequent oxidation during long-range transport may have contributed significantly to fine-mode MSA⁻ on 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 traveled over the marine regions including the East China Sea, Sea of Japan, and Pacific Ocean during long-range atmospheric transport. The 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 Scontaining species in the marine atmosphere.

NH₄⁺ in the Okinawa aerosols shows a unimodal size distribution with a peak at 0.65–1.1 µm (Fig. 4h), indicating that NH₄⁺ is mainly formed by gas-to-particle conversion via the reaction with H₂SO₄ and HNO₃. Interestingly, the size distribution of NH₄⁺ is similar to that of SO₄²⁻ and diacids such as oxalic acid (Figs. 4g and 5a). We also found a strong correlation between SO₄²⁻ and NH₄⁺ on fine mode (r = 0.99). Ion balance calculations are commonly used to evaluate acidbase balance of aerosol particles. Average equivalent ratios of total cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) to anions (Cl⁻, NO₃⁻, and SO₄²⁻) 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 on Okinawa were apparently acidic.

NH₃ is an alkaline gas that neutralizes the acidic particles in the atmosphere. Kerminen et al. (1997a) proposed that particulate NH₄⁺ is secondarily formed via heterogeneous reactions of gaseous NH₃ with acidic species (H₂SO₄ and HNO₃). The reaction of NH₃ with H₂SO₄ is favored over its reaction with HNO₃. The average NH₄⁺/SO₄²⁻ equivalent ratios in fine-mode particles on 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–



Figure 5. Size distributions of selected water-soluble dicarboxylic acids and related compounds in the aerosol samples collected on Okinawa Island.

0.65 μ m, indicating that NH₃ was not abundant enough to neutralize all SO₂. The aerosol chemical composition data obtained from the ISORROPIA II model revealed that significant amounts of SO₄²⁻, HSO₄⁻, and NH₄⁺ in fine mode were present in liquid phase, whereas SO₄²⁻ and NO₃⁻ were mainly present as solid phase in the coarse-mode aerosols in the forms of CaSO₄ and Ca(NO₃)₂, respectively. Interestingly, the average $\rm NH_4^+/SO_4^{2-}$ equivalent ratios in coarsemode 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 on Okinawa were also $\rm NH_4^+$ -poor. This result further indicates that there was not enough $\rm NH_3$ to neutralize HNO₃, and thus the shortfall of $\rm NH_3$ may be the restrictive factor for the formation of $\rm NH_4\rm NO_3$ in Okinawa aerosols. Therefore, NO_3^- reacts with coarse particles that contain alkaline species (Ca²⁺) in Okinawa aerosols.

The size distribution of SO_4^{2-} 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-} might be neutralized by NH_3 in fine mode. 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, b), who found a large and irreversible uptake between HNO₃ and various authentic dust samples including samples from the Chinese dust region.

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 (Fig. 6a 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. The WSOC concentrations showed a strong correlation with fine-mode SO_4^{2-} (r = 0.96). Because production of SO_4^{2-} is closely 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. WSOC concentrations also showed high correlation with K⁺ (r = 0.93) and NH⁺₄ (r = 0.91) in fine mode. This result suggests that direct emission from biomass burning or fast oxidation of biomass-burning-derived precursors significantly contributes to the formation of fine-mode WSOC in Okinawa aerosols during long-range transport.

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 appeared in the size range of 3.3– 4.7 µm in diameter (Fig. 6b). Primary emission from biomass burning and/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 a strong correlation (r = 0.95) with K⁺ in fine mode. The fine-mode OC showed significant positive correlations with SO₄^{2–} (r = 0.93) and NH₄⁺ (0.91), suggesting a secondary photochemical formation of OC in the fine mode of Okinawa aerosols.

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 organic aerosols especially in long-range-transported aerosols (Aggarwal and Kawamura, 2009). The WSOC / OC



Figure 6. Size distributions of water-soluble organic carbon (WSOC) and organic carbon (OC) in the aerosol samples collected on Okinawa Island.

ratios varied from 0.51 to 0.76 with an average of 0.67 ± 0.09 in the fine mode and from 0.43 to 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 significantly subjected to photochemical processing in fine aerosols during long-range transport from the Asian continent to Okinawa compared to coarse-mode aerosols.

Source contributions and secondary processes that may convert VOCs to more soluble forms on the surface area of fine particles could cause higher WSOC / OC ratios in fine mode. Biomass-burning-derived OC is highly watersoluble and usually resides in fine mode, whereas coarsemode OC contains high molecular weight organic compounds emitted by soil resuspension and emissions of pollen and fungal spores, which are less water-soluble (Wang et al., 2011; Mkoma et al., 2013). Biomass burning significantly contributed to fine-mode WSOC on Okinawa as discussed above. 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 the reaction rate is more on the surface of fine particles than 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).

The WSOC / OC ratio in fine mode showed a weak positive correlation with downward solar radiation flux (r = 0.39). This weak correlation is probably due to the fact that fine-mode WSOC can be produced in the aqueous phase of aerosols during long-range transport. Based on the year-round measurements of total suspended aerosols from Ok-inawa Island, Kunwar and Kawamura (2014) documented higher WSOC / OC ratio in winter (ave. 0.60) and spring (ave. 0.45) than summer (ave. 0.28). These observations demonstrate that WSOC can be produced from OC under a weak solar radiation condition on the transport pathway from the source region to Okinawa possibly via aqueous-phase processing.

Calculated LWC for each sample from Okinawa and average LWC in size-segregated aerosols are shown in Fig. 7. The highest LWC was found at the size of 0.65–1.1 µm in the fine mode in Okinawa samples. WSOC can also contribute to aerosol LWC, although its ability to absorb water is significantly less than that of inorganics (Ansari and Pandis, 2000; Speer et al., 2003; Engelhart et al., 2011). Moreover, organic species are not taken into account in ISOR-ROPIA II for the calculation of LWC. It is noteworthy that WSOC / OC ratio and LWC in fine mode significantly correlate with r = 0.87, whereas negative correlation was found in coarse mode (r = -0.19), suggesting a possible production of WSOC from OC in aerosol aqueous phase in the fine mode of Okinawa aerosols. There may also be another important source of fine-mode WSOC in Okinawa aerosols such as primary emission from biomass burning and secondary formation via gas-phase photochemical reactions during longrange atmospheric transport (Hagler et al., 2007; Lim et al., 2010). This result may indicate that shorter-chain diacids and related polar compounds can contribute more to fine-mode WSOC via oxidation of various organic precursors during long-range transport (Carlton et al., 2007; Kawamura et al., 2005, 2007; Miyazaki et al., 2010).

3.4 Dicarboxylic acids and related compounds

The size distributions of selected diacids and related compounds are shown in Fig. 5. Based on the sources and formation processes, their size distributions fall into two groups: a group with a dominant fine mode and a group with a dominant coarse mode, as discussed in the following sections.

3.4.1 C₂, ω C₂, Gly, Ph, and benzoic acid

The first group, including C₂, ω C₂, Gly, Ph, and benzoic acid, showed similar size distributions to maxima in fine mode. C₂ showed a peak at 0.65–1.1 µm in fine mode (Fig. 5a). The size distribution of C₂ on Okinawa is different from that observed off the coast of East Asia by Mochida et al. (2003a, 2007), who found a strong bimodal pattern of



Figure 7. Aerosol liquid water contents for each sample in sizesegregated aerosols and average liquid water contents in sizesegregated aerosols on Okinawa Island.

 C_2 with a peak in the coarse mode. They suggested that the coarse-mode peak of C_2 emerged by the uptake of gaseous diacids or heterogeneous oxidations of organic precursors on the dust and sea salt particles during long-range transport. The unimodal distribution of C_2 on Okinawa with maxima in fine mode suggests that the heterogeneous uptake of C_2 on dust and sea salt particles did not occur.

The condensation mode of C₂ is likely produced photochemically in the gas phase followed by condensation onto preexisting particles at 0.1–0.5 µm (Huang et al., 2006). The fine-mode peak of C₂ at the size of 0.65-1.1 µm in Okinawa aerosols suggests a preferential production of C₂ via the oxidation of precursors in aerosol aqueous phase during long-range atmospheric transport. We found that size distribution of C₂ diacid is similar to that of SO_4^{2-} (Figs. 4g and 5a), suggesting a secondary formation of C₂, possibly in aerosol aqueous phase. The good correlations of C2 with SO_4^{2-} (r = 0.92) and NH_4^+ (0.89) in fine mode further supports that C₂ is a secondary photochemical product. Finemode C₂ can also be produced primarily from fossil fuel combustion and biomass burning in East Asia and longrange-transported to Okinawa. C2 diacid showed a significant positive correlation with fine-mode K^+ (r = 0.85), indicating that biomass burning contributed significantly to fine-mode C₂ in Okinawa aerosols.

Lim et al. (2005) and Legrand et al. (2007) reported the formation of diacids in aqueous phase. Here we investigate the impact of LWC on the formation of diacids in Okinawa aerosols. LWC of a particle can influence the production of C₂ via the changes in gas/particle partitioning of organic precursors and subsequent heterogeneous reactions in aerosol aqueous phase. A strong positive correlation (r = 0.92) of C₂ with LWC was found in fine mode, whereas the correlation was negative in coarse mode (r = -0.29), indicating a possible aqueous-phase production of C₂ via the oxidation of C₂ precursors in fine mode. Several secondary for-

mation pathways are known to C_2 in atmospheric aerosols. C_2 is produced by the decay of its higher homologues (C_3 – C_5 diacids) or oxidation of unsaturated fatty acids such as oleic acid ($C_{18:1}$) followed by the degradation to shorterchain diacids in aqueous phase (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Pavuluri et al., 2015). C_2 can also be produced by the aqueous-phase oxidation of ωC_2 , which can be formed by aqueous oxidation of Gly and MeGly, produced by the oxidation of various VOCs including toluene, ethene, and isoprene (Zimmermann and Poppe, 1996; Volkamer et al., 2001; Lim et al., 2005; Carlton et al., 2006; Ervens et al., 2008).

The scatter plots of C₂ with C₃-C₅ diacids in fine and coarse modes are shown in Fig. S3. The robust correlations of C₂ with C₃–C₅ diacids (r = 0.89-0.92) were found in fine mode, indicating that they might have similar sources and origin or C₂ may be produced via the decay of its higher homologues (C₃-C₅ diacids) during long-range transport. The differences in the slopes of linear regression of C_2 with C_3 and C₄ diacids between fine and coarse modes are not significant but slopes are slightly higher in fine mode than the coarse mode (Fig. S3a-d and Table S1). Interestingly, a significantly higher slope was observed for the regression line between C_2 and glutaric (C_5) acid in fine mode than coarse mode (Fig. S3e-f and Table S1). It is also noteworthy that the slope of the regression line of C₂ with C₅ diacid is significantly higher than that for C₃ and C₄ diacids in fine mode (Fig. S3a, c, e and Table S2). These results indicate that finemode oxalic acid may be produced from oxidation of glutaric acid during long-range transport via succinic and malonic acids as intermediates. The laboratory studies of Hatakeyama et al. (1985) and Kalberer et al. (2010) have documented that glutaric acid is produced by the oxidation of cyclohexene by O₃, which can be further oxidized in aqueous phase to result in oxalic acid (Kawamura and Sakaguchi, 1999; Legrand et al., 2007). This interpretation is further supported by the fact that C_3 – C_5 diacids were enriched in the fine mode of most samples (Fig. 5b-d) and showed good correlations with LWC (r = 0.82 - 0.89), possibly due to the enhanced secondary production by the oxidation of its precursor compounds in aerosol aqueous phase.

The size distribution of ωC_2 and Gly is similar to that of C_2 diacid in the Okinawa samples (Fig. 5e and f). The enrichment of ωC_2 and Gly in fine mode may be associated with enhanced secondary formation via aqueous-phase processing of their precursors during long-range transport. This interpretation is evidenced by the fact that strong correlations of ωC_2 and Gly were found with SO_4^{2-} (r = 0.96 and 0.86, respectively) and LWC (0.95) in fine mode. The fine-mode ωC_2 and Gly can also be produced primarily from biomass burning in East Asia and be long-range-transported to Okinawa. Significant positive correlations between ωC_2 and K⁺ (r = 0.90), and Gly and K⁺ (0.86) suggest that biomass burning contributed significantly to the fine-mode ωC_2 and Gly in Okinawa aerosols. Gly is a well-known precursor of ωC_2

and C_2 in atmospheric aerosols (Lim et al., 2005; Ervens and Volkamer, 2010; Myriokefalitakis et al., 2011). The preferential enrichment of Gly and ωC_2 in fine mode can form C_2 in Okinawa aerosols by aqueous-phase processing.

High correlations among C_2 , ωC_2 , and Gly in fine mode (r = 0.92-0.99) also indicate their similar sources and formation processes and that C_2 diacid may be produced by the oxidation of ωC_2 and Gly in fine mode. There is no significant difference in the slope of regression line of C_2 with ωC_2 between the fine and coarse modes (Fig. S3g-h and Table S1), whereas the slope of the regression line of C_2 with Gly is significantly higher in fine mode than coarse mode (Fig. S3i-j and Table S1). It is also remarkable that the slope of linear regression of C_2 with Gly is significantly higher than that with ωC_2 in fine mode (Fig. S3g-i and Table S2). This result may indicate a possible formation of fine-mode oxalic acid from glyoxal via glyoxylic acid as an intermediate during long-range atmospheric transport in the western North Pacific.

The enrichment of C_2 , ωC_2 , and Gly in fine mode on Okinawa was probably due to the enhanced oxidation of anthropogenic precursors emitted in East Asia during long-range transport because their size distributions are consistent with that of Ph and benzoic acid (Fig. 5g and h), which are tracers of anthropogenic sources. The strong correlations of finemode C_2 , ωC_2 , and Gly with Ph (r = 0.85-0.93) and benzoic acid (r = 0.90-0.96) further suggest that anthropogenic precursors are their important sources in fine mode. Ph and benzoic acid are directly emitted from combustion sources and secondarily produced in the atmosphere by the photooxidation of aromatic hydrocarbons emitted from the incomplete combustion of fossil fuel (Kawamura et al., 1985; Kawamura and Kaplan, 1987; Ho et al., 2006).

Aromatic hydrocarbons such as naphthalene and toluene have been suggested as major precursors of Ph and benzoic acid, respectively (Schauer et al., 1996; Kawamura and Yasui, 2005). Based on the high levels of naphthalene and toluene in China (Liu et al., 2007; Tao et al., 2007; Duan et al., 2008), Ho et al. (2015) recently suggested that oxidation of naphthalene and toluene in the atmosphere is one of the major sources of Ph and benzoic acid, respectively. High levels of precursors in the source regions might favor the significant secondary production of Ph and benzoic acid during long-range transport in the western North Pacific. It may be possible that their precursors emitted in East Asia were taken up by aqueous-phase aerosol and oxidized to result in Ph and benzoic acid in fine mode during long-range transport. Moreover, enrichment of Ph and benzoic acid in fine mode further suggests that these species are associated with combustion sources either by primary emission and/or secondary production from the precursor compounds, being consistent with other anthropogenic SO_4^{2-} , NH_4^+ , and K^+ . Fine-mode Ph can also be produced from evaporation of phthalates from plastics used in populated and industrialized regions in East Asia and long-range-transported to Okinawa

as discussed earlier. This explanation is consistent with the enrichment of terephthalic acid (tPh) in fine mode (Fig. 5i), which is a tracer of plastic burning (Kawamura and Pavuluri, 2011).

3.4.2 C₉ and ωC₉

The second group of organic compounds, including C₉ and ωC_9 , showed bimodal size distribution with a major peak on coarse mode at 3.3-4.7 µm and minor peak on fine mode at $0.65-1.1\,\mu m$ (Fig. 5j and k). The strong correlations were found between C₉ and Na⁺ (r = 0.85), and ω C₉ and Na⁺ (0.83) in coarse mode, indicating that C₉ and ω C₉ may be emitted into the atmosphere from the sea surface microlayers together with sea salt particles on Okinawa. Kawamura and Gagosian (1987) suggested that C₉ and ω C₉ are also derived from the photooxidation of unsaturated fatty acids such as oleic acid $(C_{18:1})$ that are produced by phytoplankton and emitted from sea surface microlayers as sea salt particles. The laboratory experiments also documented the formation of C₉ and ω C₉ due to photooxidation of C_{18:1} (Matsunaga et al., 1999; Huang et al., 2005; Ziemann, 2005; Tedetti et al., 2007). Sea surface microlayers in the surroundings of Okinawa can also emit unsaturated fatty acids together with sea salts. Therefore, the major peaks of C_9 and ωC_9 on the coarse mode may be derived from heterogeneous oxidation of unsaturated fatty acids of marine phytoplankton origin on the sea salt particles.

Wang et al. (2011) suggested that unsaturated fatty acids can be directly emitted as fine particles from food cooking emissions in urban areas in China and be oxidized to C₉ diacid in fine mode. The minor peak of C₉ and ω C₉ in fine mode can be explained by the oxidation of fine-mode unsaturated fatty acids derived from food cooking or gaseous unsaturated fatty acids during long-range transport to the western North Pacific.

3.5 Ratios of selected diacids

Kawamura and Ikushima (1993) proposed that the malonic to succinic acid ratio (C_3 / C_4) is a tracer to evaluate the extent of photochemical processing of organic aerosols. Because C₄ is oxidized to C_3 , an increase in the C_3 / C_4 ratio indicates an increased photochemical processing. The average C₃ / C₄ 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 on 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 the tropics (3.9) (Kawamura and Sakaguchi, 1999). Figure 8a 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



Figure 8. Mass concentration ratios of malonic to succinic acid and phthalic to azelaic acid in size-segregated aerosols collected on Ok-inawa Island.

2.1–3.3 and 3.3–4.7 μ m in coarse mode. This result suggests that C₃ production via C₄ decomposition occurs more efficiently at these size ranges by aqueous-phase processing.

Ph diacid originates from various anthropogenic sources, whereas C₉ diacid is specifically produced by the oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987; Kawamura and Ikushima, 1993). Therefore, Ph/C9 ratio is most likely used as a tracer to understand the source strength of anthropogenic vs. biogenic sources of diacids. A higher Ph / C₉ ratio shows more influence of anthropogenic sources, whereas a lower ratio shows more influence of biogenic sources. Figure 8b presents changes in the ratios of Ph / C₉ as a function of particle sizes. The higher Ph / C₉ ratios were obtained on fine-mode particles rather than coarse-mode particles. These results suggest that fine aerosols on Okinawa are significantly influenced by anthropogenic sources whereas the coarse aerosols are more influenced by biogenic sources. A significant contribution of Ph on fine mode further supports that anthropogenic sources are an important source of diacids and related compounds in the fine mode of Okinawa aerosols.

4 Summary and conclusions

Nine-stage atmospheric particles from < 0.43 to $> 11.3 \,\mu$ m 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 water-soluble organic carbon (WSOC), organic carbon (OC), and inorganic ions. The molecular distributions of diacids were

characterized by the predominance of oxalic acid (C₂) followed by malonic (C₃) and succinic (C₄) 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 Cape Hedo suggested a significant contribution of anthropogenic sources including industrial emissions in East Asia to Okinawa aerosols 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 aerosol aqueous phase. Their strong correlations with LWC in fine mode further suggest an importance of the aqueous-phase production in Okinawa aerosols. They may have also been directly emitted from biomass burning as supported by strong correlations with K⁺ in fine mode. 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.

Longer-chain diacid (C₉) and ω -oxoacid (ω C₉) showed bimodal size distribution with a major peak on coarse mode, suggesting that they were directly emitted and/or produced by photooxidation of unsaturated fatty acids mainly derived from sea surface microlayers 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.

Data availability

The data from this paper can be obtained by contacting the authors of this article.

Meteorological data including ambient temperature, relative humidity, and wind speed for each sample period were obtained from the Japan Meteorological Agency (http: //www.jma.go.jp).

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