



HOKKAIDO UNIVERSITY

Title	Seasonal distributions of low molecular weight dicarboxylic acids, ketoacids and α -dicarbonyls in ambient aerosols collected at Cape Hedo, Okinawa, an outflow region of Asian dusts
Author(s)	Kunwar, Bhagawati
Degree Grantor	北海道大学
Degree Name	博士(環境科学)
Dissertation Number	甲第11342号
Issue Date	2014-03-25
DOI	https://doi.org/10.14943/doctoral.k11342
Doc URL	https://hdl.handle.net/2115/55414
Type	doctoral thesis
File Information	Bhagawati_Kunwar.pdf



**Seasonal distributions of low molecular weight dicarboxylic acids,
ketoacids and α -dicarbonyls in ambient aerosols collected at Cape
Hedo, Okinawa, an outflow region of Asian dusts**

by

Bhagawati Kunwar

Doctorate Dissertation

Division of Earth System Science

Graduate School of Environmental Science, Hokkaido University,

Japan, 2014

**A dissertation submitted for the partial fulfillment of the degree in
Environmental Science**

Acknowledgement

First and foremost, I would like to express my sincere gratitude to my honorable advisor Prof. Kimitaka Kawamura for the continuous support of my PhD study and research, and his patience, motivation, enthusiasm, and immense knowledge towards me for being a scientist in the field of atmospheric chemistry. He has been leading my way by observing, suggesting, and teaching the principle of every instrumentation, experimentation and result analysis during the paper preparation. I have immensely benefited from the discussions with him and for his critical evaluations for which I always was obliged to him. Further, I learned from my supervisor not only the academics but also the fundamental importance to thinking and working rigorously with honesty. These characters will lead through my life-long career. I am also heart-born grateful to Assoc. Prof. Dr. Seki and Assist. Prof. Dr. Yuzo Miyazaki for their critical comments and suggestions during the group seminars, which help me to improve and upgrade the scientific skills. They proposed plenty of comments toward the improvement of my study in different viewpoints during the group seminars. I am grateful to lab technicians of Kawamura's laboratory, Eri Tachiabana and Kaori Ono for teaching the analytical procedures.

In addition, I would also like to express my grateful to present postdoctoral research fellow, Dr. Chandra Mouli Pavuluri and other colleagues from our group for their support.

Finally, I would like to express my thanks to my late father Kul Bahadur Kunwar, my mother Laxmi Devi Kunwar, my husband Ambarish Pokhrel, and other family members for encouraging me to obtain the higher education. Without their constant support and inspiring words, research wouldn't have been possible for me. They support me mentally for a long-term abroad study.

Lastly, I express my thanks to my small child Abhinav Bhusan Pokhrel by giving me plenty of time while reading and writing.

Abstract

Ambient aerosol samples were collected for one year in Cape Hedo, Okinawa, the southernmost main island of Japan and studied for water-soluble dicarboxylic acids, ketoacids, and α -dicarbonyls to better understand the formation/transformation pathways of organic aerosols during long-range atmospheric transport. Here, we report the seasonal variations of diacids and related compounds in Okinawa, the outflow region of Asian dusts in the western North Pacific. We found that oxalic acid is the most abundant diacid species followed by malonic (C_3) and succinic (C_4) acids whereas glyoxylic acid is a dominant ketoacid. Total diacids and ketoacids maximized in spring when air masses originated from the Asian Continent under westerly winds. In contrast, α -dicarbonyls showed maximum concentrations in winter. The C_3/C_4 ratios were found to increase in summer, suggesting an enhanced photochemical aging of organic aerosols. Both phthalic acid (Ph)/ C_9 and C_6/C_9 ratios peaked in winter, suggesting an enhanced transport of organic pollutants from East Asia. The average total diacid-C/total carbon ratio (5.4%) is higher than that (3.1%) from the East China Sea but lower than that from the remote Pacific including tropics (8.8%), suggesting that Okinawa aerosols are more aged than East Asian aerosols. This study demonstrates that the ambient aerosols from Cape Hedo are strongly influenced by the outflow of Asian pollutants in winter/spring and by photochemical processes of marine-derived organic matter in summer.

In addition, we analysed organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), total nitrogen (WSTN) and organic nitrogen (WSON), and major inorganic ions. The average concentration of OC is higher in growing seasons; spring ($2.36 \mu\text{g m}^{-3}$) and summer ($1.79 \mu\text{g m}^{-3}$). Similarly, the highest concentrations of EC and WSOC were found in spring (av. $0.41 \mu\text{g m}^{-3}$ and $0.95 \mu\text{g m}^{-3}$, respectively) followed by winter (0.37 and $0.90 \mu\text{g m}^{-3}$) whereas the lowest concentrations were found in summer (0.19 and $0.52 \mu\text{g m}^{-3}$, respectively). Higher concentrations of WSON were observed in early summer (av. $0.26 \mu\text{g m}^{-3}$) probably due to the emission from marine biota. The relatively high OC/EC (av. 7.6) and WSOC/OC (44%) ratios suggest the secondary formation of organic aerosols. A strong positive correlation between Ca^{2+} and TSP in spring suggests a significant contribution of Asian dusts

whereas the higher concentrations of NO_3^- and nss-SO_4^{2-} in winter suggest an important influence from anthropogenic sources including biomass burning, vehicular emission and coal combustion. Moreover, stable carbon ($\delta^{13}\text{C}$) and nitrogen isotope ratios ($\delta^{15}\text{N}$) were determined for total carbon (TC) and nitrogen (TN). The annually averaged $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios are -22.1‰ and +12.2‰, respectively. The seasonally averaged $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios are higher in spring (-22.5‰ and +14‰, respectively) whereas these ratios are lower in summer (-22.9‰, +11.1‰). However, no correlation was obtained between nss-Ca/TSP and $\delta^{13}\text{C}$, suggesting that during long-range atmospheric transport organic aerosols are intermixed with various sources. A strong correlation between TC and TN in spring ($r^2=0.78$) and winter (0.70) suggests that TC and TN have similar sources. Contributions of NO_3^- to TN are higher (45%) than those (18%) of NH_4^+ , suggesting that vehicular exhaust and biomass burning emissions are more important nitrogen sources than the emissions from agricultural wastes and animal excreta.

Table of Contents

Acknowledgement.....	2
Abstract.....	3
Chapter 1: Introduction.....	8
1.1. Aerosols in the Atmosphere.....	8
1.2. Sources of Aerosols in the Atmosphere.....	9
1.3. Composition of Aerosols.....	9
1.4. Purpose of the Study.....	11
References.....	12
 Chapter 2: Seasonal Changes in Compositions of Low Molecular Weight Dicarboxylic Acids, Ketoacids, and α-Dicarbonyls and Fatty Acids in Ambient Aerosols Collected from Subtropical Okinawa Island, Japan, an Outflow Region of Asian Dusts.....	
2.1. Introduction.....	15
2.2. Samples and Analytical Procedure.....	17
2.2.1. Site Description.....	17
2.2.2. Aerosol Sampling.....	17
2.2.3. Chemical Analysis.....	18
2.2.4. Backward Air Mass Trajectory Analysis.....	20
2.3. Results.....	20
2.3.1. Molecular Distributions of Dicarboxylic Acids, Ketoacids and α -Dicarbonyls.....	20
2.3.2. Seasonal Variation of Diacids, Ketoacids and α -Dicarbonyls.....	22
2.3.3. Correlation Coefficients among Selected Diacids and Related Compounds.....	23
2.3.4. Principal Component Analysis for Concentrations of Dicarboxylic Acids and Related Compounds.....	24
2.3.5. Molecular Compositions of n-Alkanoic and Alkenoic Acids.....	26
2.4. Discussion.....	26

2.4.1 Sources of TSP.....	26
2.4.2. Concentration Ratios of Diacids and Related Compounds: Possible Sources and Formation Mechanisms.....	27
2.4.3. Possible Sources of Oxalic and Glyoxylic Acids.....	28
2.4.4. Seasonal Changes in Molecular Compositions and Photochemical Processing.....	30
2.4.5. Contributions of Diacids and Related Compounds to TSP, OC, TC and WSOC.....	33
2.4.6. Comparison of Distributions of Diacids and Related Compounds in Okinawa with East Asia and the Pacific.....	36
2.5. Summary and Conclusions.....	37
References.....	39
Chapter 3. One-Year Observations of Carbonaceous and Nitrogenous Components and Major Ions in the Aerosols from Subtropical Okinawa Island, an Outflow Region of Asian Dusts.....	69
3.1. Introduction.....	69
3.2. Samples and Analytical Procedure.....	70
3.2.1. Sampling Site and Aerosol Collection.....	70
3.2.2. Chemical Analysis.....	71
3.2.3. Estimate of Organic Matter and Secondary Organic Carbon.....	72
3.2.4. Estimate of Sea Salt and Non-Sea Salt component.....	73
3.2.5. Estimate of Chlorine Loss.....	73
3.2.6. Backward Air Mass Trajectory Analysis.....	74
3. 3. Results and Discussion.....	74
3.3.1 Aerosols Mass Loading.....	74
3.3.2. Seasonal Variations of Carbonaceous and Nitrogenous Components.....	75
3.3.3. Seasonal Variations of OC/EC and WSOC/OC ratios.....	77
3.3.4. Seasonal Variations of Inorganic Species.....	79
3.4.1. Ion Balance and Correlations among Major Ions.....	80
3.4.2. Sea Salt and Non-Sea Salt Ions.....	81

3.4.3. Anthropogenic Aerosols and Ionic Composition.....	83
3.4.4. Neutralization Factor and Ionic Composition.....	84
3.4. Summary and Conclusions.....	84
Reference.....	87
 Chapter 4. Seasonal Variations of Stable Carbon and Nitrogen Isotopic Compositions of Ambient Aerosol Samples Collected at Cape Hedo, Subtropical Okinawa Island, an Outflow Region of Asian Dusts.....	
	109
4.1. Introduction.....	109
4.2. Experimental.....	109
4.2.1. Site Description and Aerosol Sampling.....	109
4.2.2. Measurements of TC and TN, and their Stable Isotopes.....	110
4.2.3. Measurements of WSOC, WSTN, Major Ions and OC/EC.....	111
4.2.4. Results and Discussion.....	112
4.3.1. Seasonal Variations of TC, TN, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$	112
4.3.2. Sources of TC and TN and Variations of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$	115
4.3.3. Contribution of NO_3^- and NH_4^+ to TN.....	116
4.4. Summary and Conclusions.....	117
References.....	119
 Chapter 5. Summary and Conclusions.....	
	130

Chapter 1. Introduction

1.1. Aerosols in the Atmosphere

Atmospheric aerosols are two-phase colloidal system of solid or liquid particles in a gas. Most aerosols exhibit as poly disperses colloidal system, having a wide range of particle sizes. Atmospheric aerosols can affect the radiative balance by reflecting and absorbing incoming solar radiation, as well as by acting as condensation nuclei for the formation of cloud droplets, which also can reflect incoming light and result in the further reduction in solar radiation reaching the Earth's surface (indirect effect) (Twomey, 1974). Besides that, the aerosol particles can deposit in the nose, mouth, pharynx and larynx (the head airways region), deeper within the respiratory tract (from the trachea to the terminal bronchioles), or in the alveolar region. The deposition of aerosol particles within the respiratory system strongly determines the health effects of exposure to such aerosols.

The size distribution of the particles ranged from the nanometers to micrometers. Based upon the size, particles in the atmosphere exhibit various modes.

(a) Ultra-fine, nucleation, Aitken mode: The size of the particles ranges from 0.001 to 0.1 μm in radius. In the atmosphere these particles are formed from the homogenous nucleation of gasses and relatively have short life time. This conversion (gas to particle) takes place during long range photochemical atmospheric oxidation (Kawamura et al., 2010; Hagler et al., 2007). Aitken mode particles often make dominant contribution to the total particle number concentration. However, due to very small size these aerosols contribute a very few percent to the bulk aerosol mass concentration.

(b) Accumulation mode: The size of the particles in this mode ranged from 0.1 to 1.0 μm in radius. In the atmosphere, they are produced from either coagulation of smaller particles or heterogeneous condensation process.

(c) Coarse mode aerosol: Course mode aerosols are formed by windblown dust, sea salt spray and other sources. Aerosols in the atmosphere can move from one place to other place along with the air current. During long range or short range transport, aerosols can be oxidized.

The lifetime of aerosols in the atmosphere is few days to two weeks. The lifetime of aerosols in the atmosphere is still not clearly understood. The average lifetime of the aerosols mainly depends upon aerosols properties and meteorological conditions. Due to gravitational force, the large particles removed quickly. Wet deposition and dry deposition are the main processes to remove the aerosols from the atmosphere.

1.2. Sources of Aerosols in the Atmosphere

Atmospheric aerosols are the complex mixture of various chemical components that are derived from the multiple sources (Kawamura et al., 2004; Kawamura et al., 1996). Thus, it is very crucial to determine the atmospheric composition. Aerosols are directly injected to the atmosphere or indirectly formed by photochemical processes. Primary and secondary sources are the two main pathways of aerosol production. Based upon the emissions, there are two sources of aerosols in the atmosphere; anthropogenic sources and biogenic sources. Anthropogenic sources come from the human activities whereas biogenic sources come from the biological activities including plants, viruses, bacteria, fungi, phytoplankton, etc.

1.3. Composition of Aerosols

In general, aerosols consist of organics, inorganic species, sea salts, soil, dust and carbonaceous components. Organic aerosols including diacids are important product from the photo-oxidation of volatile organic compounds. Diacids including oxalic, malonic, maleic, phthalic acids can contribute to the aerosol nucleation process by binding to sulphuric acid and ammonia (Xu and Zhang, 2012). The formation of new particles and nanoparticles in the atmosphere are enhanced in the presence of organic acids [Zhang et al., 2004, Wang et al., 2010].

The carbonaceous components are mainly comprised of organic carbon (OC) and elemental carbon (EC). The main sources of carbonaceous components are fossil fuel combustions and biomass burning. Besides that, oxidation of biogenic volatile organics is the major source of organic carbon. Carbonaceous aerosols play major role in climate change and

health effect [Folinsbee, 1992]. EC has positive and negative radiative forcing in the atmosphere [Ramanathan et al., 2001]. Water soluble organic aerosols play an important role in climate forcing [Novakov and Penner, 1993] and CCN activity [Saxena et al., 1995].

Soil and dust are the main contributors to aerosol loadings. They also can affect the optical thickness. Dust is originated from deserts and dry regions having less vegetation. Tegen et al. [1995] showed that up to 50% of the current atmospheric dust loading is originated from the disturbed soil surface. The radiative effects of dust aerosols depend upon the particle size, refractive index and presence of minerals [Tegen et al., 1996]. Mineral dust can provide surface for heterogeneous reactions with trace atmospheric gases, leading to the chemical modification of the particles that ultimately affects the atmospheric chemical balance and photochemical cycle (Price et al., 2004).

Sea salt aerosols are emitted to the atmosphere by bubble bursting processes, which depend the wind speed. Sea salt aerosols affect the light scattering and cloud condensation nuclei in the marine sources in the presence of high wind speed [Quinn et al., 1998; O'Dowd et al., 1997]. SO_4^{2-} and NO_3^- aerosols play important role in the atmosphere. Both are formed from the atmospheric oxidation of gaseous precursor compounds. DMS and SO_2 are the main sources of SO_4^{2-} . SO_2 is derived from anthropogenic sources whereas DMS is from biogenic sources in the ocean. Hence, aerosols in the atmosphere are very complex. Without having the clear idea about composition of aerosols, it is difficult to identify the sources and atmospheric processes of aerosols during long-range transport.

As we stated above, lifetime of aerosols in the atmosphere is generally few days to two weeks. Aerosols are removed from the atmosphere by wet and dry deposition. The deposition process is effective for very small and large particles. Larger particles will settle down quickly through sedimentation (settling) while smaller particles are deposited by Brownian diffusion. Gravitational sedimentation, turbulence, and diffusion are the examples of dry deposition. Below-cloud scavenging and in-cloud scavenging are the two major processes of wet deposition. Wet deposition occurs in the presence of atmospheric hydrometeors. Dilution process or mixing of clean air also changes the atmospheric concentrations of aerosols.

1.4. Purpose of the Study

The world coal consumption is highest in East Asia. One fourth of the primary carbonaceous aerosols are generated in China [Streets et al., 2004]. About 70% of carbonaceous aerosols are originated from coal burning [Cooke et al., 1999]. Large amounts of low quality coal are used for house heating and cooking purposes [Wang et al., 2006]. Diacids and related compounds are found in the remote marine sites in the East Asian-Pacific region, suggesting a long-range atmospheric transport of organic pollutants from East Asian countries to the North Pacific [Simoneit et al., 2004; Sato et al., 2009]. Okinawa is situated in the outflow region of East Asia. We can trap East Asian aerosols during the long range atmospheric transport over Okinawa. Concentrations of diacids and related compounds are high in polluted aerosols. The main objectives of this study are to understand the seasonal variations, sources and atmospheric processing during long-range transport of diacids and related compound in the aerosols from Cape Hedo, Okinawa. We investigate the molecular distributions of diacids, ketoacids and α -dicarbonyls, as well as fatty acids, in the ambient aerosols collected at Cape Hedo, Okinawa to identify sources and atmospheric processes of organic aerosols. Organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), water soluble organic nitrogen (WSON) and inorganic ions were also measured in the aerosol samples. In addition, we measured the stable carbon and nitrogen isotopes for bulk carbon and nitrogen. Besides that, we measure the stable carbon isotope for diacids and related compounds. By comparing our data sets with previously published data from its surroundings and East Asian cities, we discuss the sources (anthropogenic vs. biogenic) and atmospheric processing of organic aerosols transported over Cape Hedo, Okinawa Island in the western North Pacific.

References

- Cooke, W. F., C. Lioussé, H. Cachier and J. Feichter (1999), Construction of a 1° x 1° fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model, *J. Geophys. Res.*, 104, 22137-22162.
- Folinsbee, L.J.: Human Health Effects of Air Pollution, *Environ. Health Perspect.*, 100: 45-56, 1992.
- Hagler, G. S. W., Bergin, M. H., Smith, E. A., and Dibb, J. E.: A summer time series of particulate carbon in the air and snow at Summit, Greenland, *J. Geophys. Res.*, 112 D21309, doi:10.1029/2007JD008993, 2007.
- Kawamura, K., H. Kasukabe, and L. A. Barrie (1996), Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, *Atmos. Environ.*, 30, 1709–1722.
- Kawamura, K., M. Kobayashi, N. Tsubonuma, M. Mochida, T. Watanabe, and M. Lee (2004), Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in *Geochemical Investigation in Earth and Space Science; A Tribute to Issac R. Kaplan*, The Geochemical Society Special Publication Series, vol. 9, edited by R. J. Hill, pp. 243-265, Elsevier, Amsterdam, Netherlands.
- Kawamura, K., R. Sempéré, Y. Imai, M. Hayashi, and Y. Fujii (1996b), Water soluble dicarboxylic acids and related compounds in the Antarctic aerosols, *J. Geophys. Res.*, 101, 18,721–18,728.
- Price, H. U., Jaffe, D. A., Cooper, O. R., and Doskey, P. V (2004), Photochemistry, ozone production, and dilution during long range transport episodes from Eurasia to the northwest United States, *J. Geophys. Res.*, 109, D23S13, doi:10.1029/2003JD004328, 2004.
- Quinn, P. K., Charlson, and T.S Bates (1998), Simultaneous observations of ammonia in the atmosphere and ocean, *Nature*, 335, 335, 336-338.

- Quinn, P. K., Coffman, D. J., Kapustin, V. N., Bates, T.S., and D. S. Covert (1998), Aerosol optical properties In the marine boundary layer during the First Aerosol Characterization Experiment (ACE 1) and underlying chemical and physical aerosol properties, *J. Geophys. Res.*, 103(D13), 16, 547-16, 563.
- Sato, K., H. Li, Y. Tanaka, S. Ogawa, Y. Iwasaki, A. Takami and S. Hatakeyama (2009), Long-range transport of particulate polycyclic aromatic hydrocarbons at Cape Hedo remote island site in the East China Sea between 2005 and 2008, *J. Atmos. Chem.*, 61, 243-257.
- Simoneit, B. R. T., M. Kobayashi, M. Mochida, K. Kawamura, M. Lee, H.-J. Lim, B. J. Turpin, and Y. Komazaki (2004), Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign, *J. Geophys. Res.*, 109, D19S10, doi:10.1029/2004JD004598.
- Streets, D. G., T. C. Bond, T. Lee, and C. Jang (2004), On the future of carbonaceous aerosol emissions, *J. Geophys. Res.*, 109, D24212, doi: 10.1029/2004JD004902.
- Tegen, I., and I. Fung (1996), Contribution to the atmospheric mineral aerosol load from land surface modification (1995), *J. Geophys. Res.*, 100(D9), 18, 707-18, 726.
- Tegen, I., Lacis, A. A and Fung, I (1996), The influence of climate forcing of mineral aerosols from disturbed soils, *Nature*, 380, 419-422.
- Twomey, s., 1974, Pollution and planetary albedo. *Atmospheric Environment*, 8, 1251-1256.
- Xu, W., and R. Zhang (2012), Theoretical investigation of interaction of dicarboxylic acids with common aerosol nucleation precursors, *J. Phys. Chem. A.*, 116, dx.doi.org/10.1021/jp301964u, 4539–4550.
- Wang H., K. Kawamura, K. F. Ho, and S. C. Lee (2006b), Low molecular weight dicarboxylic acids, ketoacids and dicarbonyls in the fine particles from a roadway tunnel: significant secondary production from the precursors in vehicular emissions, *Environ. Sci. Technol.*, 40, 6255-6260.

- Wang, H., K. Kawamura, and K. Yamazaki (2006a), Water soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the Southern Ocean and Western North Pacific, *J. Atmos. Chem.*, 53, 43-61.
- Wang, L., A.F. Khalizov, J. Zheng, W. Xu, V. Lal, Y. Ma, and R. Zhang (2010), Atmospheric nanoparticles formed from heterogeneous reactions of organics, *Nature Geosci.* 3, doi:10.1038/ngeo778, 238-242.
- Wang, Z. B., Hu, M., Yue, D. L., He, L. Y., Huang, X. F., Yang, Q., Zheng, J., Zhang, R. Y., and Zhang, Y. H.: New particle formation in the presence of a strong biomass burning episode at a downwind rural site in PRD, China, *Tellus*, 65,19965, doi:10.3402/tellusb.v65i0, 2013a.
- Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E., Tie, X., Molina, L., and M. Molina (2004), Atmospheric new particle formation enhanced by organic acids, *Science*, 304, (5676), 1487-1490.

Chapter 2: Seasonal Changes in Compositions of Low Molecular Weight Dicarboxylic Acids, Ketoacids, and α -Dicarbonyls and Fatty Acids in Ambient Aerosols Collected from Subtropical Okinawa Island, Japan, an Outflow Region of Asian Dusts

2.1. Introduction

Dicarboxylic acids are an important group of water-soluble organic compounds in the atmospheric aerosols [Grosjean et al., 1978; Kawamura and Ikushima, 1993; Rogge et al., 1993; Kawamura and Yasui, 2005]. Diacids, ketoacids and α -dicarbonyls have been reported in the tropospheric aerosols from urban [Grosjean et al., 1978; Kawamura and Yasui, 2005; Tran et al., 2000; Kerminen et al., 2000], rural [Limbeck et al., 2001; Legrand et al., 2007], marine [Kawamura and Sakaguchi, 1999; Mochida et al., 2003a, b; Kawamura et al., 2004; Wang et al., 2006; Rinaldi et al., 2011], Arctic [Kawamura et al., 1996a; Narukawa et al., 2003; Kerminen et al., 1999; Kawamura et al., 2005; Kawamura et al., 2010] and Antarctic regions [Kawamura et al., 1996b]. Total diacids account for about 1-3% of the particulate carbon in the urban areas and >10% in the marine atmosphere [Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1996; Kawamura and Sakaguchi, 1999; Kerminen et al., 2000].

Due to their water-soluble properties, dicarboxylic acids and related compounds have received much attention. They can act as cloud condensation nuclei (CCN) [Novakov and Penner, 1993; Saxena et al., 1995, Novakov et al., 1997] and thus contribute to the radiative balance on the Earth [Novakov and Penner, 1993]. Gierlus et al. [2012] reported an important effect of oxalic acid on CCN activity of mineral dust aerosol by laboratory experiment. Xu and Zhang [2012] reported that dicarboxylic acids can contribute to the aerosol nucleation process in the presence of sulphuric acid and ammonia and can interact with the trace nucleation species in the atmosphere [Xu et al., 2010]. Small organic acids may also have an adverse effect on human health [Highwood and Kinnersley, 2006].

Diacids and related compounds are produced from primary and secondary sources. The main primary sources of diacids are fossil fuel combustion [Ho et al., 2006], meat cooking

operation [Rogge et al., 1991; Schauer et al., 1999] and biomass burning [Yamasoe et al., 2000; Gao et al., 2003; Kundu et al., 2010a]. Their secondary sources include photo-induced oxidations of biogenic unsaturated fatty acids [Kawamura and Gagosian, 1987], aromatic hydrocarbons and cyclic olefins [Hatakeyama et al., 1987; Kawamura et al., 1996a] and biogenic volatile organic compounds (BVOCs) [Warneck 2003; Lim et al., 2005; Carlton et al., 2006]. Small diacids (C_2 - C_4) are produced by either photo-oxidation of aromatic hydrocarbons or direct emissions from fossil fuel combustion [Kawamura and Ikushima, 1993]. Further, oxalic acid is formed by the oxidation of glyoxylic acid that is photo-oxidation product of glyoxal, methylglyoxal, and pyruvic acid [Kawamura et al., 1996a; Ervens et al., 2004; Lim et al., 2005; Carlton et al., 2006; Rinaldi et al., 2011], whereas C_5 - C_6 diacids are produced by the oxidation of cyclic olefins [Kawamura et al., 1996a]. Recently Myriokefalitakis et al. [2011] reported that 79% of oxalate originates from biogenic isoprene via photochemical processes. The world coal consumption is highest in East Asia. Large amounts of low quality coal are used for house heating and cooking purposes. Diacids and related compounds are found in the remote marine sites in the East Asian-Pacific region, suggesting a long-range atmospheric transport of organic pollutants from East Asian countries to the North Pacific [Simoneit et al., 2004; Sato et al., 2009; Wang et al., 2009a,b].

Okinawa is the southernmost main island of Japan, situated on the outflow region of Central and South China. Cape Hedo is located on the northern edge of Okinawa and has been used as a supersite of Atmospheric Brown Clouds (ABC) project [Takami et al., 2007]. This site has been regarded as an ideal site to study the chemical processes (production, transformation and degradation) of organic aerosols in East Asia. At Cape Hedo, various studies have been conducted for inorganic ions [Jaffe et al., 2005], normal hydrocarbons, hopanes and polynuclear aromatic hydrocarbons (PAHs) [Sato et al., 2009; Wang et al., 2009b], trace gasses [Zhang et al., 2003], characteristics of organic aerosols [Lun et al., 2009], and stable hydrogen isotope ratios of n-alkanes [Yamamoto and Kawamura, 2011]. Studies of cloud condensation nuclei activity and hygroscopic growth were also conducted at Cape Hedo [Mochida et al., 2010]. However, there are no studies on dicarboxylic acids and related

compounds at this super site, although there are few such studies in the western North Pacific rim [Mochida et al., 2003a, 2003b; Kundu et al., 2010b].

2.2. Samples and Analytical Procedures

2.2.1. Site Description

Aerosol samples were collected at Cape Hedo Atmosphere and Aerosol Measurement Station (CHAAMS, 26° 87' N, 128° 2' E) located on the northwest coast of subtropical Okinawa Island. Figure 2.1 shows the map of Cape Hedo and Okinawa Island. Okinawa locates 1500 km south of Tokyo, 2000 km southeast of Beijing, 800 km east of Chinese coast, and 1000 km south of South Korea. Cape Hedo is surrounded by subtropical forest [Yamamoto and Kawamura, 2011]. It is situated on the outflow region of East Asia, especially China, but local anthropogenic activities are rare [Takami et al., 2007; Sato et al., 2009]. The northern Okinawa, where Cape Hedo locates, is mostly covered with subtropical rain forests, and there are no major industries [Yamamoto and Kawamura, 2011]. In the Asian Pacific region, the East Asian monsoon dominates in winter to spring, whereas the monsoon from the Pacific dominates in summer to fall [Sato et al., 2009], therefore, continental air masses from East Asian countries generally arrive over Okinawa during winter and spring.

2.2.2. Aerosol Sampling

Total suspended particles (TSP) were collected on weekly basis at CHAAMS station from 2009 October to 2010 October. Aerosol samples ($n = 50$) were collected using a high-volume air sampler (Kimoto AS-810B) and pre-combusted (450°C, 4 hours) quartz fiber filters (Pallflex 2500QAT-UP, 20×25 cm). The sampling periods were generally 7 days for each sample. Before and after sampling, sample filters were stored in a pre-combusted glass jar (150 mL) with a Teflon-lined screw cap. The sample filters were stored in darkness at -20°C in the freezer room of the Institute of Low Temperature Science (ILTS) until the analysis. Field blanks were also collected in the study area. Blank filter was put in filter cartilage in the sampler and pump was turn off. After 10 second, field blank from the filter cartilage was

removed from cartilage. Quartz fibre filters may adsorb organic vapours, causing positive artefacts on OC measurements. However, due to the relatively long period of sampling (one week), we consider that the artefacts may be minimum.

2.2.3. Chemical Analysis

Before analysis, TSP mass was measured gravimetrically at room temperature and 50% relative humidity. We analyzed the filter samples for water-soluble diacids, ketoacids, and α -dicarbonyls by the method reported previously [Kawamura and Ikushima, 1993; Kawamura et al., 1996a]. Briefly, aliquot of the filter was extracted with organic-free ultrapure water (10 ml $\times$ 3) under ultrasonication for 10 minutes. To remove insoluble particles and filter debris, the extracts were passed through glass column (Pasteur pipette) packed with quartz wool, pH-adjusted to 8.5-9.0 with 0.1 M KOH solution, and then concentrated to almost dryness using a rotary evaporator under vacuum. The extracts were reacted with 14% boron trifluoride (BF₃)/n-butanol at 100°C for 1 hour to derive carboxyl group to dibutyl ester and keto group to dibutoxy acetals. The derived esters and acetals were dissolved in n-hexane and then washed with pure water three times and extracted with n-hexane. The extracts were again concentrated using rotary evaporator under vacuum. After the dryness using nitrogen blow down, the derivatives were diluted with n-hexane (50 or 100 μ l) and determined using a capillary gas chromatograph (GC; HP 6890). By comparing GC retention times with authentic standards, the GC peaks were identified and confirmed by mass spectral examination using a GC/mass spectrometer (GC/MS) system.

Before real sample analysis, a test experiment was performed to check the recovery. Ten μ l of free C₂, C₃, C₄, C₅ and C₆ diacids in aqueous solution (1.03, 1.12, 1.46, 1.04, and 0.83 n moles/ μ l, respectively) were spiked on a pre-combusted quartz fiber filter. The spiked diacids were extracted and analyzed like a real sample. The recoveries for diacids were above 85% for C₂ and more than 90 % for C₃, C₄, C₅ and C₆. Recoveries were higher (87% for oxalic acid) when authentic standards were spiked to real aerosol filter sample [Kawamura and Yasui, 2005]. We evaluated the recovery of α -dicarbonyl (glyoxal) to be 91%. We also conducted

reproducibility test using three different parts of the same aerosol filter, which was collected on the rooftop of our institute building using a high volume air sampler. The analytical errors in the triplicate analysis were less than 2% for C₂ and C₃, 5% for C₄ and 1% for C₅ and C₆. We got small peaks of oxalic, malonic and glyoxylic acids in the field blank filters. However, the blank levels relative to real samples were less than 1% for C₂, less than 2% for C₃ and less than 5% for glyoxylic acid. Concentrations of all the species reported here are corrected for the field blanks.

The concentrations of OC and EC were measured using a Sunset Laboratory carbon analyzer following Integragency Monitoring Protected Visual Environments (IMPROVE) thermal/optical evolution protocol [Wang et al., 2005] and assuming that the carbonate carbon is negligible. A small filter punch (disk) having 1.4 cm in diameter was placed in quartz boat inside the thermal desorption chamber. In the chamber, stepwise heating was applied at first in helium flow and then, after the initial ramp, helium gas was switched to He/O₂. The evolved CO₂ during the oxidation at each temperature step was measured by a non-dispersive infrared (NDIR) detector system and the transmittance of light (red 660 nm) through the filter punch was used for setting up OC/EC split point and thereby OC correction. The analytical errors in duplicate analysis of the filter sample were less than 8% for OC and 5% for EC.

To measure WSOC, a filter disc (20 mm in diameter) was extracted with organic-free ultrapure water under ultrasonication for 15 minutes. The water extracts were passed through a syringe filter (Millex-GV, 0.45 µm, Millipore) and WSOC was measured using a Shimadzu carbon analyzer (TOC-V_{CSH}) [Miyazaki et al., 2011]. To determine major ions, a sample filter disc (20 mm in diameter) was extracted with organic-free ultrapure water (10 ml) under ultrasonication (15 min × 2 times). The extracts were filtered using a membrane disc filter (Millex-GV, 0.45 µm, Millipore). Cations and anions were determined by ion chromatograph (761 Compact IC, Metrohm, Switzerland). The field blank levels for WSOC and major ions were both less than 1% of real samples. Concentrations reported here are corrected for the blanks. The analytical errors for duplicate analysis were less than 2% for WSOC and 5% for major ions.

2.2.4. Backward Air Mass Trajectory Analysis

To find out the source regions of air masses over Cape Hedo, 5-day back trajectory analysis at 500 meter above was performed for every day during one year campaign using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (<http://www.arl.noaa.gov/ready/hysplit4.html>) NOAA Air Resources Laboratory, Silver Spring, Maryland, United States [Draxler and Hess, 1997, 1998]. Figure 2.2 shows the air mass trajectories drawn for every day for winter, spring, summer and autumn seasons. In spring and winter, our sampling site was strongly influenced by continental air masses. In contrast, in summer, the site was strongly covered by oceanic air masses whereas in autumn it was influenced by both oceanic and continental air masses. Because the sampling duration is 7 days, it is difficult to differentiate the origin of the air masses. Each sample contains either mixed continental or oceanic air masses. However, we confirmed that the continental air masses generally arrived from Russia, Mongolia, Northeast China, Korea and Japan to the sampling site based on 5 day backward air mass trajectory analysis.

2.3. Results

We found relatively high aerosol mass concentrations in spring with the highest value ($286 \mu\text{g m}^{-3}$) in March 2010. Generally the aerosol mass concentrations are below $125 \mu\text{g m}^{-3}$ throughout the year. Concentrations of OC in this study ranged from $0.76\text{--}7.12 \mu\text{g m}^{-3}$ (average, $1.74 \pm 1.03 \mu\text{g m}^{-3}$). The highest average value was found in spring ($2.36 \mu\text{g m}^{-3}$) followed by summer and winter whereas the lowest value was found in autumn ($1.42 \mu\text{g m}^{-3}$).

2.3.1. Molecular Distributions of Dicarboxylic Acids, Ketoacids and α -Dicarbonyls

We detected a homologous series of α,ω -dicarboxylic acids (oxalic, C2-dodecanoic, C₁₂), aromatic unsaturated diacids (phthalic, isophthalic, and terephthalic acids), aliphatic unsaturated diacids (maleic, fumaric and methyl maleic), branched chain diacids (methyl malonic, methyl succinic and methyl glutaric) and multifunctional dicarboxylic acids (malic, ketomalonic, and 4-ketopimelic). We also detected ketocarboxylic acids (C₂–C₉ ω -

oxocarboxylic acids and pyruvic acid), and α -dicarbonyls (glyoxal and methylglyoxal) in the aerosol samples. Oxalic acid (C_2) was found as the most abundant diacid species followed by malonic (C_3) and succinic (C_4) acids in autumn, spring, and winter. However, in most summer samples, azelaic acid (C_9), which is a specific oxidation product of unsaturated fatty acids [Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1987; Rogge et al., 1991; Stephanou and Stratigakis, 1993], became the third most abundant species following C_3 . It is of interest to note that in two summer samples C_9 was found as the second most abundant diacid following C_2 .

Table 2.1 presents concentration ranges and average concentrations of diacids, ketoacids and α -dicarbonyls detected in the aerosols from Cape Hedo as well as abbreviations of each compounds. Concentrations of total diacids ranged from 26 to 671 ng m^{-3} (average $\pm$ standard deviation, $246 \pm 150 \text{ ng m}^{-3}$) throughout one-year observation. Total diacids showed the highest concentration in spring (range: 208-533 ng m^{-3} , average: 344 ng m^{-3}) followed by winter (162 - 513 ng m^{-3} , 313 ng m^{-3}). Lower concentrations were found in summer (26-671 ng m^{-3} , 131 ng m^{-3}) and autumn (41-318 ng m^{-3} , 190 ng m^{-3}). Figure 2.3 shows seasonally averaged molecular distributions of diacids and related compounds in the Okinawa aerosols during the entire sampling period.

Concentrations of C_2 , the most abundant organic species, ranged from 17 to 496 ng m^{-3} with an average of 191 ng m^{-3} . Malonic (C_3) or glyoxylic (ωC_2) acid were found as the second most abundant species, followed by C_4 . Methylglyoxal (MeGly), phthalic acid (Ph), glyoxal (Gly), pyruvic acid (Pyr) were among the most abundant species after C_4 in winter whereas MeGly, Gly, Pyr, Ph, C_9 and glutaric acid (C_5) were abundant in spring. In contrast, C_9 , MeGly, Ph, 7-oxoheptanoic acid (ωC_7), Pyr, Gly became more abundant than C_5 in summer. Similarly MeGly, 4-oxobutanoic acid (ωC_4), Gly, Ph, Pyr, C_9 were abundant in autumn after C_4 (Figure 2.3). The concentrations of longer chain diacids decrease with an increase in the carbon chain length, except for C_9 and C_{11} . C_9 is the most abundant species in the range of C_7 - C_{12} diacids.

Figure 2.4 shows pie diagrams for the relative abundances of straight-chain C₂-C₁₀ diacids for all seasons. The relative abundances of C₂ in total diacids showed a maximum in winter (55-83%, average 80%) and minimum in summer (65-84%, 73%). In contrast, the highest relative abundances of C₃ (2.54-17.6%, 10.7%) and C₉ (1.13-7.30%, 4 %) were found in summer and the lowest values were in winter. Similarly, C₆ (0.35-1.64%, 0.9%), Ph (0.99-6.33%, 3%), and tPh (0.14-1.0%, 0.46%) showed the highest relative abundances in winter. Glutaric acid (C₅) showed the highest average relative abundance in autumn (Figure 2.4d). The abundances of branched chain diacids, i.e., methylmalonic (iC₄) and methylsuccinic (iC₅), relative to corresponding straight chain diacids became higher in autumn, although branched diacids are less abundant than the normal structures (Table 2.2).

Concentrations of total ketoacids ranged from 1.75-95 ng m⁻³ (average, 26 ng m⁻³). Although their concentrations varied from one season to another, ωC₂ was found as the most abundant ketoacid in all seasons. The concentrations of ωC₂ ranged from 0.76-65.6 ng m⁻³ (15.2 ng m⁻³). The highest concentration was found in spring (8.83-65.6 ng m⁻³, 21.3 ng m⁻³) and the lowest value in summer (0.76-46.7 ng m⁻³, 7.14 ng m⁻³). The second most abundant ketoacid was Pyr (0.23-17 ng m⁻³, 3.3 ng m⁻³). The distributions of ketoacids showed that ωC₂ and 9-oxononanoic acid (ωC₉) in total ketoacids maximized in autumn, whereas 3-oxopropanoic (ωC₃) and 4-oxobutanoic (ωC₄) acids peaked in summer. Concentrations of total α-dicarbonyls (Gly and MeGly) ranged from 0.38-54 ng m⁻³ (average, 13 ng m⁻³). α-Dicarbonyls were found to maximize in winter. However, their concentrations are significantly lower than those of diacids and ketoacids. We found that methylglyoxal is always more abundant than glyoxal.

2.3.2. Seasonal Variation of Diacids, Ketoacids and α-Dicarbonyls

Monthly averaged variations in the concentrations of total diacids, ketoacids and α-dicarbonyls in Okinawa aerosols are given in Figure 2.5. Total diacids show a peak in winter to spring although they slightly declined in February (Figure 2.5a), whereas ketoacids peaked in

January and April (Figure 2.5b). In contrast, α -dicarbonyls show maximum concentration in January with the second peak in April (Figure 2.5c).

Figure 2.6 presents monthly averaged concentrations of individual diacids. Although concentrations of diacids and related compounds are generally higher in winter and lower in summer, their seasonal variations are compound specific. Short-chain saturated diacids (C_2 - C_4) show maxima in winter to spring and minima in summer (Figures 2.6a-c) whereas long-chain diacids such as C_7 , C_8 and C_{10} show springtime maxima (Figures 2.6f-i). In contrast, C_9 maximized in summer (Figure 2.6h). Aromatic diacids such as Ph and tPh and aliphatic unsaturated diacids such as maleic (M), fumaric (F) and methylmaleic (mM) acids show winter maxima (Figure 2.6m-r), whereas isophthalic acid (iPh) shows spring maximum and summer minimum (Figure 2.6n). Branched chain diacids, i.e., iC_4 and iC_5 acids, are characterized by winter to spring maxima and methylglutaric (iC_6) are by wintertime maxima. Multifunctional diacids such as kC_3 and kC_7 showed maximum concentrations in spring whereas hydroxylsuccinic acid (hC_4) peaked in summer.

Monthly averaged concentrations of ketoacids and α -dicarbonyls are presented in Figure 7. Concentrations of Pyr, ωC_2 , ωC_3 , and ωC_4 acids showed maxima in spring and minima in summer (Figures 2.7a-d). Glyoxal (Gly) showed two peaks in January and April whereas MeGly maximized in January.

2.3.3. Correlation Coefficients among Selected Diacids and Related Compounds

Tables 2.3 to 2.6 show the results of correlation coefficients among diacids and related compounds for four seasons. In winter, C_2 is correlated with its precursor compounds such as C_3 ($r=0.83$), C_4 (0.68), and Gly (0.73) (Table 2.3). Although there is no direct correlation between C_2 and Pyr, we found a strong correlation between ωC_2 and its precursors such as Pyr (0.95) and Gly (0.95). In spring, similar correlations are found between C_2 and its precursors such as C_3 (0.91), C_4 (0.84), kC_3 (0.73), Pyr (0.70) and ωC_2 (0.72) (Table 2.4). A strong relation was also found between ωC_2 and Pyr (0.97). In summer, strong relationships were observed between C_2 and its precursors such as ωC_2 (0.99), C_3 (0.95), C_4 (0.86), kC_3 (0.96),

Pyr (0.98), MeGly (0.82) (Table 2.5). Similarly, a very strong relation was found between Pyr and ω C₂ (0.98) during summer. We also found a strong correlation between C₂ and its precursors in autumn (Table 2.6). However, the correlations for α -carbonyls were not so strong for some combinations of organic species (e.g., oxalic acid) for one-year data sets (data are not shown as a table).

2.3.4. Principal Component Analysis for Concentrations of Dicarboxylic Acids and Related Compounds

Principal component analysis (PCA) is a mathematical algorithm that reduces dimensionality of the data while retaining most of the variation in the data set. It accomplishes reduction by identifying directions, called principal components, along which the variation in the data is maximal. By using a few components, each sample can be represented by relatively few numbers instead of thousands of variables. Principal component analysis is a useful statistical tool for data analysis to find out the sources of aerosols. This method has been applied especially when sources of aerosols are different [Hopke, 1985; Kawamura and Sakaguchi, 1999; Mochida et al., 2003a]. In this study, the data sets of diacids over Okinawa (n=50) were subjected to principal component analysis to investigate their sources and possible formation pathways. The term “loading” in PCA represents the correlation coefficient between the component and individual species.

As seen in Table 2.7, we found three components in winter, two components in spring, two components in summer, and three components in autumn for Okinawa aerosols. In winter, the high loadings of C₂ to C₅, M, C₉, and ω C₂ were found in Component 1, whereas C₇, C₈ and Gly showed high loadings in Component 2. The high loadings of C₁₀, Ph and ω C₂ were found in Component 3. These results indicate that the winter aerosols of Cape Hedo are influenced by anthropogenic sources because Components 1 and 3 may be mainly associated with anthropogenic sources whereas Component 2 may be associated with photo-oxidation of unsaturated fatty acids. Unsaturated fatty acids can also be emitted from meat cooking

operation and wood burning [Rogge et al., 1993; Rogge et al., 1998]. Small diacids and Ph are formed from the photo-oxidation of aromatic hydrocarbons and PAHs.

During spring, the high loadings of C₂, C₃, C₄, C₅, and C₆ and negative loading of C₉ (biogenic tracer) were found in Component 1, suggesting the influence of anthropogenic emissions because C₂ to C₆ are formed from the oxidation of aromatic hydrocarbons such as toluene, benzene and cyclic olefins followed by photo-oxidation [Kawamura et al., 1996a]. Component 1 also has a high loading with C₁₀, M, Ph and ω C₂, indicating an intensive photo-oxidation from aromatic hydrocarbons because Ph is formed by the oxidation of PAHs and ω C₂ is the intermediate oxidation product of aromatic hydrocarbons. Component 2 in spring shows high loadings with C₇, C₈ and C₉, which are formed by photo-oxidation of unsaturated fatty acids that are present in terrestrial plant leaves and also emitted from the ocean via phytoplankton. Spring is a growing season for terrestrial higher plants and phytoplankton, the latter is known as spring bloom. Hence, unsaturated fatty acids are more emitted from both lands and ocean to the atmosphere in spring.

During summer, C₂ to C₁₀ diacids have highest loadings in Component 1, suggesting that the biogenic origins from the oceans. Potential sources for these compounds include unsaturated fatty acids [Kawamura et al., 1996a; Kawamura and Sakaguchi, 1999], isoprene [Lim et al., 2005], ethene and acetylene [Lim et al., 2005; Crahan et al., 2004]. The highest loadings with Ph, M, and ω C₂ in Component 1 suggest an important contribution from biogenic sources followed by photo-oxidation because ω C₂ is also an oxidation product of isoprene and other BVOCs and Ph has dual origin; one from anthropogenic activities and the other from natural sources. Ph can be produced by the oxidation of biogenic phenolic compounds [Kawamura and Sakaguchi, 1999; Kawamura et al., 1996b], which are present in sea surface slicks [Carlson, 1982] and emitted to the atmosphere. Hence, the high loading of Ph in Component 1 may suggest that its precursors are emitted from ocean surface. In contrast, high loading of Gly in Component 2 suggests a significant contribution of photochemical oxidation of marine-derived compounds because Gly is the intermediate in the oxidation of volatile organic compounds.

In autumn, C₂, C₃, C₄, C₇, C₈, M and ω C₂ showed high loadings with Component 1, suggesting that their precursors are associated with anthropogenic sources followed by oxidation except for C₇ and C₈ because short chain diacids and ω C₂ are oxidized from various anthropogenic organic compounds as stated above. Currently, we cannot explain the high loadings of C₇ and C₈ in Component 1. C₅ and C₆ diacids correlate with Component 2, suggesting that they are emitted either from anthropogenic or biogenic sources [Kawamura and Sakaguchi, 1999]. Component 3 has a high loading with Ph, which may indicate an anthropogenic input.

2.3.5. Molecular Compositions of n-Alkanoic and Alkenoic Acids

A homologous series of straight chain fatty acids (C_{14:0}-C_{24:0}) including unsaturated fatty acid (C_{18:1}) were detected in the Okinawa aerosols (see Table 2.8). Figure 2.8 shows the seasonally averaged molecular composition of fatty acids. Their distribution is generally characterized by the even carbon number predominance with a peak at palmitic acid (C_{16:0}) followed by stearic (C_{18:0}) or oleic (C_{18:1}) acid. C_{16:0} and C_{18:0} acids showed peaks in summer. In contrast, longer chain fatty acids (C₂₀, C₂₂, and C₂₄), which are specific to terrestrial higher plants [Kawamura et al., 2003], maximized in spring. The concentration of total fatty acids ranged from 1.1-23.3 ng m⁻³ (average, 8.1 ± 7.3 ng m⁻³). The carbon preference index (CPI) was calculated with homologous series of fatty acids (C_{14:0} to C_{24:0}) as Σ even carbon numbered fatty acids / Σ odd carbon numbered fatty acids [Zheng et al., 2000; Ho et al., 2011]. We found the highest CPI value during summer (average, 49) and the lowest value (average, 18) during winter.

2.4. Discussions

2.4.1 Sources of TSP

The higher concentrations of TSP during spring are caused by the westerly winds via the uplift of the mineral dusts from the arid regions in China and Mongolia and the transport to the Pacific. The outflow of Asian dust from East Asia including arid region of China and

Mongolia is common in spring. Crustal elements like calcium, iron, aluminium, barium, etc. are abundant in Asian dusts and loess deposits [Nishikawa et al., 2000; Mori et al., 2002]. Very high aerosol mass concentrations ($> 400 \mu\text{g m}^{-3}$) were also found in Gosan site, Jeju Island during spring 2002 [Kawamura et al., 2004]. Mori et al. [2003] and Duncan et al. [2007] reported elevated levels of Asian dust in Okinawa in spring by long-range atmospheric transport. We found a strong correlation between Ca^{2+} and TSP ($r=0.81$) in spring, suggesting that spring aerosols are significantly influenced by dust particles. A similar positive correlation was observed in summer (0.91). However, no statistically important relation was found between Ca^{2+} and TSP in winter and autumn. To find out the source region, we further analysed the air mass back trajectories, which demonstrated that the air masses in spring mostly originated from the arid regions in China and Mongolia (see Fig. 2.2). In contrast, in summer most of the air masses originated from the Pacific Ocean.

2.4.2. Concentration Ratios of Diacids and Related Compounds: Possible Sources and Formation Mechanisms

Many studies have been conducted to interpret the production mechanisms of C_2 , C_3 and C_4 from long-chain diacids [Kawamura and Ikushima, 1993; Carlton et al 2006; Legrand et al., 2007; Charbouillot et al., 2012]. These organic acids have been proposed to associate with atmospheric chain reactions during the production of diacids. Hence, concentration ratios of $\text{C}_2/\omega\text{C}_2$, C_2/Pyr , C_2/Gly , C_2/C_4 , C_2/C_3 and C_3/C_4 could be used as indicators of secondary production of oxalic acid. The C_2/Gly and $\omega\text{C}_2/\text{Gly}$ ratios show maxima in spring (Figure 2.9f,g). C_3/C_4 ratios show a small peak in February with a large peak in August (Figure 2.9d). In contrast, $\text{C}_2/\omega\text{C}_2$ ratios increase from winter to spring and stay high in summer although a drop was observed in April (Figure 2.9h). These results suggest a production of oxalic acid by the oxidation of its precursors such as glyoxylic acid, pyruvic acid and glyoxal in spring.

Both Ph and C_6 are primarily derived from the incomplete combustion of aromatic hydrocarbons (e.g., naphthalene) and cyclic olefins such as cyclohexene, respectively; both are emitted as vehicular exhaust [Kawamura et al., 1996a]. In contrast, C_9 is a specific oxidation

product of biogenic unsaturated fatty acids as stated above. Hence, Ph/C₉ and C₆/C₉ have been used as tracers to better discuss anthropogenic versus biogenic emissions [e.g., Kawamura and Yasui, 2005]. The highest C₆/C₉ ratio was found in winter (average 1.5) followed by spring (0.61). The averaged ratio in spring (0.61) is higher than in summer (0.1). The average Ph/C₉ and C₆/C₉ ratios (Figure 2.9a,b) were highest in winter followed by spring, suggesting that Cape Hedo is strongly influenced by the anthropogenic sources during winter than spring. Seasonal variations of Ph/C₉ show a similar trend with C₆/C₉ ratios, again suggesting that the long-range transport of organic pollutants is enhanced in winter. In contrast, the lowest C₆/C₉ and Ph/C₉ ratios in summer indicate a decreased anthropogenic sources and/or an enhanced biogenic input from the ocean. The medium ratios of Ph/C₉ and C₆/C₉ were obtained in spring, suggesting that the aerosols are of both biogenic and anthropogenic origin. The biogenic emissions from terrestrial higher plants are active during the growing season in East Asia.

2.4.3. Possible Sources of Oxalic and Glyoxylic Acids

The predominance of C₂ has been reported in many aerosol samples collected from urban [Kawamura and Ikushima, 1993; Miyazaki et al., 2007, Pavuluri et al., 2010], remote marine [Kawamura and Sakaguchi, 1999; Mochida et al., 2003a, 2003b, Kundu et al., 2010b], and background sites in Africa [Limbeck et al., 2001; Mkoma and Kawamura, 2013]. In contrast, C₄ was the most abundant species in summertime Antarctic aerosols [Kawamura et al., 1996b] and ice core samples from Greenland [Kawamura et al., 2001]. Jung et al. [2010] reported that tPh acid, a tracer of plastic burning, was the most abundant species in the urban aerosols from Ulaanbaatar, Mongolia. The highest concentration of diacids at Cape Hedo was found in spring followed by winter, suggesting the more formation of diacids in spring and winter. The lowest concentration was observed in summer probably due to a significant influence of the clean air masses from the Pacific. The higher relative abundances of C₂ in winter (Figure 2.4a) suggest an enhanced photochemical ageing of organic aerosols during long-range atmospheric transport from the Asian Continent although the ambient temperature in inland China is very low (e.g., -14°C) in winter [Ho et al., 2007].

The highest relative abundance of C₉ in summer (Figure 2.4c) indicates that Okinawa Island is heavily affected by biogenic emissions from the ocean surface. In contrast, the highest relative abundances of C₆ and aromatic diacids (Ph and tPh) in winter (Figure 2.4a and Table 2.1) suggest a significant anthropogenic contribution in winter. These aromatic diacids are derived from combustion sources [Koebel and Elsener, 1998] and/or atmospheric photochemical degradation of PAHs [Kawamura and Ikushima, 1993]. Because the local anthropogenic emission is insignificant in our sampling site as stated above, these aromatic acids are originated from large cities in East Asia. In fact, large amounts of PAHs were reported in Chinese megacities during winter season [Wang et al., 2006].

Glyoxylic acid (ω C₂) was found as the most abundant ketoacid followed by pyruvic acid in the Okinawa aerosols. The predominance of ω C₂ was also found in other samples from many geographical locations such as Mongolia [Jung et al., 2010], urban megacities in China [Ho et al., 2007], Jeju Island in the East China Sea [Kundu et al., 2010b], the southern Ocean [Wang et al., 2005], the western Pacific [Sempéré and Kawamura, 2003], Chennai, India [Pavuluri et al., 2010], New Delhi, India [Miyazaki et al., 2009], Sapporo, Japan [Aggarwal and Kawamura, 2008], Arctic [Kawamura et al., 2010] and Antarctic regions [Kawamura et al., 1996b]. ω C₂ has been proposed as one of the major precursors of oxalic acid [Kawamura et al., 1996a; Warneck, 2003]. The highest concentration of ω C₂ in spring may be in part due to the emission of isoprene from the local forests because ω C₂ is the intermediate oxidation product of isoprene to C₂ [Legrand et al., 2007]. Tambunan et al. [2006] reported that the Moraceae family including the genus *Ficus* is very common in the Okinawa forests and emits isoprene at higher rates than other plant families. Similarly, the highest relative abundances of ω C₃, ω C₄ were found in summer, suggesting that they are formed by the oxidation of unsaturated fatty acids containing a double bond at C-3 or C-4 position.

α -Dicarbonyls showed the highest concentration in winter. The photochemical degradation of α -dicarbonyls may be restricted in winter. In contrast, photochemical oxidation of α -dicarbonyls is probably enhanced under the conditions of higher temperature and stronger solar radiation. Gly and MeGly are gas-phase oxidation products of VOCs such as benzene,

toluene, xylene [Birdsall et al., 2011; Bandow et al., 1985; Volkamer et al., 2001, 2006], isoprene [Zimmermann and Poppe, 1996], ethylene [Ervens et al., 2004], terpene [Fick et al., 2004], acetylene, ethene [Warneck, 2003], and naphthalene and alkylnaphthalenes [Wang et al., 2007 and Chan et al., 2009]. The α -dicarbonyls can be further oxidized to final product, i.e., oxalic acid. Gly and MeGly exist as dimer in aerosols [Krizner et al., 2009]. They can be found in cloud water and are expected to remain largely in the aerosol phase when cloud droplets evaporate or non-volatile oligomers are formed during the evaporation process [Hasting et al., 2005; Loeffler et al., 2006]. Gly shows hydration and self-oligomerization in the presence of acid and higher relative humidity [Zhang et al., 2012]. These oligomers can be rapidly decomposed to Gly during the analytical procedure (BF_3 /n-butanol treatment) and then derivatized to dibutoxy acetals that are less volatile than glyoxal.

2.4.4. Seasonal Changes in Molecular Compositions and Photochemical Processing

The concentrations of short-chain saturated diacids (C_2 - C_4) showed the winter to spring maxima (see Figure 2.6), suggesting a significant production of these diacids during late winter to spring. In contrast, long-chain diacids such as C_7 , C_8 and C_{10} show springtime maxima in April or May. The spring maxima may be caused by the enhanced emissions of their precursors (unsaturated fatty acids) from terrestrial vegetation followed by the subsequent oxidation in the atmosphere. However, C_9 did not show a maximum in spring, but maximized in June (Figure 6h). This difference between C_9 and other long-chain diacids may indicate that the source of C_7 , C_8 and C_{10} is different from that of C_9 . Unsaturated fatty acids are enriched in sea surface micro layers due to phytoplankton activity and emitted to the atmosphere followed by photochemical oxidation to result in C_9 [Kawamura and Gogosian, 1987]. Hence, C_9 may be formed from marine-derived unsaturated fatty acids via photochemical processing in summer.

Fatty acids including unsaturated structure are major lipid components of marine organic matter, which are abundant in micro layers of seawater surface [Marty et al., 1979] and are abundantly emitted to the atmosphere by bubble bursting process in summer. In fact, 9-oxononanoic acid (ωC_9) is the intermediate precursor of C_9 via the oxidation of oleic acid.

Thus, the photochemical oxidation of ω C₉ is enhanced in summer and more C₉ is produced. Hence, the concentrations of ω C₉ become lower in summer and higher in winter. In summer, a maritime high-pressure system dominates over the Pacific where the air mass is less influenced by the continental outflow from Asia. On the other hand, the highly polluted air masses are transported from East Asian countries to the Pacific by northeast Asian monsoon in winter [Sato et al., 2009]. The large variations of diacid concentrations found in autumn, winter and spring, may be caused by the frequent passages of low- and high-pressure systems, which are also associated with changes in air mass origins and the extent of wet scavenging of aerosols from the atmosphere. In contrast, the maritime high-pressure system dominates in the western North Pacific in summer, leading to the smaller variability of diacid concentrations.

Kawamura et al. [1996a] proposed the production scheme of ketoacids, that is, ω C₂, ω C₃ and ω C₄ are formed by the oxidation of unsaturated fatty acids. These intermediate compounds also can act as the precursors of C₂, C₃, and C₄ diacids via the oxidation of aldehyde group, respectively. It is interesting to note that the seasonal variations (springtime maxima) of these ketoacids are similar with the diacids having same carbon numbers, suggesting that they have same or similar sources probably from biogenic origin in spring.

Gly and MeGly are gas phase oxidation products of VOCs and they can act as precursors for secondary organic aerosol (SOA) formation via heterogeneous processes [Kroll et al., 2005; Liggio et al., 2005]. Gly and MeGly exist in both gaseous phase and particulate phase depending on atmospheric conditions. High abundances of MeGly and Gly in winter aerosols from Cape Hedo can be explained by long-range atmospheric transport of polluted air masses originated in Asian megacities via fossil fuel combustion and photochemical oxidation of aromatic hydrocarbons.

Correlation analysis is a powerful tool for determining the sources and transformation process of diacids and related compounds. Oxalic acid is accumulated in atmospheric aerosols as a result of direct emissions from anthropogenic sources and atmospheric secondary oxidation of various precursors. Kawamura and Ikushima [1993] proposed that C₂ could be formed by the oxidation of C₃ via ketomalonic acid (kC₃). Similarly, C₃ can be formed from C₄

via malic acid (hC_4), whereas C_4 and longer-chain diacids are the oxidation products of biogenic unsaturated fatty acids [Kawamura and Gagosian, 1987]. Hence, it is reasonable to consider that good correlation between oxalic acid and its precursor compounds would imply that the formation of C_2 is involved with photochemical oxidation processes in the atmosphere. C_2 can be produced by the oxidation of Gly, MeGly and Pyr [Kawamura et al., 1996a]. They have been considered as precursors of C_2 through ωC_2 in aqueous phase reaction [Lim et al., 2005; Carlton et al., 2006].

In winter, strong and good correlation of C_2 with its precursors such as C_3 , C_4 , and Gly were obtained (Table 2.3), suggesting the secondary formation of C_2 from aromatic hydrocarbon including benzene, toluene and PAHs. In spring, similar correlations were found between C_2 and its precursors (C_3 , C_4 , kC_3 , Pyr and ωC_2) as well as a very strong relation between ωC_2 and Pyr ($r=0.97$) (Table 2.4). These results suggest that there is a chain reaction to produce small diacids. In summer, strong correlations were found between C_2 and its precursor compounds (ωC_2 , C_3 , C_4 , kC_3 , Pyr and MeGly) (Table 2.5). Similarly, very strong correlations (0.82-0.99) were obtained between Pyr and ωC_2 . These results suggest that C_2 may be formed through gas phase oxidation of BVOCs such as isoprene followed by further oxidation in aqueous (aerosol) phase. Both terrestrial and marine emissions of isoprene are significant in summer in and around Okinawa. We found a strong correlation between C_2 and its precursors in autumn (Table 2.6). From the above discussion, we can further conclude that production of SOA is more significant than the primary emissions in our sampling site during the whole period.

To better understand the sources of organic aerosols and their atmospheric processes, we further analyze a correlation between concentrations of diacids and EC. EC is a tracer of primary anthropogenic emission from fossil fuel combustion [Jung et al., 2010]. We found good correlation between total diacids and EC with the highest correlation coefficient ($r=0.70$) in winter (see Figure 2.10). However, the least correlations were found in autumn (0.62) and summer (0.61). The good correlation between total diacids and EC in winter, suggests that they have similar sources. No statistically significant correlation was found between Na^+ and diacids

in all seasons even in summer, although all the summer air masses originated from the Pacific. This result suggests that diacids are not directly emitted from the ocean. Na^+ is primarily emitted from the ocean as sea salt, but direct contribution of diacids from the ocean is not important although seawater contains oxalic and other diacids [Tedetti et al., 2006]. Diacids may be largely formed through secondary oxidation processes during whole seasons. However, primary emission from fossil fuel combustion is somehow important especially in East Asian megacities in winter and spring and the emission products are long-range transported to the western North Pacific via the atmosphere.

Unsaturated aliphatic diacids, i.e., maleic (M, *cis*-), fumaric (F, *trans*-) and methylmaleic (mM) acids, are proposed as photochemical oxidation products of aromatic hydrocarbons such as benzene and toluene [Kawamura et al., 1996a]. Bandow et al. [1985] have shown the formation of maleic anhydride from the oxidation of benzene and toluene. M may be further converted to F by photo-induced isomerisation [Kawamura and Ikushima, 1993]. The F/M ratios at Cape Hedo maximized in summer (3.3) followed by autumn (1.6), spring (1.19) and winter (1.16). The F/M ratios show on average the highest value in August (Figure 2.9c), suggesting that the isomerisation reaction more proceeds under higher solar radiation and temperature. *Cis* to *trans* isomerisation reaction has been reported to occur in the aerosols from urban Tokyo in summer [Kawamura and Ikushima, 1993], Gosan site, Jeju Island [Kundu et al., 2010b] and Chichi-jima Island [Mochida et al., 2003a].

The strong C_3/C_4 peak in August (Figure 2.9d) suggests an enhanced oxidation of C_4 to C_3 during long-range atmospheric transport under higher temperature and solar radiations. Meanwhile the second peak in February may be caused by scattered concentrations of C_4 (Fig. 2.6c). Summertime maximum of C_3/C_4 ratios has been reported in urban Tokyo [Kawamura and Ikushima, 1993] and Chichijima [Mochida et al., 2003a]. The highest ratios of C_2/Gly (Figure 2.9f) and $\omega\text{C}_2/\text{Gly}$ (Figure 2.9g) were found in spring, indicating a significant photochemical production of C_2 and ωC_2 from Gly. In contrast, we found that $\text{C}_2/\omega\text{C}_2$ (Figure 2.9h) ratios increased from winter to spring and stayed high in summer although a small drop

was observed in April. This result suggests more production of C_2 from ωC_2 in summer probably via aqueous aerosol phase reaction.

2.4.5. Contributions of Diacids and Related Compounds to TSP, OC, TC and WSOC

We found that total diacids comprised 0.06-1.6% (average 0.40%) of total suspended particle (TSP). Figure 2.11 shows the monthly averaged variation of diacids to TSP (%). The highest ratio was obtained in January. Based on seasonal average of total diacids/TSP ratios, we found the highest (0.47%) in winter and the lowest ratio (0.06%) in summer. The higher loading of diacids in winter is probably due to biofuel burning and fossil fuel combustion in East Asia followed by long-range transport. Total diacids comprised 0.9-20.6% (average 5.8%) of OC and 2.2- 22.9% (average 8.17%) of WSOC. The highest average values were found in spring whereas lowest values were found in summer for both diacid-C to OC (spring 7.9%, winter 6.2%, autumn 5.8%, summer 3.4%) and diacid-C to WSOC (spring 10.1, winter 8.4%, autumn 8.8%, and summer 5.3%).

Total diacid-C/TC ratios, where TC means OC + EC, ranged from 1.03-12.8% (average 5.4%) (Figure 12a). The average ratio is highest in spring (7.3%) and lowest in summer (3.3%). The springtime maximum suggests an important formation of diacids in spring. Spring maximum was observed for normal saturated diacids (i.e., C_2 , C_3 , C_4 , C_7 , C_8 , and C_{10}) (Figures 2.12b-d, 2.12g-h and 2.12j). In contrast, C_6 showed a peak in December and decreased towards January with a slight increase in March (Figure 2.12f). C_9 showed a gradual increase from January toward summer with a peak in July (Figure 2.12i) due to the enhanced formation from biological activities. Ph peaked in December and gradually decreased toward April (Figure 2.12n), suggesting a direct emission from fossil fuel combustions and secondary formation from PAHs. tPh-C/TC ratios (Figure 2.12p) stayed high in December to March, suggesting an enhanced plastic burning that is very common in Mongolia and China in winter [Jung et al., 2010]. Unsaturated aliphatic diacids showed a broad peak in March (Figures 2.12q and 2.12s), except for M, which also showed a peak in August (Figure 2.12r), suggesting a photo-induced *cis-to-trans* isomerisation under strong UV radiation. Branched chain diacids (except for iC_6)

and multi-functional diacids also showed maxima in spring (Figures 2.12k,l,t), further supporting a significant oxidation of aromatic hydrocarbon. Similar seasonal variations were also observed for diacid-C/WSOC (not shown as a figure).

Figure 2.13 shows seasonal variations in the contributions of ketoacids and α -dicarbonyls to TC (%). Total ketoacid-C/TC and dicarbonyl-C/TC ratios ranged from 0.02-0.82% (average 0.19%) and 0.005-0.35% (0.10%), respectively. The contributions of individual ketoacids to TC were found to maximize in spring (e.g., ω C₄), except for ω C₉ that showed a peak in February. The seasonal variations of ketoacid-C/WSOC showed maxima in winter whereas α -dicarbonyl-C/WSOC showed winter and spring peaks (not shown as a figure).

To better understand the sources and transformation processes, we performed correlation analyses for the concentrations of total diacids, ketoacid and α -dicarbonyls, and the ratios (%) of total diacid-C/TC, ketoacid-C/TC, and α -dicarbonyl-C/TC. Total concentrations of the compound classes show strong and fair correlations (e.g., $r = 0.93$ for total diacids versus total ketoacids and $r = 0.50$ for total diacids versus total α -dicarbonyls), and their contribution to aerosol total carbon (TC) also show strong and good correlations (e.g., $r = 0.92$ for total diacid-C/TC versus total ketoacid-C/TC and $r = 0.75$ for total diacid-C/TC versus total α -dicarbonyl-C/TC). The correlation analysis suggests that these organic compounds are originated from the similar sources and/or similar formation pathways [Wang et al., 2006a].

The average ratio of total diacid-C/TC (5.4%) in this study (Figure 2.12a) is 3 times higher than that (1.8%) reported over the southern Ocean [Wang et al., 2006a] but slightly lower than that (7%) of the western Pacific [Wang et al., 2006a]. The average contribution of diacids to TC (5.4%) in our sampling site is much lower than that (8.8%) reported in remote marine aerosols including tropics [Kawamura and Sakaguchi, 1999]. However, our average value is higher than those reported in the aerosol samples from the western Pacific (3.2%) [Sempéré and Kawamura, 2003], Arctic (4%) [Kawamura et al., 2010], Sapporo (1.8%) [Aggrawal and Kawamura, 2008], Chennai (1.6%) [Pavuluri et al., 2010], Tokyo (0.95%) [Kawamura and Ikushima, 1993], and Mongolia (0.6%) [Jung et al., 2010]. These comparison

may indicate that photochemical production of diacids in the Cape Hedo aerosols is more significant than the aerosols from the Southern Ocean, the Arctic, Sapporo, Chennai, Tokyo, and Mongolia, but less significant than remote marine aerosols including tropics.

Unsaturated diacids (M, F and mM) are formed by the photochemical oxidation of aromatic hydrocarbons such as benzene and toluene as stated above. The broad peak of unsaturated aliphatic diacid-C/TC ratios (%) for M and mM was detected in March, whereas a sharp peak of F was obtained in August, again suggesting a photo-induced *cis-to-trans* isomerisation under strong UV radiation. The highest ratios (%) of branched chain diacid-C/TC and multi-functional diacid-C/TC were observed in spring, further supporting the significant oxidation of aromatic hydrocarbon during long-range atmospheric transport.

2.4.6. Comparison of Distributions of Diacids and Related Compounds in Okinawa with East Asia and the Pacific Ocean

To better understand the atmospheric processes during the long-range transport, concentrations of diacids from Cape Hedo, Okinawa are compared with those reported in East Asian countries and the Pacific Rim. Although there are few studies on diacids and related compounds for four seasons, we compare our results with the available data sets from East Asia and the western Pacific. Figure 2.14 shows geographical distributions of diacids, ketoacids and α -dicarbonyls in aerosols collected in East Asian cities and coastal and remote marine sites from remote islands, and in the Pacific during oceanic cruises.

The concentrations of total diacids observed in Okinawa (26 - 671 ng m⁻³, average 246 ng m⁻³) are about 2 folds less than those reported in Mongolia [Jung et al., 2010], 3.5 folds less than 14 Chinese cities [Ho et al., 2007], 3.4 folds less than the East China Sea [Mochida et al., 2003b], 2.6 folds less than Gosan, Jeju Island [Kawamura et al., 2004; Kundu et al., 2010b], and 4.8 folds less than the Sea of Japan [Mochida et al., 2003b]. On the other hand, the concentration of total diacids from Okinawa is 1.7 times higher than that of aerosol samples from remote Chichi-jima Island [Mochida et al., 2003a], which is located about 1000 km east of our sampling site. The average concentration is 4 times higher than that of the western North

to Central Pacific [Kawamura and Sakaguchi, 1999] and 6.4 times higher than the western Pacific including the areas of the Southern Hemisphere (35N°-50S°) [Wang et al., 2006]. The average concentrations of diacids, ketoacids and α -dicarbonyls show a decrease with increasing distance from the continent (Figure 2.14).

We compare the C_3/C_4 ratios in the Okinawa aerosols with those from different locations to discuss the photochemical ageing of organic aerosols during the transport of the Asian out flow over the Pacific. The average C_3/C_4 ratio (3.3) obtained at Cape Hedo is higher than those (0.56-2.9, average 1.6) obtained in urban Tokyo [Kawamura and Ikushima, 1993], but lower than those (1-11, 5) from the Pacific including tropics [Kawamura and Sakaguchi, 1999]. The C_3/C_4 ratios in our sampling site are much higher than Mongolia (winter average, 0.2) [Jung et al., 2010], Chinese cities (average, 0.86 in summer and 0.61 in winter) [Ho et al., 2007] and Gosan (autumn 1.3, winter 1.3, spring 1.2, summer 2.6) [Kundu et al., 2010b]. These comparisons further support that as the distance from the continent increases, photochemical oxidation of C_4 occurs to results in more C_3 in the atmosphere.

2.5. Summary and Conclusions

A homologous series of α , ω -dicarboxylic acids (C_2 - C_{12}), ketocarboxylic acids (ωC_2 - ωC_9 and Pyr), aromatic diacids (phthalic, isophthalic, and terephthalic acids), and α -dicarbonyls (glyoxal and methylglyoxal), as well as fatty acids, were studied in aerosol samples collected in Okinawa Island in 2009 to 2010 to better understand their seasonal distributions. The results are discussed in terms of photochemical processing of organic aerosols and also biogenic versus anthropogenic sources. Oxalic acid (C_2) was found as the most abundant diacid species followed by malonic (C_3) and succinic (C_4) acid in all seasons. The seasonal variation of C_2 , C_3 and C_4 showed winter to spring maxima. The summertime maximum ratios of C_3/C_4 and fumaric to maleic acid were due to photochemical processing of diacids during warmer season. Enhanced phthalic to C_9 (Ph/ C_9) and C_6/C_9 ratios were observed in winter due to an important anthropogenic emissions followed by long-range atmospheric transport from East Asian megacities. The declined Ph/ C_9 and C_6/C_9 ratios and increased $C_{18:1}$ concentration in

summer demonstrates a significant contribution of oceanic organic matter to the Okinawa aerosols in warm season. The increased C_3/C_4 ratio and strong correlations of C_2 to its precursors indicate that photochemical processing of organic aerosols is significant in summer.

Averaged total diacid-C/TC ratio (5.4%) in the Okinawa aerosols was found to be much higher than the values (<2%) reported in urban aerosols from Japan and China, but lower than that (8.8%) reported in the remote marine aerosols from the western Pacific including tropics. These comparisons explain that Okinawa aerosols are photochemically much more aged than urban aerosols, but less aged than the remote marine aerosols in the open ocean. Total diacids accounted for on average 5.8% of OC and 8.2% of WSOC in the aerosols from Okinawa. The relatively high ratios demonstrate that the organic aerosols from the western Pacific Rim are enriched with water-soluble organic acids as a result of photochemical aging during long-range atmospheric transport in the outflow region of East Asia. Finally, although the aerosol concentrations of diacids from Okinawa were several time lower than those from Gosan site, Jeju Island, South Korea, detailed analyses of molecular compositions (e.g., C_3/C_4 ratios) demonstrated that the Okinawa aerosols are photochemically more aged than the Gosan aerosols due to the longer distance from the source regions in East Asia and higher ambient temperature and solar radiation because Okinawa is located in subtropical region.

References

- Aggarwal, S. G., and K. Kawamura (2008), Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: Implications for photochemical aging during long-range atmospheric transport, *J. Geophys. Res.*, 113, D14301, doi: 10.1029/2007JD009365.
- Bandow, H., N. Washida, and H. Akimoto (1985), Ring cleavage reactions of aromatic hydrocarbons studied by FT-IR spectroscopy: I. Photooxidation of toluene and benzene in the NO_x-air system, *Bull. Chem. Soc. Jpn.*, 58, 2531-2540.
- Birdsall, A.W. and Matthew J. Elrod (2011), Comprehensive NO-dependent study of the products of the oxidation of atmospherically relevant aromatic compounds *The J. of Phys. Chem.*, 115, 5397–5407.
- Carlson, D. J. (1982), Surface microlayer phenolic enrichments indicate sea surface slicks, *Nature*, 296, 426-429, doi:10.1038/296426a0.
- Carlton, A. G., B. J. Turpin, H.-J. Lim, K. E. Altieri, and S. Seitzinger (2006), Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, *Geophys. Res. Lett.*, 33, L06822, doi: 10.1029/2005GL025374.
- Chan, A.W. H., K. E. Kautzman, P. S. Chhabra, J. D. Surratt, M. N. Chan, J. D. Crounse, A. Kurten, P. O. Wennberg, R. C. Flagan, and J. H. Seinfeld (2009), Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs), *Atmos. Chem. Phys.*, 9, 3049-3060.
- Charbouillot, T., Gorini, S., Vyard, G., Parazols, M., Brigante, M., Deguillaume, L., Delort, A. M. and Mailhot, G.: Mechanism of carboxylic acid photooxidation in atmospheric aqueous phase: Formation, fate and reactivity, *Atmos Environ*, 56, 1-8, 2012.
- Cooke, W. F., C. Liousse, H. Cachier and J. Feichter (1999), Construction of a 1° x 1° fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model, *J. Geophys. Res.*, 104, 22137-22162.

- Crahan, K. K., D. Hegg, D. S. Covert, and H. Jonsson (2004), An exploration of aqueous oxalic acid production in the coastal marine atmosphere, *Atmos. Environ.*, 38, 3757–3764.
- Draxler, R. R., Hess, G. D. (1997), Description of the HYSPLIT_4 Modeling System. NOAA Technical Memorandum ERL ARL-224.
- Draxler, R. R., Hess, G. D. (1998), An overview of the HYSPLIT_4 modelling system for trajectories, dispersion and deposition. *Australian Meteorological Magazine* 47, 295-308.
- Duncan, F., Jacob, D. G., and Park R. J. (2007), The impact of transpacific transport of mineral dust in the united states, *Atmos. Environ.*, 41, 1251-1266.
- Ervens, B., G. Feingold, G. J. Frost, and S. M. Kreidenweis (2004), A modelling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, *J. Geophys. Res.*, 109, D15205, doi: 10.1029/2003JD004387.
- Fick, J., C. Nilsson, and B. Andersson (2004), Formation of oxidation products in a ventilation system, *Atmos. Environ.*, 38, 5895-5899.
- Gao, S., D. A. Hegg, P. V. Hobbs, T. W. Kirchstetter, B. I. Magi, and M. Sadilek (2003), Water-soluble organic components in aerosols associated with savanna fires in southern Africa: Identification, evolution, and distribution, *J. Geophys. Res.*, 108(D13), 8491, doi: 10.1029/2002JD002324.
- Gierlus, K. M., O. Laskina, T. L. Abernathy, V. H. Grassian (2012), Laboratory study of the effect of oxalic acid on the cloud condensation nuclei activity of mineral dust aerosol, *Atmos. Environ.*, 46, 125-130.
- Grosjean, D., K. V. Cauwenberghe, J. P. Schmid, P. E. Kelly, and J. N. Pitts (1978), Identification of C₃-C₁₀ aliphatic dicarboxylic acids in airborne particulate matter, *Environ. Sci. Technol.*, 12, 313-317, doi: 10.1021/es60139a005.
- Hastings, W., C. Koehler, E. Bailey, and D. Dehaan (2005), Secondary organic aerosol formation by glyoxal hydration and oligomer formation: Humidity effects and equilibrium shifts during analysis, *Environ. Sci. Technol.*, 39, 8728-8735.

- Hatakeyama, S., M. Ohno, J. Weng, H. Takagi, and H. Akimoto (1987), Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air, *Environ. Sci. Technol.*, 21, 52-57.
- He, N., and Kawamura K., Distributions and diurnal changes of low molecular weight organic acids and α -dicarbonyls in suburban aerosols collected at Mangshan, North China, *Geochemical Journal*, 44, e17-e22, 2010.
- Highwood, E. J., and R. P. Kinnersley (2006), When smoke gets in our eyes: The multiple impacts of atmospheric black carbon on climate, air quality and health, *Environmental International*, 32, 560-566.
- Ho, K. F., J. J. Cao, S. C. Lee, K. Kawamura, R. J. Zhang, J. C. Chow, and J. G. Watson (2007), Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China, *J. Geophys. Res.*, 112, D22S27, doi: 10.1029/2006JD008011.
- Ho, K. F., S. C. Lee, J. J. Cao, K. Kawamura, T. Watanabe, Y. Cheng, and J. C. Chow (2006), Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong, *Atmos. Environ.*, 40, 3030-3040.
- Ho, K. F., S. S. H. Ho, S. C. Lee, K. Kawamura, S. C. Zou, J. J. Cao, and H. M. Xu (2011), Summer and winter variations of dicarboxylic acids, fatty acids and benzoic acid in PM_{2.5} in Pearl Delta River Region, China, *Atmos. Chem. Phys.*, 11, 2197-2208.
- Hopke, P. K. (1985), *Receptor Modelling in Environmental Chemistry*. Wiley, New York.
- Jaffe, D., E. Prestbo, P. Swartzendruber, P. W. Penzias, S. Kato, A. Takami, S. Hatakeyama, and Y. Kajii (2005), Export of atmospheric mercury from Asia, *Atmos. Environ.*, 39, 3029-3038.
- Jung, J., B. Tsatsral, Y. J. Kim, and K. Kawamura (2010), Organic and inorganic aerosol compositions in Ulaanbaatar, Mongolia, during the cold winter of 2007 to 2008: Dicarboxylic acids, ketocarboxylic acids, and α -dicarbonyls, *J. Geophys. Res.*, 115, D22203, doi: 10.1029/2010JD014339.

- Kawamura, K., and R. B. Gagosian (1987), Implications of ω - oxocarboxylic acids in the remote marine atmosphere for photo - oxidation of unsaturated fatty acids, *Nature*, 325, 330-332.
- Kawamura, K., and F. Sakaguchi (1999), Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropic, *J. Geophys. Res.*, 104, 3501-3509.
- Kawamura, K., and K. Ikushima (1993), Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, 27, 2227-2235.
- Kawamura, K., and O. Yasui (2005), Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, *Atmos. Environ.*, 39, 1945-1960.
- Kawamura, K., H. Kasukabe, and L. A. Barrie (1996a), Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, *Atmos. Environ.*, 30, 1709–1722.
- Kawamura, K., R. Sempéré, Y. Imai, M. Hayashi, and Y. Fujii (1996b), Water soluble dicarboxylic acids and related compounds in the Antarctic aerosols, *J. Geophys. Res.*, 101, 18,721–18,728.
- Kawamura, K., Y. Imai, and L. A. Barrie (2005), Photochemical production and loss of organic acids in high Arctic aerosols during long range transport and polar sunrise ozone depletion events. *Atmos. Environ.* 39, 599-614.
- Kawamura, K., H. Kasukabe, and L. A. Barrie (2010), Secondary formation of water-soluble organic acids and α -dicarbonyls and their contribution to total carbon and water-soluble organic carbon: Photochemical ageing of organic aerosols in the Arctic spring, *J. Geophys. Res.*, 115, D21306, doi: 10. 1029/2010JD014299.
- Kawamura, K., H. Kasukabe, O. Yasui, and L. A. Barrie (1995), Production of dicarboxylic acids in the arctic atmosphere at polar sunrise, *Geophys. Res. Lett.*, 22, 1253-1256.
- Kawamura, K., K. Yokoyama, Y. Fujii and O. Watanabe (2001), A Greenland ice core record of low molecular weight dicarboxylic acids, ketocarboxylic acids, and α -dicarbonyls: A

- trend from little ice age to the present (1540 to 1989 A.D.), *J. of Geophys Res.*, 106, 1331-1345.
- Kawamura, K., M. Kobayashi, N. Tsubonuma, M. Mochida, T. Watanabe, and M. Lee (2004), Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in *Geochemical Investigation in Earth and Space Science; A Tribute to Issac R. Kaplan*, The Geochemical Society Special Publication Series, vol. 9, edited by R. J. Hill, pp. 243-265, Elsevier, Amsterdam, Netherlands.
- Kerminen, V.-M., C. Ojanen, T. Pakkanen, R. Hillamo, M. Aurela, and J. Merilainen (2000), Low-molecular weight dicarboxylic acids in an urban and rural atmosphere, *J. Aerosol. Sci.*, 31, 349-362.
- Kerminen, V.-M., K. Teinila, R. Hillamo, and T. Makela (1999), Size segregated chemistry of particulate dicarboxylic acids in the Arctic atmosphere, *Atmos. Environ.*, 33, 2089-2100.
- Koebel, M., and M. Elsener (1998), Oxidation of diesel-generated volatile organic compounds in the selective catalytic reduction process. *Industrial and Engineering Chemistry Research* 37, 3864-3868.
- Krizner, H. E., D. O. De Haan, and J. Kua (2009), Thermodynamics and kinetics of methylglyoxal dimer Formation: a computational study, *J. Phys. Chem. A.*, 113, 6994–7001.
- Kroll, J. H., N. L. Ng, S. M. Murphy, V. Varutbangkul, R. C. Flagan, and J. H. Seinfeld (2005), Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, *J. Geophys. Res.*, 110, D23207, doi: 10.1029/2004JD005113.
- Kundu, S., K. Kawamura, T. W. Andreae, A. Hoffer, and M. O. Andreae (2010a), Molecular distributions of dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls in biomass burning aerosols: Implications for photochemical production and degradation in smoke layers, *Atmos. Chem. Phys.*, 10, 2209-2225.
- Kundu, S, K. Kawamura and M. Lee (2010b), Seasonal variations of diacids, ketoacids and α -dicarbonyls in marine aerosols at Gosan, Jeju Island: Implications for their formation and

- degradation during long-range transport, *J. Geophys. Res.*, 115, D19307, doi: 10.1029/2010JD013973.
- Legrand, M., S. Preunkert, T. Oliveira, C. A. Pio, S. Hammer, A. Gelencsér, A. Kasper-Giebl, and P. Laj (2007), Origin of C₂-C₅ dicarboxylic acids in the European atmosphere inferred from year-around aerosol study conducted at a west-east transect, *J. Geophys. Res.*, 112, D23S07, doi: 10.1029/2006JD008019.
- Liggio, J., S. M. Li, and R. McLaren (2005), Reactive uptake of glyoxal by particulate matter, *J. Geophys. Res.* 110, D10304, doi: 10.1029/2004JD005113.
- Lim, H.-J., A. G. Carlton, and B. J. Turpin (2005), Isoprene forms secondary organic aerosol through cloud processing: Model simulations, *Environ. Sci. Technol.*, 39, 4441-4446.
- Limbeck, A., H. Puxbaum, L. Otter, and M. C. Scholes (2001), Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA), *Atmos. Environ.*, 35(10), 1853-1862.
- Loeffler, K., C. Koehler, N. Paul and D. Dehaan (2006), Oligomer formation in evaporating aqueous glyoxal and methyl glyoxal solutions, *Environ. Sci. Technol.*, 40, 6318-6323.
- Lun, X., A. Takami, T. Miyoshi, and S. Hatakeyama (2009), Characteristic of organic aerosol in a remote area of Okinawa Island, *J. Environmental Science*, 21, 1371-1377.
- Marty, J. C., A. Saliot, P. Buat, R. Chesselet, and K. A. Hunter (1979), Relationship between the lipid compositions of marine aerosols, the sea surface microlayer, and subsurface water, *Journal of Geophysical Research.*, 84(C9), 0148-0227.
- Miyazaki, Y., P. Fu, K. Kawamura, Y. Mizoguchi, and K. Yamanoi (2011) Seasonal variations of stable carbon isotopic ratios and biogenic tracer compounds of water-soluble organic aerosols in a deciduous forest, *Atmos. Chem. Phys.*, 11, 30773–30795, doi:10.5194/acpd-11-30773.
- Miyazaki, Y., S. G. Aggarwal, K. Singh, P. K. Gupta, and K. Kawamura (2009), Dicarboxylic acids and water-soluble organic carbon in aerosols in New Delhi, India, in winter: Characteristics and formation processes, *J. Geophys. Res.*, 114, D19206, doi: 10.1029/2009JD011790.

- Miyazaki, Y., Y. Kondo, S. Han, M. Koike, D. Kodama, Y. Komazaki, H. Tanimoto, and H. Matsueda (2007), Chemical characteristics of water-soluble organic carbon in the Asian outflow, *J. Geophys. Res.*, 112, D22S30, doi: 10.1029/2007JD009116.
- Mkoma S. L. and Kawamura K. (2013), Molecular composition of dicarboxylic acids, ketocarboxylic acids, α -dicarbonyls and fatty acids in atmospheric aerosols from Tanzania, East Africa during wet and dry seasons, *Atmos. Chem. and Physics*, 13, 2235–2251.
- Mochida M., C. Nishita-Hara, H. Furutani, Y. Miyazaki, J. Jung, K. Kawamura, and M. Uematsu (2010), Hygroscopicity and cloud condensation nucleus activity of marine aerosol particles over the western North Pacific, *J. Geophys. Res.*, 116, D06204, doi: 10.1029/2010JD014759.
- Mochida, M., A. Kawabata, K. Kawamura, H. Hatsushika, and K. Yamazaki (2003a), Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific, *J. Geophys. Res.*, 108(D6), 4193, doi: 10.1029/2002JD002355.
- Mochida, M., K. Kawamura, N. Umemoto, M. Kobayashi, S. Matsunaga, H. - J. Lim, B. J. Turpin, T. S. Bates, and B. R. T. Simoneit (2003b), Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia: Continental outflow of organic aerosols during the ACE-Asia campaign, *J. Geophys. Res.*, 108(D23), 8638, doi:10.1029/2002JD003249.
- Mori, I., Nishikawa, M., Quan, H., Morita, M., 2002. Estimation of the concentration and chemical composition of kosa aerosols at their origin. *Atmos. Environ.*, 36, 4569-4575.
- Mori, I., Nishikawa, M., Tanimura, T., and H. Quan (2003), Change in size distribution and chemical composition of kosa (Asian dust) aerosol during long-range transport, *Atmos. Environ.*, 37, 4253–4263.
- Myriokefalitakis, S., K. Tsigaridis, N. Mihalopoulos, J. Sciare, A. Nenes, K. Kawamura, A. Segers, and M. Kanakidou (2011), In-cloud oxalate formation in the global troposphere: A 3-D modeling study, *Atmos. Chem. Phys.*, 11, 5761-5782.

- Narukawa, M., K. Kawamura, K. G. Anlauf, and L. A. Barrie (2003), Fine and coarse modes of dicarboxylic acids in the arctic aerosols collected during the Polar Sunrise Experiment 1997, *J. Geophys. Res.*, 108(D18), 4575, doi:10.1029/2003JD003646.
- Narukawa, M., K. Kawamura, N. Takeuchi, and T. Nakajima (1999), Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.*, 26(20), 3101-3104.
- Nishikawa, M., Hao, Q., Morita, M., 2000. Preparation and evaluation of certified reference materials from Asian mineral dust, *Global Environ. Res.* 4, 103-113.
- Novakov, T., and J. E. Penner (1993), Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, *Nature*, 365, 823-826.
- Novakov, T., C. E. Corrigan, J. E. Penner, C. C. Chuang, O. Rosario, and O. L. Mayol Bracero (1997), Organic aerosols in the Caribbean trade winds: A natural source?, *J Geophys. Res.*, 102,21, 307-21,313.
- Pavuluri, C., M., K. Kawamura, and T. Swaminathan (2010), Water-soluble organic carbon, dicarboxylic acids, ketoacids, and α -dicarbonyls in the tropical Indian aerosols, *J. Geophys. Res.*, 115, D11302, doi: 10.1029/ 2009JD012661.
- Rinaldi, M., et al. (2011), Evidence of a natural marine source of oxalic acid and a possible link to glyoxal, *J. Geophys. Res.*, 116, D16204, doi:10.1029/2011JD015659.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1991), Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations, *Environ. Sci. Technol.*, 25, 1112-1125.
- Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit (1993), Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation, *Atmos. Environ., Part A*, 27, 1309-1330.
- Sato, K., H. Li, Y. Tanaka, S. Ogawa, Y. Iwasaki, A. Takami and S. Hatakeyama (2009), Long-range transport of particulate polycyclic aromatic hydrocarbons at Cape Hedo remote island site in the East China Sea between 2005 and 2008, *J. Atmos. Chem.*, 61, 243-257.

- Saxena, P., L. Hildemann, P. McMurry, and J. Seinfeld (1995), Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, 100(D9), 18,755-18,770.
- Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit (1999), Measurement of emissions from air pollution sources - I, C₁ through C₂₉ organic compounds from meat charboiling, *Environ. Sci. Technol.*, 33, 1566-1577.
- Sempéré, R., and K. Kawamura (1996), Low molecular weight dicarboxylic acids and related polar compounds in the remote marine rain samples collected from western Pacific, *Atmos. Environ.*, 30, 1609-1619.
- Sempéré, R., and K. Kawamura (2003), Trans-hemispheric contribution of C₂-C₁₀ α , ω -dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions, *Global Biogeochem. Cycles*, 17(2), 1069, doi: 10.1029/2002GB001980.
- Simoneit, B. R. T., M. Kobayashi, M. Mochida, K. Kawamura, M. Lee, H.-J. Lim, B. J. Turpin, and Y. Komazaki (2004), Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign, *J. Geophys. Res.*, 109, D19S10, doi:10.1029/2004JD004598.
- Stephanou, E. G., and N. Stratigakis (1993), Oxocarboxylic and α , ω -dicarboxylic acids: Photooxidation products of biogenic unsaturated fatty acids present in urban aerosols, *Environ. Sci. Technol.*, 27, 1403-1407.
- Streets, D. G., T. C. Bond, T. Lee, and C. Jang (2004), On the future of carbonaceous aerosol emissions, *J. Geophys. Res.*, 109, D24212, doi: 10.1029/2004JD004902.
- Takami, A., T. Miyoshi, A. Shimono, N. Kaneyasu, S. Kato, Y. Kajii, and, S. Hatakeyama (2007), Transport of anthropogenic aerosols from Asia and subsequent chemical transformation, *J. Geophys. Res.* 112, D22S31, doi:10.1029/2006jd008120.
- Tambunan, P., S. Baba, A. Kuniyoshi, H. Iwasaki, T. Nakamura, H. Yamasaki, and H. Oku, Isoprene emission from tropical trees in Okinawa Island, Japan (2006), *Chemosphere*, 65, 2138–2144.

- Tedetti, M., K. Kawamura, B. Charriere, N. Chevalier, and R. Sempéré (2006), Determination of low molecular weight dicarboxylic acids in seawater samples, *Anal. Chem.*, 78, 6012-6018.
- Tran, N. K., S. M. Steinberg, and B. J. Johnson (2000), Volatile aromatic hydrocarbons and dicarboxylic acid concentrations in air at an urban site in the South western US, *Atmos. Environ.*, 34, 1845-1852.
- Volkamer, R., J. L. Jimenez, F. S. Martini, K. Dzepina, Q. Zhang, D. Salcedo, L. T. Molina, D. R. Worsnop, and M. J. Molina (2006), Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, *Geophys. Res. Lett.*, 33, L17811, doi: 10.1029/2006GL026899.
- Volkamer, R., U. Platt, and K. Wirtz (2001), Primary and secondary glyoxal formation from aromatics: Experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene, and p-xylene, *J. Phys. Chem. A.*, 105, 7865-7874.
- Wang, G. H., K. Kawamura, S.C. Lee, K.F. Ho, and J.J. Cao (2006), Molecular, seasonal and spatial distribution of organic aerosols from fourteen Chinese cities, *Environ. Sci. Technol.*, 40, 4619-4625.
- Wang, G., K. Kawamura, and M. Lee (2009a), Comparison of organic compositions in dust storm and normal aerosol samples collected at Gosan, Jeju Island, during spring, *Atmos. Environ.*, 43, 219-227.
- Wang, G., K. Kawamura, M. Xie, S. Hu, S. Gao, J. Cao, Z. An, and Z. Wang (2009b), Size-distributions of n-alkanes, PAHs and hopanes and their sources in the urban, mountain and marine atmospheres over East Asia. *Atmos. Chem. Phys.*, 9(22), 8869-8882.
- Wang, H., K. Kawamura and D. Shooter (2005), Carbonaceous and ionic components in wintertime atmospheric aerosols from two New Zealand cities: Implication for solid fuel combustion, *Atmos. Environ.*, 39, 5865-5875.
- Wang, H., K. Kawamura, and K. Yamazaki (2006a), Water soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the Southern Ocean and Western North Pacific, *J. Atmos. Chem.*, 53, 43-61.

- Wang H., K. Kawamura, K. F. Ho, and S. C. Lee (2006b), Low molecular weight dicarboxylic acids, ketoacids and dicarbonyls in the fine particles from a roadway tunnel: significant secondary production from the precursors in vehicular emissions, *Environ. Sci. Technol.*, 40, 6255-6260.
- Wang, L., A.F. Khalizov, J. Zheng, W. Xu, V. Lal, Y. Ma, and R. Zhang (2010), Atmospheric nanoparticles formed from heterogeneous reactions of organics, *Nature Geosci.* 3, doi:10.1038/ngeo778, 238-242.
- Wang, L., R. Atkinson and J. Arey (2007), Dicarbonyl products of the OH radical-initiated reactions of naphthalene and the C₁- and C₂-alkylnaphthalenes, *Environ. Sci. Technol.*, 2007, 41, 2803-2810.
- Warneck, P. (2003), In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere, *Atmos. Environ.*, 37, 2423-2427.
- Xu, W., and R. Zhang (2012), Theoretical investigation of interaction of dicarboxylic acids with common aerosol nucleation precursors, *J. Phys. Chem. A.*, 116, dx.doi.org/10.1021/jp301964u, 4539–4550.
- Xu, Y., Nadykto, A. B., Yu, F., Herb, J., and W. Wang (2010), Interaction between common organic acids and Trace Nucleation Species in the Earth's Atmosphere, *J. Phys. Chem. A.*, 114, 387-396.
- Yamamoto, S., and K. Kawamura (2011), Stable hydrogen isotopic compositions of fossil fuel-derived n-alkanes in the atmospheric aerosols from Okinawa, Japan, *Res. Org. Geochem.*, 27, 81-89.
- Yamasoe, M. A., P. Artaxo, A. H. Miguel, and A. G. Allen (2000), Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: Water-soluble species and trace elements, *Atmos. Environ.*, 34, 1641-1653.
- Yokouchi, Y., and Y. Ambe (1986), Characterization of polar organics in airborne particulate matter, *Atmos. Environ.*, 20, 1727–1734.
- Zhang, M., I. Uno., G. R. Carmichael, H. Akimoto, Z. Wang, Y. Tang, J-H Woo, D. G. Streets, G. W. Sachse, M. A. Avery, R. J. Weber, and R. W. Talbot (2003), Large-scale

- structure of trace gas and aerosol distributions over the western Pacific Ocean during the Transport and Chemical Evolution Over the Pacific (TRACE-P) experiment, *J. Geophys. Res.*, 108, 8820, doi: 10.1029/2002JD002946.
- Zhang, R., Khalizov, A.F., Wang, L., Hu, M., and X. Wen (2012), Nucleation and growth of nanoparticles in the atmosphere, *Chem. Rev.* **112**, 1957-2011, DOI: 10.1021/cr2001756.
- Zheng, M., M. Fang, F. Wang, and K. L. To (2000), Characterization of the solvent extractable organic compounds in PM_{2.5} aerosols in Hong Kong, *Atmos. Environ.*, 34, 2691-2702.
- Zimmermann, J. and D. A. Poppe (1996), A supplement for the RADM2 chemical mechanism: The photooxidation of isoprene, *Atmos. Environ.*, 30, 1255-1269.

Table 2.1. Concentrations (ng m^{-3}) of diacids, ketoacids, and α -dicarbonyls in the TSP samples collected from 2009 October to 2010 October

Compounds	Concentrations (ng m^{-3})			
	Winter Range (Ave.)	Spring Range (Ave.)	Summer Range (Ave.)	Autumn Range (Ave.)
Diacids				
Oxalic, C_2	91-415 (244)	165-414 (272)	17-496 (96)	24-261 (148)
Malonic, C_3	12-47 (25)	16-40 (29)	2.0-68 (15)	6.6-32 (19)
Succinic, C_4	0.95-41 (16)	7.7-32 (18)	0.72-57 (6.5)	1.3-15 (8.7)
Glutaric, C_5	1.5-5.8 (3.1)	1.4-6.8 (2.9)	0.06-8.1 (0.99)	0.21-8.7 (1.9)
Adipic, C_6	0.77-4.0 (1.9)	0.75-3.4 (1.6)	0.07-2.5 (0.63)	0.24-1.6 (0.86)
Pimelic, C_7	0.17-1.6 (0.75)	0.21-3.0 (0.99)	0.05-2.0 (0.59)	0.27-1.1 (0.66)
Suberic, C_8	0.05-0.50 (0.21)	0.25-0.78 (0.41)	0.04-0.57 (0.20)	0.07-0.32 (0.20)
Azelaic, C_9	0.53-3.8 (1.5)	1.1-5.9 (3.2)	1.0-7.6 (3.9)	1.24-6.7 (2.4)
Sebacic, C_{10}	0.04-0.34 (0.19)	0.12-0.81 (0.33)	0.06-0.33 (0.17)	0.05-0.28 (0.15)
Undecanedioic, C_{11}	BDL-1.1 (0.38)	0.20-0.62 (0.43)	0.03-1.1 (0.25)	0.03-0.45 (0.20)
Dodecanedioic, C_{12}	BDL-0.46 (0.10)	BDL-0.26 (0.07)	BDL-0.09 (0.01)	0.00-0.15 (0.04)
Methylmalonic, iC_4	0.35-1.1 (0.66)	0.37-1.2 (0.69)	0.05-0.83 (0.29)	0.17-0.72 (0.45)
Methylsuccinic, iC_5	0.68-3.0 (1.9)	0.93-3.5 (1.8)	0.08-2.1 (0.67)	0.47-1.8 (1.1)
Methylglutaric, iC_6	0.13-2.4 (0.47)	0.19-0.77 (0.40)	0.03-0.96 (0.25)	0.04-0.43 (0.23)
Maleic, M	0.50-3.3 (1.4)	0.67-4.5 (1.8)	0.08-2.2 (0.44)	0.17-1.3 (0.67)
Fumaric, F	0.65-2.7 (1.6)	1.1-3.2 (1.8)	0.19-3.3 (0.97)	0.42-1.8 (1.1)
Methylmaleic, mM	0.18-1.5 (0.66)	0.09-1.8 (0.53)	0.02-1.3 (0.26)	0.07-0.58 (0.26)
Phthalic, Ph	2.5-15 (8.4)	1.34-8.3 (3.8)	0.40-7.6 (1.9)	0.69-8.0 (2.5)
Isophthalic, iPh	0.01-1.7 (1.1)	0.44-2.3 (1.0)	0.08-1.5 (0.35)	0.17-0.88 (0.44)
Terephthalic, tPh	0.37-2.4 (1.5)	0.19-2.5 (1.1)	0.05-1.2 (0.37)	0.06-1.1 (0.52)
Hydroxysuccinic, hC_4	BDL-0.09 (0.05)	0.03-0.10 (0.05)	BDL-0.29 (0.06)	0.02-0.08 (0.03)
Ketomalonic, kC_3	0.54-1.9 (1.0)	0.51-2.5 (1.06)	0.03-2.2 (0.36)	0.08-1.8 (0.65)
Ketopimelic, kC_7	0.10-2.8 (1.1)	0.83-2.7 (1.4)	0.02-4.0 (0.50)	0.07-1.1 (0.57)
Total diacids	163-513 (313)	208-532 (344)	26-671 (131)	41-318 (190)
Ketoacids				
Pyruvic	2.2-9.5 (4.9)	1.8-17 (4.5)	0.23-6.4 (1.4)	0.54-4.2 (2.4)
Glyoxylic, $[\text{C}_2]$	10-38 (21)	8.8-66 (21)	0.76-46 (7.1)	1.6-21 (12)
3-oxopropanoic, $[\text{C}_3]$	0.69-1.9 (1.3)	0.73-2.4 (1.5)	0.08-2.7 (0.65)	0.24-1.3 (0.79)
4-oxobutanoic, $[\text{C}_4]$	0.01-1.9 (0.88)	0.51-2.1 (1.2)	0.18-1.1 (0.45)	0.21-37 (3.4)
5-oxopentanoic, $[\text{C}_5]$	0.11-0.53 (0.31)	0.10-0.55 (0.28)	0.04-0.35 (0.14)	0.05-0.32 (0.13)
7-oxoheptanoic, $[\text{C}_7]$	1.3-6.4 (2.8)	1.3-4.8 (2.9)	0.22-5.1 (1.3)	0.12-3.3 (1.2)
8-oxooctanoic, $[\text{C}_8]$	0.21-4.5 (1.4)	0.09-2.8 (1.8)	0.02-6.1 (0.89)	0.10-2.0 (1.1)
9-oxononoic, $[\text{C}_9]$	0.14-5.3 (2.3)	0.71-3.0 (1.6)	0.02-5.3 (0.71)	0.13-2.3 (0.99)
Total Keto acid	17-58 (34)	17-95 (35)	1.75-74 (13)	3.6-67 (22)
α -Dicarbonyls				
Glyoxal, Gly	1.8-19 (6.0)	1.3-30 (5.0)	0.26-6.6 (1.3)	0.39-6.8 (2.6)
Methylglyoxal, MeGly	6.1-35 (16)	3.1-16 (8.7)	0.14-14 (3.0)	0.56-15 (8.2)
Total dicarbonyls	8.9-54 (22)	4.9-37 (14)	0.39-21 (4.2)	1.2-22 (11)

Note: BDL means Below Detection Limit (0.001 ng m^{-3}) and Ave. means average.

Table 2.2. The relative abundances (%) of individual compound in total diacids, ketoacids, and α -dicarbonyls in aerosols over Okinawa

Compounds	Relative Abundances (%)			
	Winter	Spring	Summer	Autumn
	Range (Ave.)	Range (Ave.)	Range (Ave.)	Range (Ave.)
Diacids				
Oxalic, C ₂	56-83 (80)	74-82 (79)	66-84 (73)	58-83 (75)
Malonic, C ₃	6.3-15 (7.2)	7.2-10 (8.1)	2.5-18 (11)	8.1-21 (9.6)
Succinic, C ₄	0.35-10 (3.9)	3.2-7.3 (5.4)	0.41-8.5 (4.3)	2.6-6.7 (5.3)
Glutaric, C ₅	0.61-2.13 (0.85)	0.40-1.3 (0.86)	0.14-1.2 (0.62)	0.40-6.9 (2.2)
Adipic, C ₆	0.35-1.6 (0.90)	0.25-0.63 (0.51)	0.23-0.70 (0.52)	0.26-1.2 (0.69)
Pimelic, C ₇	0.06-0.48 (0.22)	0.05-0.56 (0.15)	0.09-1.1 (0.51)	0.21-0.85 (0.30)
Suberic, C ₈	0.01-0.14 (0.06)	0.07-0.24 (0.09)	0.08-0.45 (0.17)	0.05-0.23 (0.11)
Azelaic, C ₉	0.28-0.77 (0.47)	0.38-2.2 (0.65)	1.13-7.3 (4.0)	0.53-5.5 (0.96)
Sebacic, C ₁₀	0.01-0.21 (0.08)	0.04-0.15 (0.09)	0.05-0.37 (0.22)	0.02-0.28 (0.08)
Undecanedioic, C ₁₁	0.00-0.21 (0.06)	0.09-0.16 (0.13)	0.09-0.26 (0.18)	0.02-0.27 (0.10)
Dodecanedioic, C ₁₂	0.00-0.17 (0.01)	0.00-0.06 (0.02)	0.00-0.01 (0.00)	0.00-0.05 (0.01)
Methylmalonic, iC ₄	0.18-0.42 (0.21)	0.12-0.29 (0.23)	0.12-0.48 (0.24)	0.14-0.45 (0.31)
Methylsuccinic, iC ₅	0.24-1.1 (0.65)	0.25-0.66 (0.58)	0.29-1.6 (0.80)	0.21-1.4 (0.95)
Methylglutaric, iC ₆	0.06-0.46 (0.11)	0.06-0.23 (0.10)	0.03-0.40 (0.24)	0.03-0.52 (0.09)
Maleic, M	0.22-1.0 (0.43)	0.28-0.86 (0.66)	0.13-0.47 (0.38)	0.12-0.63 (0.43)
Fumaric, F	0.30-1.0 (0.48)	0.38-0.75 (0.57)	0.34-3.2 (0.65)	0.18-2.0 (0.79)
Methylmaleic, mM	0.09-0.63 (0.23)	0.04-0.34 (0.22)	0.03-0.35 (0.20)	0.04-0.41 (0.18)
Phthalic, Ph	0.99-6.3 (3.0)	0.52-1.58 (1.5)	0.78-3.3 (1.6)	0.36-2.9 (1.2)
Isophthalic, iPh	0.00-0.87 (0.3)	0.12-0.79 (0.29)	0.18-0.45 (0.31)	0.08-0.40 (0.26)
Terephthalic, tPh	0.14-1.0 (0.46)	0.08-0.48 (0.35)	0.12-0.74 (0.33)	0.12-0.58 (0.37)
Hydroxysuccinic, hC ₄	0.00-0.04 (0.02)	0.01-0.03 (0.01)	0.00-0.18 (0.02)	0.00-0.19 (0.01)
Ketomalonic, kC ₃	0.21-0.67 (0.38)	0.19-0.57 (0.30)	0.11-0.35 (0.32)	0.15-0.67 (0.34)
Ketopimelic, kC ₇	0.04-0.54 (0.27)	0.26-0.55 (0.33)	0.04-0.59 (0.25)	0.15-0.51 (0.29)
Ketoacids				
Pyruvic	9.1-20 (15)	8.8-18 (12)	8.5-16 (13)	6.4-19 (12)
Glyoxylic, ω C ₂	48-66 (61)	44-69 (54)	41-63 (53)	31-71 (63)
3-oxopropanoic, ω C ₃	2.7-5.7 (4.3)	2.4-6.7 (4.7)	3.6-12 (7.6)	1.8-11 (4.4)
4-oxobutanoic, ω C ₄	0.01-4.8 (2.0)	1.9-5.9 (4.7)	1.5-14 (5.3)	0.75-54 (3.1)
5-oxopentanoic, ω C ₅	0.25-2.1 (1.0)	0.28-1.5 (1.1)	0.47-5.8 (1.5)	0.26-2.9 (0.77)
7-oxoheptanoic, ω C ₇	4.5-13 (6.4)	3.0-16 (11)	6.9-21 (10)	0.27-16 (7.5)
8-oxooctanoic, ω C ₈	0.87-9.0 (2.7)	0.36-11 (6.1)	0.36-12 (4.3)	2.5-11 (4.9)
9-oxononoic, ω C ₉	0.78-11 (6.6)	2.4-9.3 (6.6)	0.59-7.1 (4.2)	2.3-6.9 (4.5)
α -Dicarbonyls				
Glyoxal, Gly	14-45 (24)	12-80 (24)	21-65 (34)	12-56 (22)
Methylglyoxal, MeGly	55-85 (76)	20-88 (75)	35-79 (65)	44-87 (78)

Note: The relative abundances of individual diacids is calculated as % of total diacids. Same for those of individual ketoacids and individual α -dicarbonyls.

Table 2.3. Correlation coefficients (r) among selected diacids and related compounds in winter

Compounds	C ₂	C ₃	C ₄	hC ₄	kC ₃	Pyr	Gly	MeGly	ωC ₂
C ₂	1								
C ₃	0.83	1							
C ₄	0.68	0.80	1						
hC ₄	0.20	0.54	0.64	1					
kC ₃	0.42	0.49	0.43	0.56	1				
Pyr	0.39	0.54	0.48	0.38	0.83	1			
Gly	0.73	0.01	0.01	0.41	0.60	0.01	1		
MeGly	0.10	0.02	0.23	0.23	0.49	0.20	0.70	1	
ωC ₂	0.45	0.64	0.55	0.55	0.79	0.95	0.95	0.23	1

Note: We categorized the r-values in Tables 3-6 as strong ($r \geq 0.80$), good ($0.60 \leq r \leq 0.80$), fair ($0.3 \leq r \leq 0.5$), and very weak correlation ($r \leq 0.30$).

Table 2.4. Correlation coefficients (r) among selected diacids and related compounds in spring

Compounds	C ₂	C ₃	C ₄	hC ₄	kC ₃	Pyr	Gly	MeGly	ωC ₂
C ₂	1								
C ₃	0.89	1							
C ₄	0.84	0.74	1						
hC ₄	-0.33	-0.30	0.68	1					
kC ₃	0.68	0.55	0.75	-0.29	1				
Pyr	0.83	0.78	0.93	-0.30	0.63	1			
Gly	0.27	0.01	0.55	-0.28	0.41	0.48	1		
MeGly	0.38	0.12	0.53	-0.01	0.11	0.55	0.75	1	
ωC ₂	0.76	0.68	0.88	-0.33	0.66	0.95	0.37	0.43	1

Table 2.5. Correlation coefficient (r) among selected diacids and related compounds in summer

Compounds	C ₂	C ₃	C ₄	hC ₄	kC ₃	Pyr	Gly	MeGly	ωC ₂
C ₂	1								
C ₃	0.95	1							
C ₄	0.96	0.90	1						
hC ₄	0.25	0.43	0.2	1					
kC ₃	0.99	0.93	0.97	0.10	1				
Pyr	0.98	0.93	0.96	0.20	0.98	1			
Gly	-0.07	-0.20	-0.09	-0.20	-0.04	-0.10	1		
MeGly	0.82	-0.26	-0.10	-0.20	-0.05	-0.10	0.96	1	
ωC ₂	0.99	0.93	0.98	0.20	0.99	0.98	-0.08	-0.10	1

Table 2.6. Correlation coefficient (r) among selected diacids and related compounds in autumn

Compounds	C ₂	C ₃	C ₄	hC ₄	kC ₃	Pyr	Gly	MeGly	ωC ₂
C ₂	1								
C ₃	0.91	1							
C ₄	0.84	0.80	1						
hC ₄	0.16	0.10	0.01	1					
kC ₃	0.73	0.62	0.74	0.17	1				
Pyr	0.70	0.62	0.79	0.00	0.66	1			
Gly	-0.03	0.09	0.05	0.00	-0.30	-0.10	1		
MeGly	-0.07	-0.29	0.00	0.09	-0.20	-0.10	0.05	1	
ωC ₂	0.72	0.68	0.82	-0.30	0.68	0.97	-0.07	0.16	1

Table 2.7. Results of principal component analysis (Varimax rotation with Kaiser Normalization) on concentration of the selected diacids and related compounds in the marine aerosols collected in Cape Hedo, Okinawa, Japan during winter, spring, summer and autumn

Compounds	Winter			Spring		Summer		Autumn		
	Component			Component		Component		Component		
	1	2	3	1	2	1	2	1	2	3
C ₂	0.69	0.55	-0.20	0.93	0.11	0.98	-0.03	0.85	0.78	0.26
C ₃	0.90	0.32	-0.30	0.83	0.26	0.95	-0.20	0.86	-0.71	0.10
C ₄	0.88	0.15	0.10	0.93	0.22	0.94	-0.06	0.80	0.42	0.22
C ₅	0.89	0.29	0.20	0.87	0.36	0.95	-0.06	-0.10	0.92	0.91
C ₆	0.17	0.06	0.01	0.93	0.20	0.99	-0.08	0.46	0.80	-0.10
C ₇	0.46	0.78	0.33	0.27	0.90	0.93	0.10	0.64	0.17	0.10
C ₈	0.01	0.94	0.04	0.43	0.80	0.89	-0.01	0.87	0.13	0.00
C ₉	0.90	-0.01	-0.20	-0.30	0.90	0.79	0.10	-0.10	-0.16	0.22
C ₁₀	-0.20	-0.15	0.78	0.91	0.17	0.79	0.46	0.18	-0.93	0.89
M	0.94	-0.64	0.10	0.92	-0.17	0.97	-0.09	0.82	0.20	0.14
Ph	0.22	0.45	0.78	0.94	-0.03	0.96	0.01	0.41	0.23	0.78
ωC ₂	0.51	0.51	0.59	0.72	0.60	0.97	-0.47	0.89	0.31	0.18
Gly	0.18	0.73	-0.10	0.02	-0.49	0.08	0.96	0.12	0.66	0.24
Variance %	46	19	8.0	59	19	74	15	50	14	13

Table 2.8. Concentrations of fatty acids found in the atmospheric aerosols over Okinawa Island during winter, spring, summer and autumn

Fatty acids	Concentration (ng m ⁻³)							
	Winter (n=13)		Spring (n=13)		Summer (n=12)		Autumn (n=12)	
	Range	Ave±SD	Range	Ave±SD	Range	Ave±SD	Range	Ave±SD
C14:0	0.57-3.9	2.2±0.82	1.2-4.2	2.5±0.80	0.41- 3.4	1.1±0.84	0.43-2.2	1.20±0.55
C16:0	0.23-6.7	1.5±1.6	0.03-7.8	3.3±2.2	0.96- 11	5.3±2.8	0.17-6.3	1.8±1.7
C17:0	0.04-0.25	0.09±0.06	0.04-0.19	0.12±0.05	0.03- 0.55	0.11±0.14	0.02-0.15	0.08±0.04
C18:0	0.28-2.28	0.93±0.51	0.19-2.8	1.1±0.67	0.39- 3.6	2.0±0.99	0.03-2.2	0.71±0.59
C18:1	0.02-2.2	0.36±0.58	0.10-1.7	0.67±0.50	0.37- 6.1	2.4±1.7	0.02-5.9	0.96±1.7
C20:0	0.06-0.33	0.19±0.09	0.06-1.5	0.39±0.45	0.04- 0.34	0.18±0.10	0.03-0.21	0.09±0.06
C21:0	BDL-0.41	0.13±0.12	BDL-0.17	0.02±0.05	BDL- 0.04	0.01±0.02	BDL-0.18	0.04±0.05
C22:0	0.04-0.87	0.39±0.27	0.08-2.7	0.60±0.84	0.03- 0.57	0.23±0.15	0.03-0.34	0.13±0.09
C23:0	BDL-0.35	0.09±0.11	BDL-0.7	0.12±0.23	BDL- 0.50	0.07±0.14	BDL-0.03	0.01±0.01
C24:0	0.04-1.0	0.33±0.29	BDL-2.6	0.57±0.83	0.04- 0.64	0.31±0.18	BDL-0.34	0.12±0.10
Total	1.3-18	6.2±4.5	1.7-24	9.4±6.6	2.3- 26	12±7.1	0.73-18	5.1±4.9

Note: BDL means Below Detection Limit (0.001ng/m⁻³). Concentrations of C15:0 and C19:0 are below detection limit.

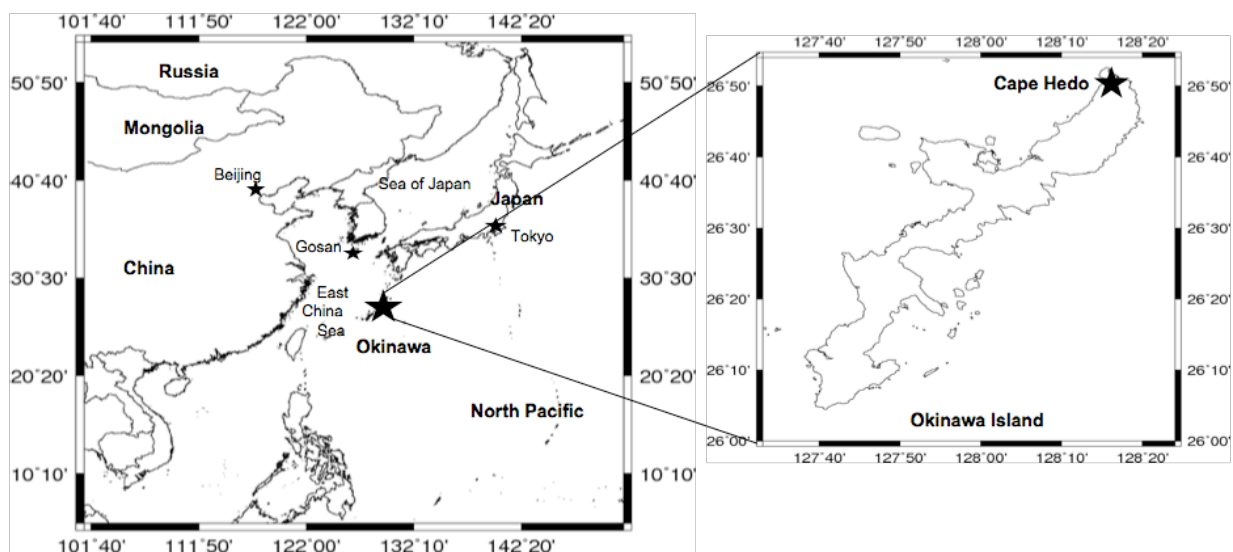
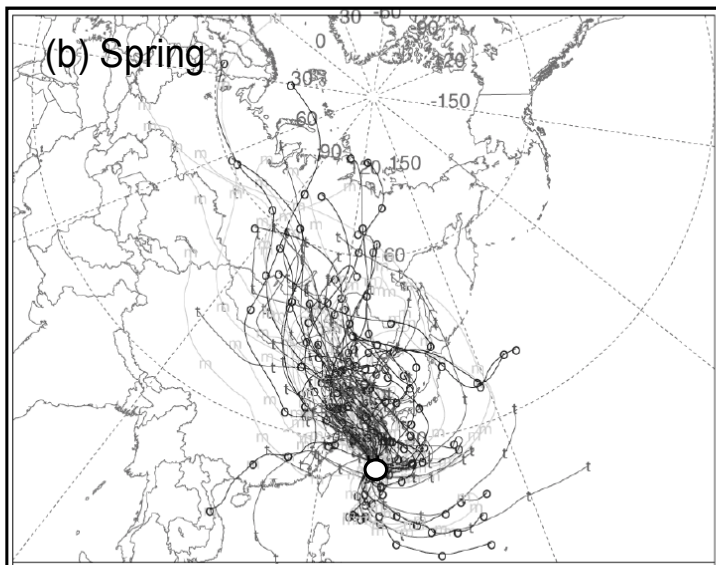
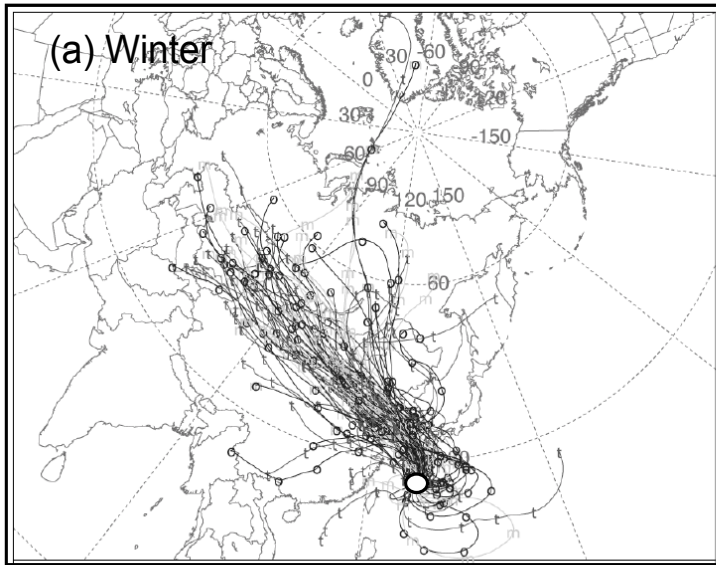


Figure 2.1. Map showing the geographical region of Cape Hedo, Okinawa, where aerosol sampling was performed. Cape Hedo is situated in the northwest coast of Okinawa Island.



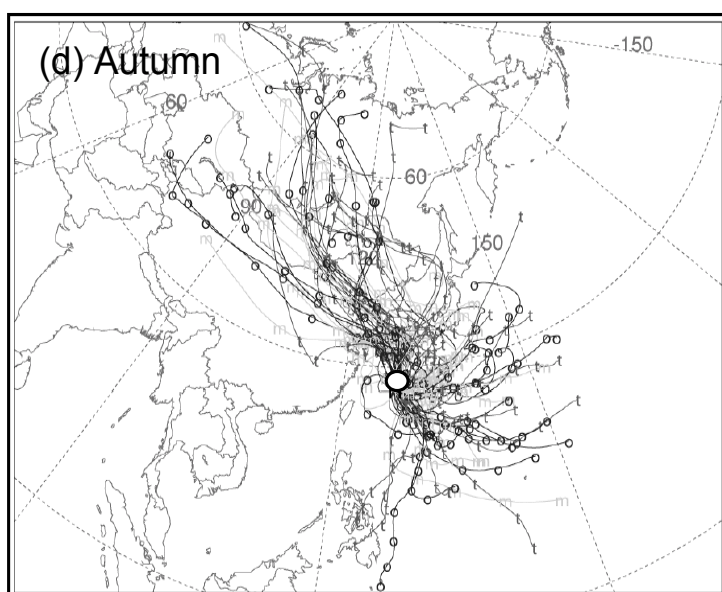
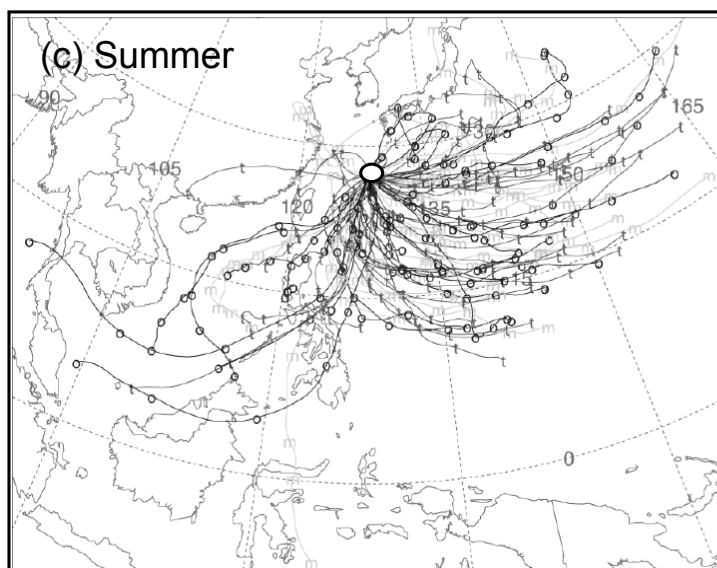


Figure 2.2. Five-day backward trajectory analysis for (a) winter (December, January and February), (b) spring (March, April and May), (c) summer (June, July and August) and (d) autumn (September, October and November). Backward trajectories at 500 m above ground level were drawn with the NOAA HYSPLIT model.

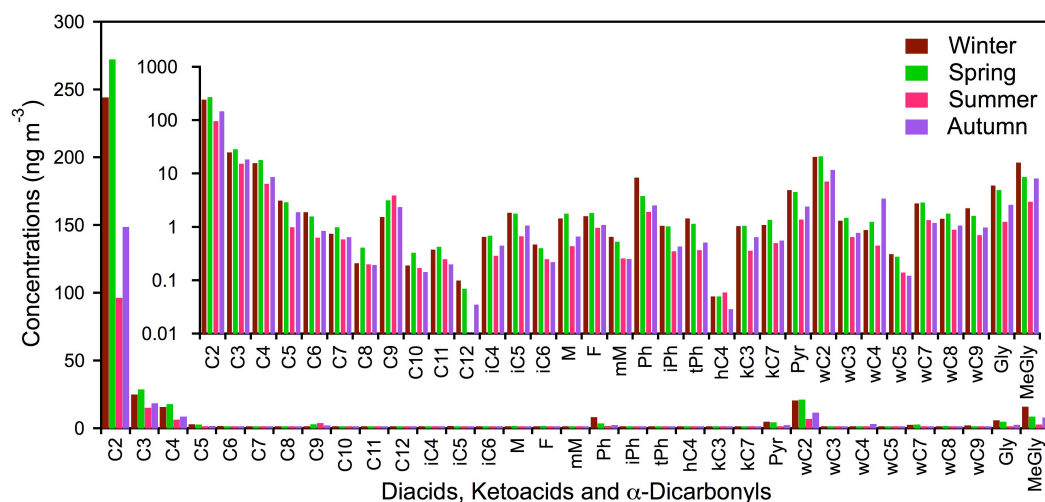


Figure 2.3. Seasonally averaged molecular distributions of straight chain diacids (C₂ -C₁₂), branched chain diacids (iC₄- iC₆), unsaturated dicids (M, F, mM, Ph, iPh, and tPh), multifunctional diacids (hC₄, kC₃ and kC₇), ketoacids (ωC₂-ωC₉, and pyruvic), and α-dicarbonyls (Gly and MeGly) in aerosols collected at Cape Hedo from October 2009 to October 2010. Lower panel represents normal scale and upper panel represents log scale.

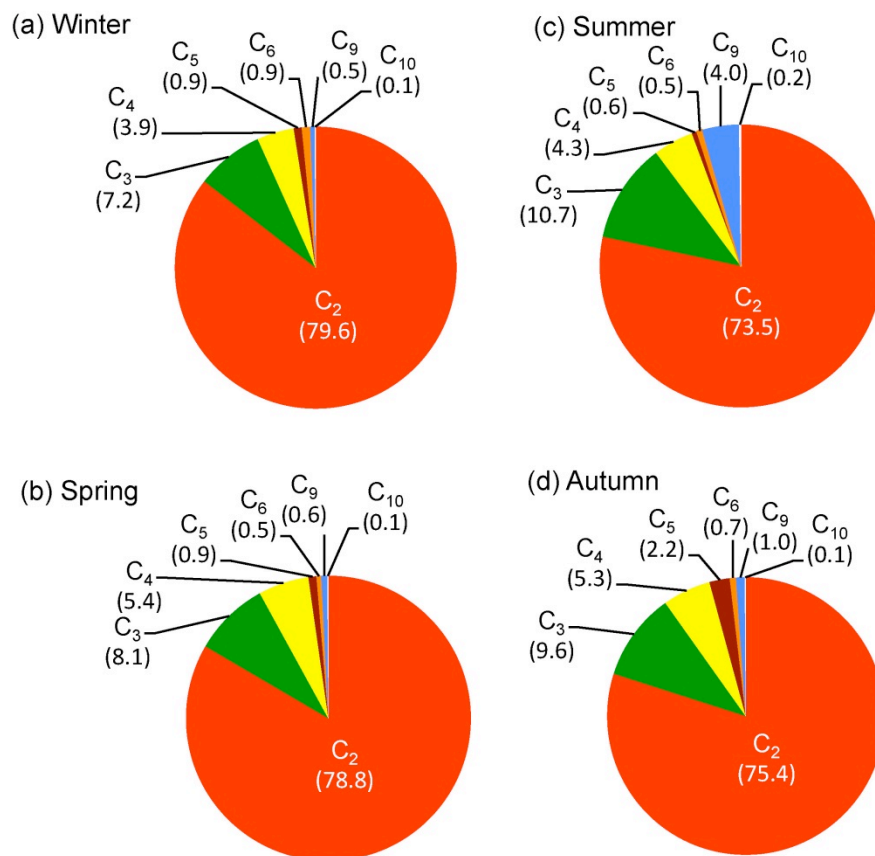


Figure 2.4. Seasonal differences in relative abundances (%) of individual diacid species in total straight-chain diacids in aerosols collected from Cape Hedo. (a) winter, (b) spring, (c) summer, and (d) autumn.

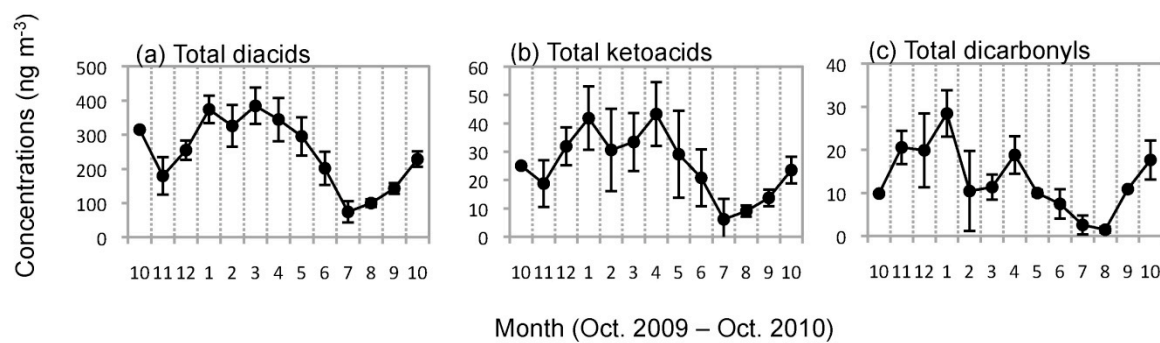


Figure 2.5. Seasonal variations in the concentration of (a) total diacids, (b) total ketoacids, and (c) total α -dicarbonyls in aerosols collected from Cape Hedo, Okinawa.

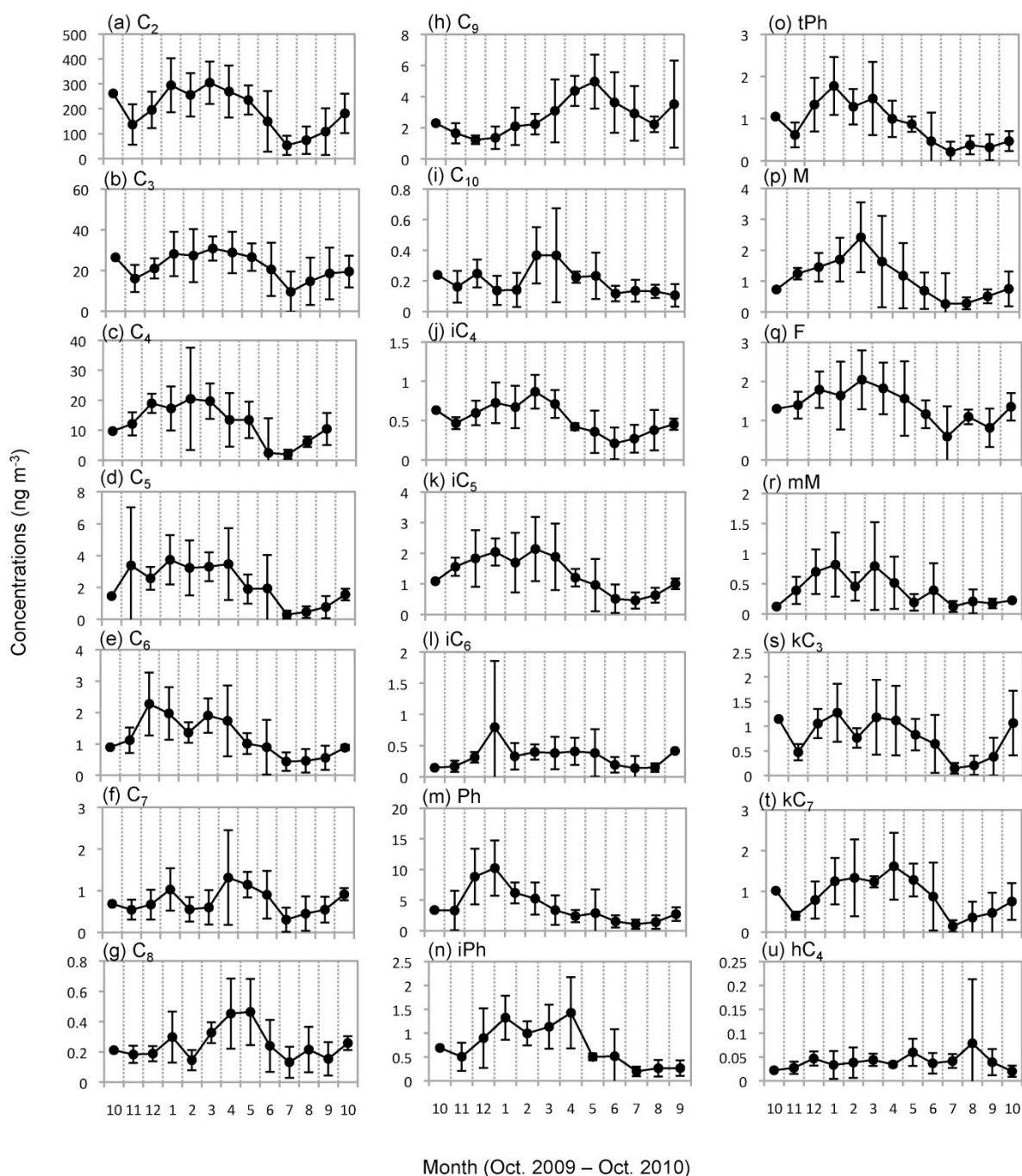


Figure 2.6. Seasonal variations of (a) oxalic acid (C_2), (b) malonic acid (C_3), (c) succinic acid (C_4), (d) glutaric acid (C_5), (e) adipic acid (C_6), (f) pimelic acid (C_7), (g) suberic acid (C_8), (h) azelaic acid (C_9), (i) sebacic acid (C_{10}), (j) methylmalonic acid (iC_4), (k) methylsuccinic acid (iC_5), (l) 2-methylglutaric (iC_6) (m) phthalic acid (Ph), (n) isophthalic acid (iPh), (o) terephthalic acid (tPh), (p) maleic acid (M), (q) fumaric acid (F), (r) methylmaleic acid (mM), (s) ketomalonic acid (kC_3), (t) 4-ketopimelic acid (kC_7), and (u) malic acid (hC_4) in the ambient aerosols from Cape Hedo, Okinawa.

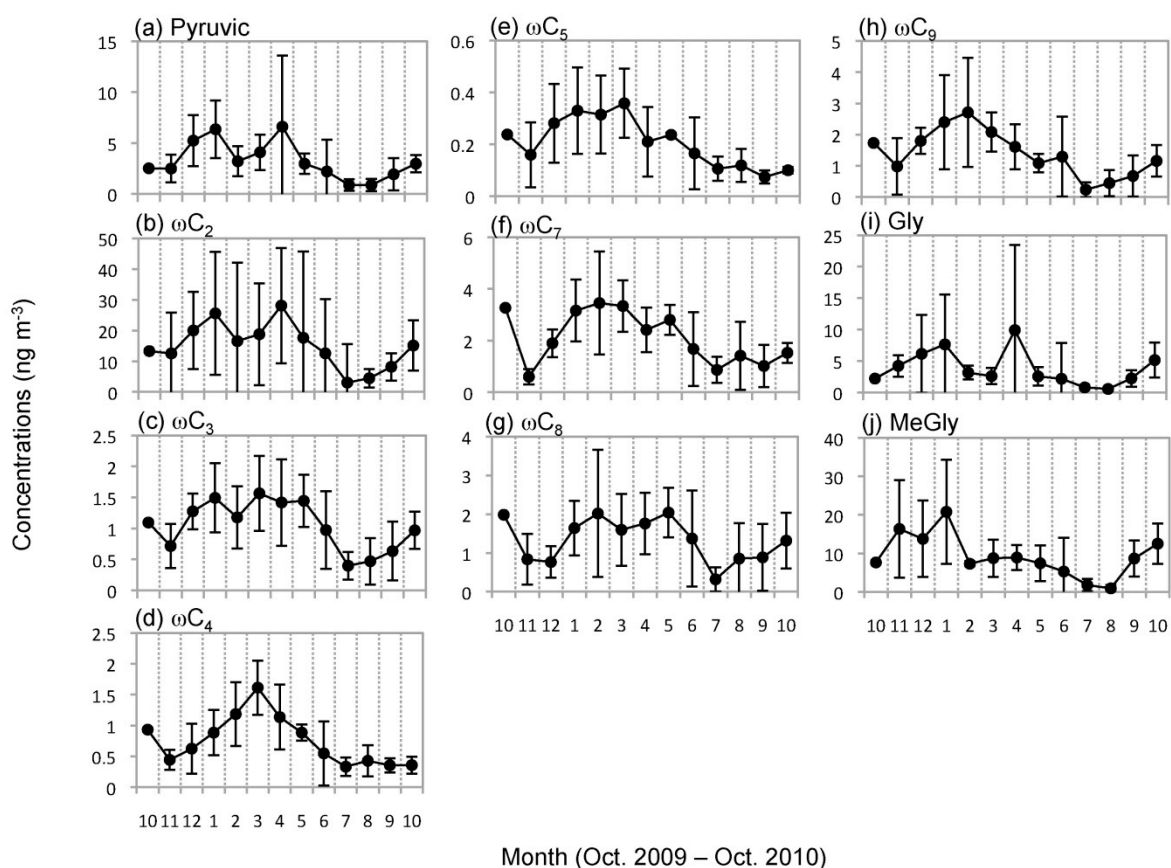


Figure 2.7. Seasonal variations of (a) pyruvic acid (Pyr), (b) glyoxylic acid (ωC_2), (c) 3-oxopropanoic acid (ωC_3), (d) 4-oxobutanoic acid (ωC_4), (e) 5-oxopentanoic acid (ωC_5), (f) 7-oxoheptanoic acid (ωC_7), (g) 8-oxooctanoic acid, (ωC_8), (h) 9-oxononanoic acid (ωC_9), (i) glyoxal (Gly), and (j) methylglyoxal (MeGly) in the ambient aerosols from Cape Hedo, Okinawa.

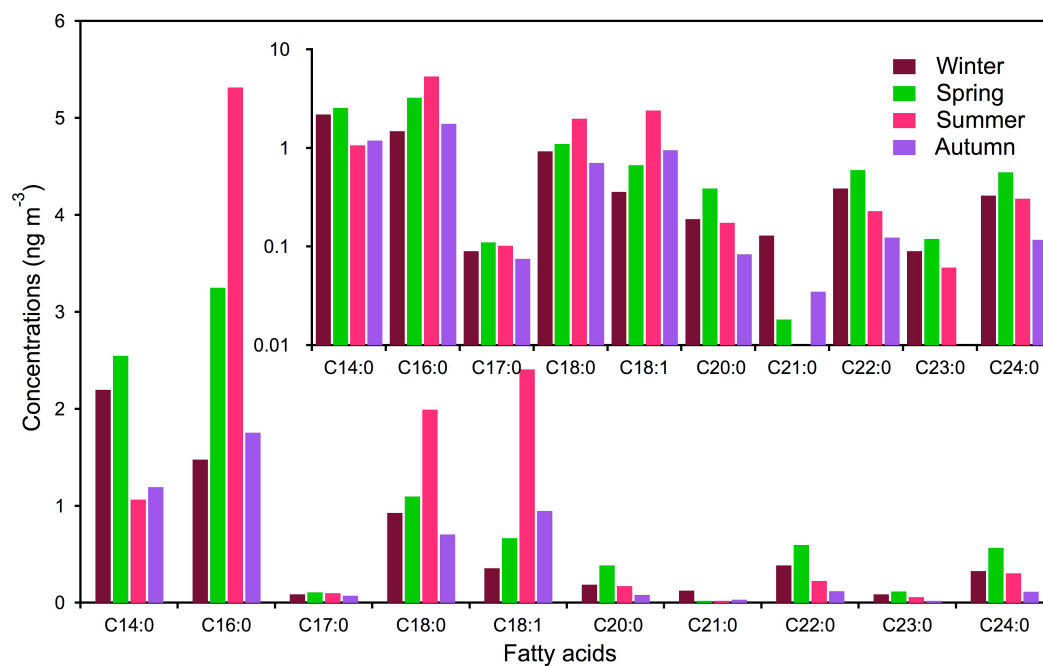


Figure 2.8. Seasonally averaged molecular distributions of fatty acids in aerosols collected from Cape Hedo, Okinawa during 2009 October to 2010 October. The first number of fatty acid indicates the number of carbon atom whereas the second number indicates the number of double bonds. Lower panel represents normal scale and upper panel represents log scale. C15:0 and C19:0 were not shown here because they were not detected in the samples.

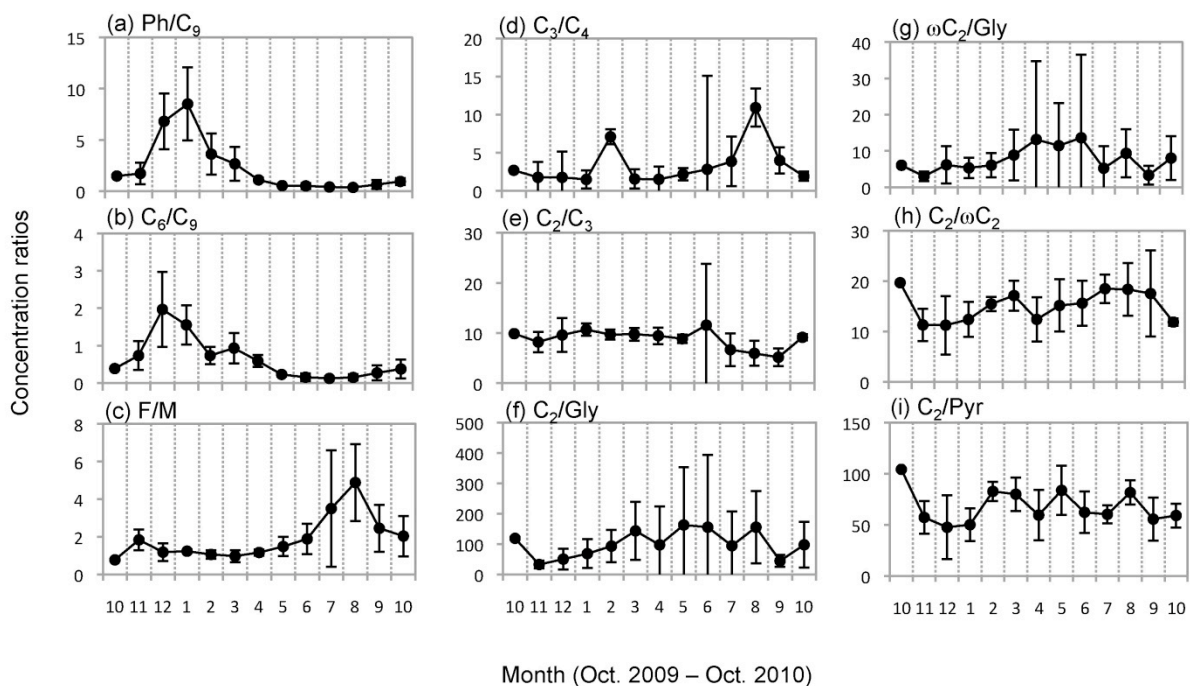


Figure 2.9. Monthly averaged seasonal variations in the concentration ratios of (a) phthalic/azelaic (Ph/C_9), (b) adipic/azelaic (C_6/C_9), (c) fumaric/maleic (F/M) (d) malonic/succinic (C_3/C_4) (e) oxalic/malonic (C_2/C_3), (f) oxalic/glyoxal (C_2/Gly), (g) glyoxylic/glyoxal ($\omega\text{C}_2/\text{Gly}$), (h) oxalic/ glyoxylic ($\text{C}_2/\omega\text{C}_2$), and (i) oxalic/pyruvic (C_2/Pyr) in the aerosols collected from Cape Hedo, Okinawa.

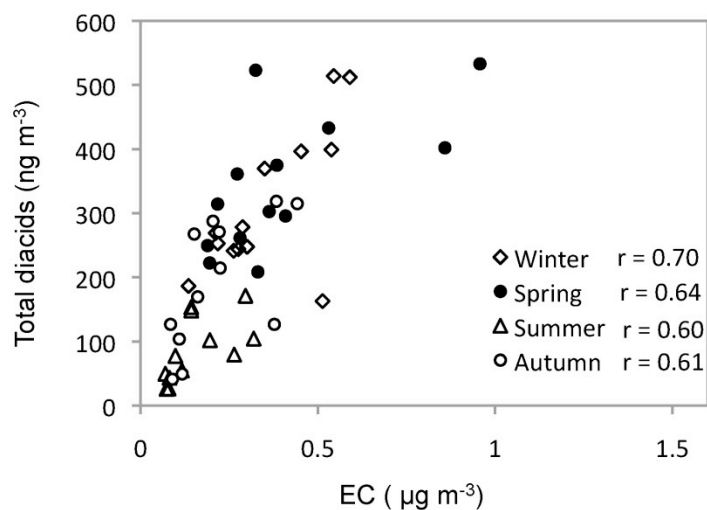


Figure 2.10. Correlation between elemental carbon (EC) and total diacids in aerosol samples collected from Cape Hedo, Okinawa.

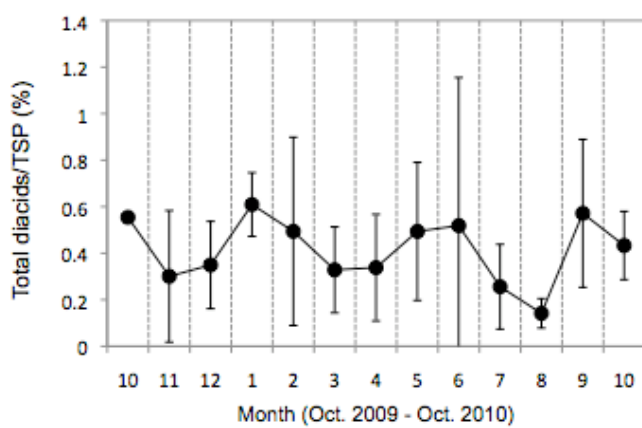


Figure 2.11. Monthly averaged variation of total diacids to total suspended particles in aerosols collected in Cape Hedo, Okinawa. The error bars represent standard deviations.

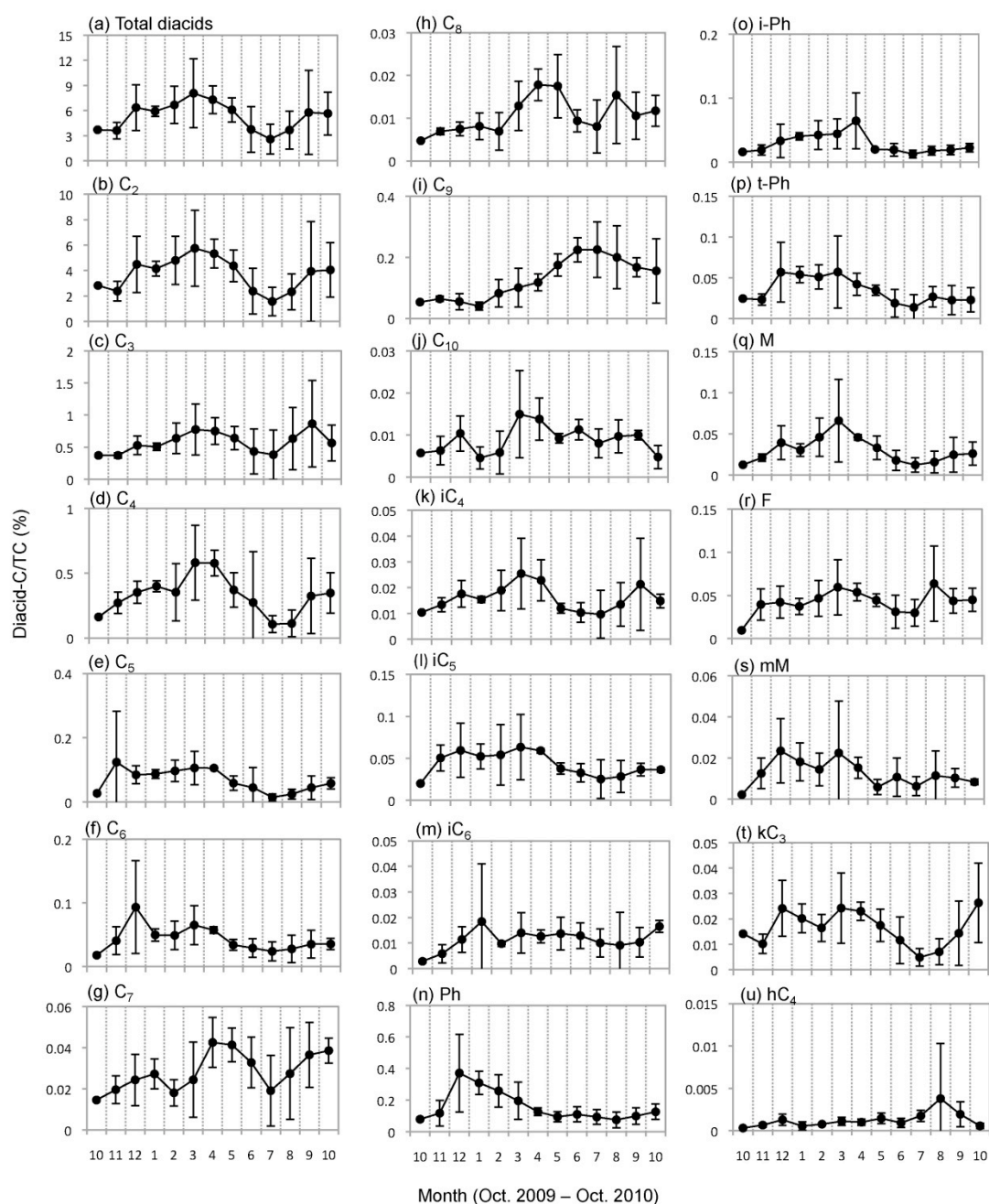


Figure 2.12. Seasonal variations in the contribution of dicarboxylic acid carbon to total carbon (TC). (a) total diacids, (b) oxalic acid (C_2), (c) malonic acid (C_3), (d) succinic acid (C_4), (e) glutaric acid (C_5), (f) adipic acid (C_6), (g) pimelic acid (C_7), (h) suberic acid (C_8), (i) azelaic acid (C_9), (j) sebacic acid (C_{10}) (k) methyl malonic acid (iC_4), (l) methylsuccinic acid (iC_5), (m) 2-methylglutaric acid (iC_6) (n) phthalic acid (Ph), (o) isophthalic acid (iPh), (p) terephthalic acid (tPh), (q) maleic acid (M), (r) fumaric acid (F), (s) methylmaleic acid (mM), (t) ketomalonic acid (kC_3), and (u) malic acid (hC_4) in the ambient aerosols from Cape Hedo, Okinawa.

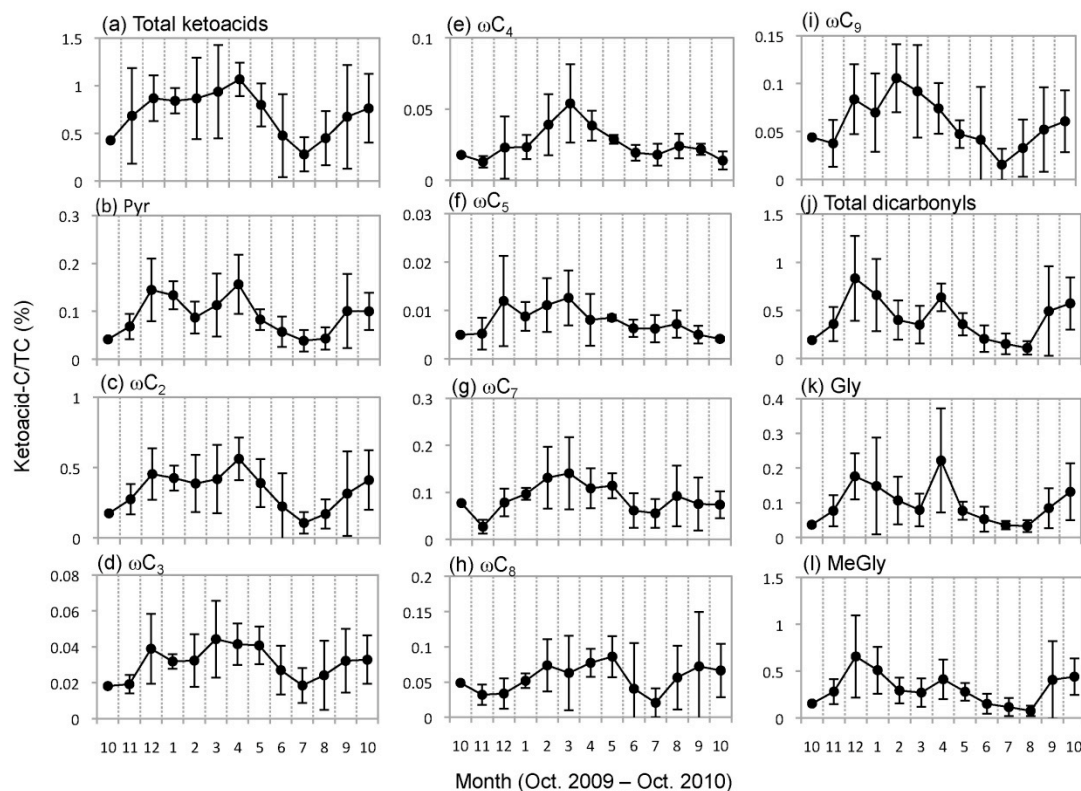


Figure 2.13. Seasonal variations of ketoacid-C and α -dicarbonyl-C to total carbon (TC) (a) total ketoacids, (b) pyruvic acid (Pyr), (c) glyoxylic acid (ωC_2), (d) 3-oxopropanoic acid (ωC_3), (e) 4-oxobutanoic acid (ωC_4), (f) 5-oxopentanoic acid (ωC_5), (g) 7-oxoheptanoic acid (ωC_7), (h) 8-oxooctanoic acid (ωC_8), (i) 9-oxononanoic acid (ωC_9), (j) total dicarbonyls, (k) glyoxal (Gly), and (l) methylglyoxal (MeGly) in the ambient aerosols from Cape Hedo, Okinawa.

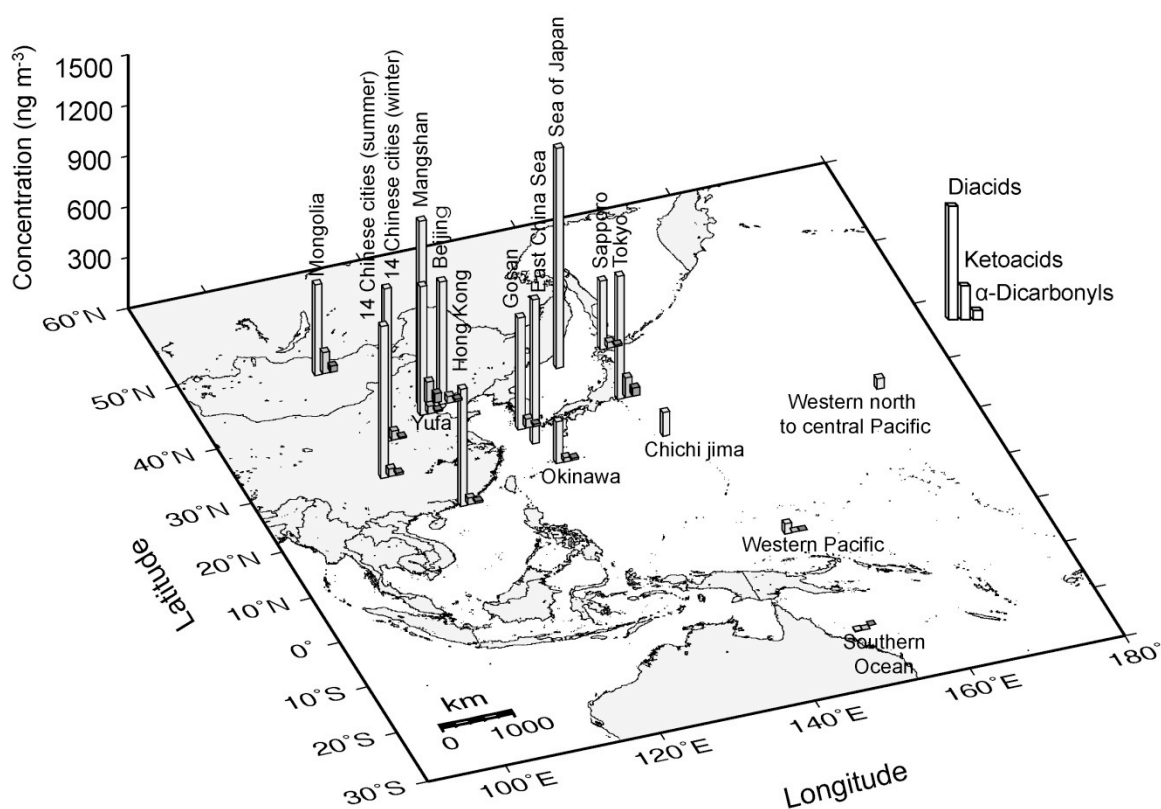


Figure 2.14. Average concentrations of diacids, ketoacids and α -dicarbonyls detected in the aerosols from different locations in East Asia and the Pacific Ocean. The average value can be obtained from Jung et al., 2010 (Mangolia), Ho et al., 2007 (14 Chinese cities during winter and summer), Ho et al., 2006 (Hong Kong road side), Ho et al., 2010 (Yufa and Beijing), He and Kawamura, 2010 (Mangshan), Kawamura et al., 2004 (Gosan), Mochida et al., 2003a (Chichijima), Mochida et al., 2003b (the East China sea and Sea of Japan), Aggarwal and Kawamura, 2008 (Sapporo), Kawamura and Yasui 2005 (Tokyo), Wang et al., 2006 (the western Pacific and Southern Ocean), Kawamura and Sakaguchi., 1999 (the western North to central Pacific).

Chapter 3: One-Year Observations of Carbonaceous and Nitrogenous Components and Major Ions in the Aerosols from Subtropical Okinawa Island, an Outflow Region of Asian Dusts

3.1. Introduction

Aerosols affect the Earth's radiative forcing directly by scattering and absorbing light and indirectly by acting as cloud condensation nuclei (Buseck and Posfai, 1999). The role of atmospheric aerosols in radiative budget, however, has not been well understood despite many studies (e.g., Ramanathan et al., 2001). Carbonaceous aerosols play major role in climate change and health effect (Folinsbee, 1992). Although EC is minor component in carbonaceous aerosols, it has positive radiative forcing at the top of the atmosphere (TOA) and negative radiative forcing at the surface (Ramanathan et al., 2001). Organic aerosols that contain water-soluble species play an important role in climate forcing (Novakov and Penner, 1993) and cloud condensation nuclei (CCN) activity (Saxena et al., 1995). Large amounts of water-soluble organic compounds including dicarboxylic acids are present in the tropospheric aerosols from urban (Kawamura and Kaplan, 1987), rural (Limbeck et al., 2001), marine (Kawamura et al., 2004), Arctic (Kawamura et al., 1996a, 2010) and Antarctic regions (Kawamura et al., 1996b), supporting that they are important chemical constituents in the atmosphere.

About one fourth of the global anthropogenic carbonaceous aerosols are emitted from China, 70% of which are originated solely from coal burning (Cooke et al., 1999). Large amounts of low quality coal are used for house heating and cooking purposes (Wang et al., 2006). Light absorbing EC and light scattering OC have been abundantly reported in Chinese aerosols (Ho et al., 2007; Cao et al., 2007), which are subjected to long-range transport over the western North Pacific. Okinawa Island is located in the outflow region of Asian aerosols and on the pathway to the Pacific. Cape Hedo is located on the northern edge of Okinawa and has been used as a supersite of Atmospheric Brown Clouds (ABC) project to study the atmospheric transport of Chinese aerosols and their chemical transformation in East Asia (Takami et al.,

2007). In the Asian Pacific region, the East Asian monsoon dominates in winter to spring, whereas the monsoon from the Pacific Ocean dominates in summer to fall (Sato et al., 2009), therefore, continental air masses from East Asian countries including Russia, Mongolia, China, and Korea generally arrive over Okinawa during winter and spring.

In this study, we report one-year observations of OC, EC, WSOC, WSTN and major ions in ambient atmospheric aerosols collected at Cape Hedo, Okinawa. We calculate water-soluble organic nitrogen (WSON) based on the difference between WSTN and inorganic nitrogen (NO_3^- and NH_4^+). We discuss the seasonal changes of these components and transformations of organic aerosol (OA) during the long-range transport of Asian aerosols. Many studies related to the atmospheric chemistry have been conducted at Cape Hedo (Sato et al., 2009; Wang et al., 2009; Zhang et al., 2003; Jaffe et al., 2005; Verma et al., 2011; Lun et al., 2009; Yamamoto and Kawamura, 2011; Ueda et al., 2011; Arakaki et al., 2006; Handa et al., 2010; Mochida et al., 2010). However, no studies were conducted for a long-term measurement of OC, EC, WSOC, WSTN, WSON and major ions in atmospheric aerosols from Cape Hedo, Okinawa Island.

3.2. Samples and Analytical Procedure

3.2.1. Sampling Site and Aerosol Collection

Using a high-volume air sampler (Kimoto AS-810B) and pre-combusted (450°C, 4 hours) quartz fiber filters (Pallflex 2500QAT, 20×25 cm), total suspended aerosol (TSP) samples (n=50) were collected on weekly basis at Cape Hedo Atmosphere and Aerosol Measurement Station (CHAAMS, 26°9'N, 128°2'E) from 2009 October to 2010 October. The sampling period of each sample was 7 days. Figure 2.1 shows a map of East Asia with the geographical location of Cape Hedo in Okinawa. CHAAMS is located at the northwestern part of Okinawa Island, Japan and it is surrounded by subtropical forest (Yamamoto and Kawamura, 2011) where local anthropogenic emissions are insignificant (Takami et al., 2007). Aerosol filter samples were placed in a preheated glass jar (150 mL) with a Teflon-lined screw cap and stored in darkness at -20°C until the analysis. Field blanks were also collected at the

site. Blank filter was placed in the filter cartridge of sampler without pumping air. After 10 seconds, field blank filter was recovered from the cartridge. Quartz fibre filters may adsorb organic vapours, causing positive artefacts on OC measurements. However, due to the relatively long sampling period (one week), we consider that the artefacts may be minimal.

3.2.2. Chemical Analysis

Before the analysis, TSP mass was gravimetrically determined at room temperature of 20°C and 50% relative humidity. However, the TSP mass may be overestimated due to the water contained in the marine aerosol filters. OC and EC were measured using a Sunset Laboratory carbon analyzer following Interagency Monitoring Protected Visual Environments (IMPROVE) thermal/optical evolution protocol (Wang et al., 2005). Presence of carbonate carbon is assumed to be negligible, except for two spring samples, which showed that the pH of the filter extracts were alkaline. A filter disk (1.5 cm² punch) was put in quartz boat inside the thermal desorption chamber and stepwise heating was applied in a helium flow at first and then after the initial ramp, helium gas was switched to He/O₂. The evolved CO₂ during the oxidation at each temperature step was measured with non-dispersive infrared (NDIR) detector system. The transmittance of light (red 660 nm) through the filter punch was used for setting up OC/EC split point and thereby OC correction. The analytical errors in duplicate analysis of the filter sample were less than 8% for OC and 5% for EC. OC and EC concentrations reported here are corrected for the field blanks.

WSOC and WSTN were determined using a Shimadzu carbon/nitrogen analyzer (TOC-V_{CSH}) (Miyazaki et al., 2011). A filter disc (3.14 cm²) was extracted with organic-free pure water under ultrasonication for 15 minutes. The water extracts were filtrated on a syringe filter (Millex-GV, 0.45 µm, Millipore). Before the analysis, the extracts were acidified with 1.2 M HCl and purged with pure air to remove dissolved inorganic carbon and volatile organics. The analytical error in triplicate analysis of laboratory standards was within 5% (Miyazaki et al., 2011).

Major cations and anions were measured using an ion chromatograph (761 Compact IC,

Metrohm, Switzerland). A sample filter disc (20 mm diameter) was extracted with organic-free pure water (10 ml) under ultrasonication (15 min $\times$ 2 times). The extracts were filtrated using a membrane disc filter (Millex-GV, 0.45 μ m, Millipore) and injected to IC for measuring major ions. 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 at a flow rate of 1.2 mL min⁻¹ as an eluent and 40 mM H₂SO₄ for suppressor. For cation measurements, a Metrosep C2-150 (Metrohm) column was used by using a mixture of 4 mM tartaric acid and 1 mM dipicolinic acid as an eluent at a flow rate of 1.0 mL min⁻¹. The injection loop volume was 200 μ L. The analytical errors in duplicate analysis of the authentic standards were within 5%. We determined total 11 ions including methanesulfonate (MSA⁻). The detection limits for anions and cations were ca. 0.1 ng m⁻³. The field blanks for Na⁺ and Ca²⁺ are 0.078 and 0.144 ng L⁻¹, respectively, whereas those for MSA⁻, Cl⁻, NO₃⁻ and SO₄²⁻ were 0.003, 0.01, 0.001 and 0.011 ng L⁻¹, respectively. Here, we report the concentrations of all species after the blank correction.

3.2.3. Estimate of organic matter and secondary organic carbon

Abundances of organic matter (OM) in the atmosphere are generally estimated by multiplying the measured OC concentrations with the conversion factor of 1.6 $\pm$ 0.2 for urban and 2.1 $\pm$ 0.2 for aged aerosols (Turpin and Lim, 2001). As mentioned above, our sampling site is located in the outflow region of East Asian aerosols and local anthropogenic activities are negligible. During the atmospheric transport, aerosols are subjected to aging processes to result in more oxygenated organic species (Kawamura et al., 2004; Kundu et al., 2010). Thus, it is better to take 2.1 $\pm$ 0.2 instead of 1.6 $\pm$ 0.2 for the Cape Hedo samples.

The contributions of the primary and secondary organic carbon (SOC) to carbonaceous aerosols are calculated by EC-tracer method. EC is used as a tracer of incomplete combustions generated from primary sources (e.g., Turpin and Huntzicker, 1991). The EC-tracer method assumes the relatively constant OC/EC ratios for given area, season and local meteorology because EC and primary OC (POC) typically have the same sources (Pavuluri et al., 2011). Thus, we can use the minimum OC/EC ratios to estimate the contribution of SOC in the

atmospheric aerosol for a specific region of interest (Castro et al., 1999). This method is also applied in several atmospheric researches (Turpin and Huntzicker, 1995; Castro et al., 1999; Pavuluri et al., 2011) although it involves some degree of uncertainty. In this study, the concentrations of SOC and POC were calculated by the following equations,

$$\text{POC} = \text{EC} \times (\text{OC/EC})_{\min} + k \quad [1]$$

$$\text{SOC} = \text{OC}_{\text{meas}} - \text{POC} \quad [2]$$

, where $(\text{OC/EC})_{\min}$ is the observed minimum OC/EC ratio during the sampling period, k is a parameter for non-combustion sources contributing to the POC that is assumed to be negligible, and OC_{meas} is the measured OC concentration. The minimum OC/EC ratios in winter, spring, summer and autumn are 3, 4, 5, and 3, respectively.

3.2.4. Estimate of sea salt and non-sea salt component

In order to determine whether it is oceanic or continental, sea salt (ss) and non-sea salt (nss) concentrations were calculated using Na^+ as a reference element. The mass concentrations of non-sea salt component X ($M_{\text{nss-x}}$) can be estimated as follows (George et al., 2008).

$$M_{\text{nss-x}} = M_x - (\text{X/Na})_{\text{sw}} \times M_{\text{Na}}$$

, where M_x and M_{Na} mean the total mass loading of X and Na, respectively. $(\text{X/Na})_{\text{sw}}$ represents the mass ratio of species X to Na in seawater. The ratios of X/Na for SO_4^{2-} , K^+ , Ca^{2+} and Mg^{2+} are 0.25, 0.037, 0.038 and 0.12, respectively, assuming that sea salt is the only source of water-soluble Na^+ (Berg and Winchester, 1978). By using above equation, the mass concentrations of ss- and nss- SO_4^{2-} , K^+ , Ca^{2+} , and Mg^{2+} are calculated.

3.2.5. Estimate of chlorine loss

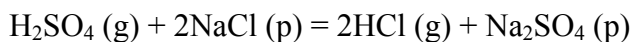
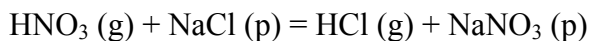
Chlorine depletion can be estimated using following formula (Yao and Zhang, 2012).

$$\text{Cl}_{\text{loss}} (\mu\text{g m}^{-3}) = 1.798 \times [\text{Na}^+]_{\text{measured}} - [\text{Cl}^-]_{\text{measured}}$$

$$\text{Cl}_{\text{loss}} (\%) = [\text{Cl}_{\text{loss}}]/1.798[\text{Na}^+]_{\text{measured}} \times 100$$

, where $[\text{Na}^+]_{\text{measured}}$ and $[\text{Cl}^-]_{\text{measured}}$ represent measured concentrations of Na^+ and Cl^- in $\mu\text{g m}^{-3}$, respectively. The mass concentration ratio of Cl^- to Na^+ in seawater is 1.798 (George et al.,

2008). The following two reactions are associated with the loss process of Cl.



3.2.6. Backward Air Mass Trajectory Analysis

Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) model (<http://www.arl.noaa.gov/ready/hysplit4.html>) was used to find the source regions of air masses at Okinawa during one-year campaign (Draxler and Rolph, 2003). 5-day back trajectory analysis at 500 meter above the ground was performed every day using the HYSPLIT model. Figure 2.2 shows the 5-day air mass trajectories for winter, spring, summer and autumn seasons. In spring and winter, Cape Hedo was strongly influenced by continental air masses (Figure 2.2a and 2.2b). In contrast, in summer, the site was covered with oceanic air masses (Figure 2.2c) whereas in autumn it was affected by both oceanic and continental air masses (Figure 2.2d). As described previously, the sampling period is 7 days for each sample. Thus, each sample contains mixed air masses from continent and ocean.

3.3. Results and Discussion

3.3.1 Aerosols mass loading

The aerosol mass loading at Okinawa ranged from 19.2 to 286 $\mu\text{g m}^{-3}$ with an average of 74.3 $\mu\text{g m}^{-3}$ during one-year observation period. Figure 3.1 shows the monthly averaged aerosol mass concentrations at Okinawa with error bars denoting the standard deviation. The average mass concentration shows a peak ($109 \pm 69.9 \mu\text{g m}^{-3}$) during spring season (March, April and May) and decrease towards the summer ($44 \pm 36 \mu\text{g m}^{-3}$). The westerly winds are responsible for such a high peak in spring, by uplifting the mineral dusts from the arid regions in China and Mongolia followed by a transport to the Pacific together with pollutants emitted from Chinese cities. During the Asian dust outflow, crustal elements (calcium, iron, aluminium, barium, etc.) are abundant in dust particles and loess deposits (Nishikawa et al., 2000). A good correlation between Ca^{2+} and TSP ($r=0.81$) in spring suggests that the spring

aerosols are significantly influenced by dust particles from arid regions in China and Mongolia. During spring, Asian dust is the source of Ca^{2+} . Air mass back trajectories also demonstrated that in spring, air masses mostly originated from the arid regions of the Asian continent.

3.3.2. Seasonal Variations of Carbonaceous and Nitrogenous Components

Table 3.1 gives the concentrations of carbonaceous components with statistical summaries in the TSP samples ($n=50$) collected from Cape Hedo, Okinawa. Their monthly variations are shown in Figure 3.2. The average concentrations of OC, EC, WSOC and WSTN ranged from 0.76 to 7.12 $\mu\text{g m}^{-3}$ (av. 1.78 $\mu\text{g m}^{-3}$), 0.07-0.96 $\mu\text{g m}^{-3}$ (0.28 $\mu\text{g m}^{-3}$), 0.27-1.9 $\mu\text{g m}^{-3}$ (0.73 $\mu\text{g m}^{-3}$) and 0.07-3.02 $\mu\text{g m}^{-3}$ (0.58 $\mu\text{g m}^{-3}$), respectively. Seasonally average concentration of OC was found highest in spring (2.36 $\mu\text{g m}^{-3}$) followed by summer (1.79 $\mu\text{g m}^{-3}$) and winter (1.53 $\mu\text{g m}^{-3}$) whereas the lowest concentration was observed in autumn (1.42 $\mu\text{g m}^{-3}$). Similarly, the highest concentrations of EC and WSOC were found in spring (0.41 $\mu\text{g m}^{-3}$ and 0.95 $\mu\text{g m}^{-3}$) followed by winter (0.70 and 0.90 $\mu\text{g m}^{-3}$). In contrast, the lowest concentrations of EC and WSOC were obtained in summer (0.19 and 0.52 $\mu\text{g m}^{-3}$).

OC showed higher concentration during winter in Chinese aerosols (Wang et al., 2011; Cao et al., 2007; 2003; Ho et al., 2007) because low quality coals are commonly used for heating and cooking purposes. Very high concentration of OC was reported in winter than spring in urban regions of China (Wang et al., 2011). In contrast, we found higher concentration of OC in spring although most of the air parcels came from China, suggesting the additional contribution to OC from biogenic sources because biogenic emissions are significant in spring season (Pavuluri et al., 2010). The springtime maxima of OC (Figure 3.2a) and WSOC (Figure 3.2c) suggest that they are formed by extensive photochemical oxidation of various organic precursors emitted from fossil fuel combustion and biomass burning as well as biogenic volatile organic compounds (BVOCs) from terrestrial plants. Wang et al. (2011) reported the levoglucosan concentration during spring season from Cape Hedo. EC also maximized in spring followed by winter, suggesting significant contributions of EC from China through long-range atmospheric transport by westerly winds. Water-insoluble organic

carbon ($\text{WIOC} = \text{OC} - \text{WSOC}$) showed the highest concentration in spring ($1.41 \mu\text{g m}^{-3}$) followed by summer ($1.27 \mu\text{g m}^{-3}$).

EC and WSOC show similar seasonal variations (Figure 3.2b, and 3.2c), suggesting that they are formed from similar sources. The average highest concentration of primary organic carbon (POC) is found in spring followed by winter whereas the higher concentration of secondary organic carbon (SOC) was found in spring and summer, as shown in Figure 3.2e and 2f. The highest concentration of SOC was observed in March with an increase toward July. The average highest concentration of SOC in summer may be caused by photochemical oxidation of organic precursors under a strong solar radiation as well as emission of marine volatile organic carbon (Shaw et al., 2010). The higher wind speed during spring may be responsible for higher POC concentration.

WSTN showed higher concentrations during winter ($0.86 \mu\text{g m}^{-3}$) followed by spring ($0.77 \mu\text{g m}^{-3}$) although the concentrations during spring months are almost constant whereas they showed lower concentrations during summer and autumn (0.37 and $0.34 \mu\text{g m}^{-3}$). The higher concentration of WSTN during winter suggests that WSTN is abundantly present in polluted air. Meanwhile, concentrations of water-soluble organic nitrogen ($\text{WSO} = \text{WSTN} - \text{NO}_3\text{-N} - \text{NH}_4\text{-N}$) ranged from 0 to $2.2 \mu\text{g m}^{-3}$ (av. $0.11 \mu\text{g m}^{-3}$). WSON comprised on average 18.9% of WSTN. Marine organisms are probably the main sources of WSON. Terrestrial and marine organisms emit nitrogenous components, which contain certain amount of WSON (Wang et al., 2013a). Marine bacteria and degraded proteins are the sources of WSON (Wedyan and Preston, 2008). Marine biota also can emit amino acids, urea and proteins. WSON is emitted to the atmosphere by bubble bursting process in the ocean surface (Cape et al., 2011). We found the highest concentration of WSON in summer (av. $0.21 \mu\text{g m}^{-3}$) followed by spring (0.13) and autumn (0.07) and lowest concentration in winter (0.06). The summertime maximum of WSON suggests that they are emitted from marine biota.

We found that the contribution of OM to TSP is on average $6.27 \pm 3.7\%$. The highest average contribution of OM to TSP was found in summer (9.5%) followed by autumn (5.31%) and spring (4.85%), and the lowest (4.48%) in winter (Figure 3.3). The contribution of WSOM

to TSP was found highest in winter (2.71%) followed by summer (2.60%). In contrast, the contribution of WIOM (water insoluble organic matter) to TSP became highest in summer (6.9%), suggesting more emission of WIOM in summer probably from biological sources (Miyazaki et al., 2011). The average contribution of EC to TSP was found highest in winter (0.54%), and lowest in summer (0.42%). In this study, a strong correlation was found between OC and EC in winter ($r=0.93$) and spring (0.81), suggesting that they are formed from similar sources (Turpin et al., 1991). However, such a strong relation was not found in summer (0.44) (Figure 3.4), indicating that OC has at least two independent sources that distort the correlation. During winter and spring, our sampling site is significantly influenced by the outflow of polluted air masses from East Asian countries, thus we obtained strong correlation between OC and EC. However, in summer, anthropogenic contributions are negligible in Cape Hedo, hence the correlation between OC and EC is rather weak.

3.3.3. Seasonal Variations of OC/EC and WSOC/OC Ratios

OC/EC ratio has been used to study the emission and transformation characteristics of carbonaceous aerosols (Cao et al., 2003). The OC/EC ratios exceeding 2.0 have been considered to indicate the contribution of secondary organic aerosols (Cao et al., 2003). In our study, OC/EC ratios ranged from 3.5 to 21 with average of 7.6 ± 4.7 . The season-averaged OC/EC ratios are 4.4 (winter), 5.7 (spring), 12.5 (summer) and 7.7 (autumn). Most of the world's urban OC/EC ratios range from 1 to 4 (Turpin et al., 1991). A ratio of 4.0 is also assumed for emissions from fossil fuel combustion (Koch, 2001). The average ratio is still higher in spring than winter although EC showed higher concentration in spring. The OC/EC ratios obtained in this study, except for summer samples, are comparable to those from Mongolia and Chinese cities (Jung et al., 2010; Cao et al., 2007). Compared to the world's urban OC/EC ratios, our summer OC/EC ratio (12.5) is extremely high, suggesting an extra source of OC from the ocean and/or secondary OC formation via the oxidation of BVOCs in summer. Tambunan et al. (2006) showed that the emissions of isoprene and other BVOCs maximize in Okinawa during summer. Generally, their emissions are higher in summer (Kim et

al., 2005).

Figure 3.5a shows the monthly variation of OC/EC ratios. In November we obtained relatively high OC/EC ratio. This may be caused by long-range atmospheric transport of biomass burning plumes from Southeast Asia because biomass burning is very common in the region in autumn (Wang et al., 2013b) and the air masses mostly came from Southeast Asia including Philippines (Figure 2.2d). OC/EC ratios from biomass burning give higher values of 5 to 8 (Andreae and Merlet, 2001). We found a strong correlation ($r=0.87$) between OC and biomass burning tracer (nss-K^+) in autumn, indicating a significant influence of biomass burning on organic aerosols. The enhanced OC/EC ratios were found in summer with a peak in July. The summer maximum may be caused by the secondary formation of OC via the oxidation of various VOCs during long-range atmospheric transport. Cao et al. (2005) showed that aerosols from residential coal combustion contain high OC/EC ratio (12). The average OC/EC ratios for winter (4.4) and spring (5.7) samples are comparable with the value (3.8) reported in 14 Chinese cities (Cao et al., 2007), indicating that our sampling site is significantly influenced by anthropogenic aerosols from China.

WSOC to OC ratio is useful to discuss the potential sources (Jung et al., 2010) and to understand photochemical oxidation (Miyazaki et al., 2010b) and extent of gas to particle formation of secondary WSOC (Hagler et al., 2007). Figure 3.5b shows the monthly averaged variation of WSOC/OC. The annual average ratio in Cape Hedo was $43 \pm 15\%$ (range, 15 to 90%). This value is lower than the ratios reported in Mongolian aerosols (31-97%, av. 53%) (Jung et al., 2010), Christchurch, New Zealand (48%, Wang et al., 2005) but similar to those from Sapporo, Japan (44%, Aggarwal and Kawamura, 2008) and from 14 Chinese cities (summer 48% and winter 40%, Ho et al., 2007). However, lower WSOC/OC ratios were reported from Gosan, Korea (30%) during the ABC campaign (Miyazaki et al., 2007), from New Delhi, India (25%) in nighttime (Miyazaki et al., 2009), and from Tokyo (summer 20% and winter 35%, Miyazaki et al., 2006). Mayol-Bracero et al. (2002) reported higher WSOC/OC ratios (45%–75%) in biomass burning aerosols over Amazonia. The smouldering biomass combustion produces WSOC abundantly (Andreae et al., 1996). The higher

WSOC/OC ratio in winter (Figure 3.5b) suggests that significant fractions of organic aerosols were derived from biomass burning together with atmospheric oxidation of fossil fuel combustion products.

Kawamura et al. (2010) reported an increase of WSOC/TC ratios in the Arctic aerosols after polar sunrise due to extensive photochemical oxidation of organic precursors. The enhanced WSOC/OC ratios (av. 81%) were also reported for summit Greenland aerosol (Hagler et al., 2007). We found highest WSOC/OC ratios in winter (60%) followed by spring (45%) and autumn (41%). The lowest WSOC/OC ratio was observed in summer (28%). The low ratio in summer may be caused by the sea-to-air emissions of water-insoluble organic compounds that are produced by marine phytoplankton, because the summertime air masses are derived from the oceanic region (Figure 2.2c). Miyazaki et al. (2010b) reported high abundance of WIOC in the western North Pacific during summer. The highest ratios in winter (60%) may be due to the enhanced oxidation of primary organic compounds during long-range atmospheric transport and/or gas-to-particle conversion of anthropogenic semi-volatile polar compounds (Kawamura et al., 2010).

The previous studies of East Asian aerosols often showed wintertime maxima of OC. However, it is not the case in our samples from Cape Hedo. Table 3.3 compares the concentration of OC and EC together with OC/EC ratios in East Asia. The annual average concentration of OC in Cape Hedo ($1.78 \mu\text{g m}^{-3}$) is significantly less than those reported in Mongolia during winter (Jung et al., 2010), Chinese cities (Cao et al., 2007), Pearl Delta region, China (Cao et al., 2003), Kaohsiung, Taiwan (Lin and Tai, 2001) and Seoul, Korea (Park et al., 2002), and is also lower than that of Jeju Island (Lee et al., 2001) where Asian outflow is important. Based on these comparisons, we can insist that concentrations of OC decrease during long-range atmospheric transport via atmospheric dilution and/or dry and wet scavenging. The major sources of carbonaceous components include industrial and vehicular emissions, fossil fuel combustions and biomass burnings in East Asia (Wang et al., 2006).

3.3.4. Seasonal Variations of Inorganic Species

The statistical summaries of water-soluble ionic species in the marine aerosol samples from Okinawa are given in Table 3.2. Their seasonal variations of cations and anions are shown in Figure 3.6. The dominant cation in our samples was Na^+ followed by Mg^{2+} and Ca^{2+} . The annual average concentrations of Na^+ , Mg^{2+} and Ca^{2+} are 5.78, 0.71 and 0.66 $\mu\text{g m}^{-3}$, respectively, whose relative contributions to total aerosol mass are 9.3, 1.1 and 0.8%, respectively. The dominant anion was Cl^- followed by SO_4^{2-} and NO_3^- . Their annual average concentrations are 10.8, 2.4 and 1.6 $\mu\text{g m}^{-3}$, respectively, whose relative contributions to total aerosol mass were 17.1, 3.7 and 2.5%, respectively. Similarly, the contributions of Na^+ and Cl^- to total ions were on average 26.2% and 47%, respectively. Average concentration of Cl^- is 6 times higher than that of OC, suggesting that inorganic loading is very important throughout the year. MSA^- , a tracer of marine biogenic sources, showed high concentration in spring, suggesting the emissions from biogenic marine sources. The summertime concentration of MSA^- in Cape Hedo is comparable with those in the western North Pacific during summer (Miyazaki et al., 2010a). Similarly, nss-K^+ , a tracer of biomass burning, showed a good correlation with OC in winter (0.72) and spring (0.65). The stronger correlation in winter suggests that biomass burning significantly contributes in winter than spring. Most cations and anions showed the highest concentrations in winter months and the lowest in summer (Figure 3.6).

The relative abundances of NO_3^- , SO_4^{2-} , NH_4^+ in TSP showed a maximum in winter. These results suggest that contributions from fossil fuel combustion, industrial emission, and biomass burning are significant (Kundu et al., 2010) as well as animal excreta for NH_3 (Pavuluri et al., 2011). In contrast, relative abundances of Ca^{2+} in TSP maximized in spring (Figure 3.6d), suggesting a significant influence from crustal dust during spring. Concentrations of Ca^{2+} (a tracer of crustal material) also maximized in spring.

3.4.1. Ion Balance and Correlations among Major Ions

Ion balance calculation is used to evaluate the ion deficit between cations and anions in aerosols (Pavuluri et al., 2011). The following equations are used to derive the charge balance

between cations and anions.

$$\text{Cation equivalents} = [\text{Na}^+]/23 + [\text{NH}_4^+]/18 + [\text{K}^+]/39 + 2x[\text{Mg}^{2+}]/24 + 2x[\text{Ca}^{2+}]/40$$

$$\text{Anion equivalents} = 2x[\text{SO}_4^{2-}]/96 + [\text{NO}_3^-]/62.04 + [\text{Cl}^-]/35.5 + [\text{Br}^-]/79.9 + [\text{MSA}^-]/95.1 + 3x[\text{PO}_4^{3-}]/94.8$$

Average equivalent ratios of total cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) to total anions (SO_4^{2-} , NO_3^- , Cl^- , Br^- , MSA^- and PO_4^{3-}) were 0.96 with standard deviation of 0.14 (n=50) as shown in Figure 3.7. The slope (0.87) of less than 1 indicates that almost all of the ions had been quantified, although CO_3^{2-} , HCO_3^- , H^+ and organic anions were not determined.

Because the concentration of the ions emitted from the same source or similar reaction pathway should show a good correlation, correlation analyses among the ions would provide important information for their sources. Tables 3.4, 3.5, and 3.6 show the results of correlation analyses of major ions for winter, spring, and summer, respectively. Throughout the year, we found strong correlations among Na^+ , sea salt (ss)- K^+ , ss- Ca^{2+} , ss- Mg^{2+} , ss- SO_4^{2-} and Cl^- , indicating that these ions are derived from the sea spray.

In winter, NO_3^- , a tracer of anthropogenic source, strongly correlates with NH_4^+ , nss- K^+ , and well correlates with nss- Mg^{2+} (Table 3.4), suggesting that they are derived from anthropogenic sources in the Asian Continent. In spring, we did not find any significant correlation between Na^+ and NO_3^- (Table 3.5). However, nss- Ca^{2+} , a tracer of crustal dust, was found to well correlate with nss- K^+ and nss- Mg^{2+} , indicating that they are derived from similar sources or reaction pathways. There is no correlation between nss- Ca^{2+} and Na^+ in spring (Table 5). In summer, NO_3^- showed a strong correlation with nss- Mg^{2+} and nss- SO_4^{2-} (Table 3.6), suggesting that they are formed from similar sources and/or reaction pathways. Both NO_3^- and nss- SO_4^{2-} are produced by photochemical reactions in the atmosphere (Pavuluri et al., 2011). It should be noted that ss- SO_4^{2-} showed good correlations with NH_4^+ and NO_3^- as well as other anthropogenic tracers (nss- K^+ , nss- Mg^{2+}) during winter and spring (Tables 3.4 and 3.5). NH_3 and HNO_3 probably react with sea salt in the marine atmosphere.

3.4.2. Sea Salt and Non-Sea Salt Ions

Sea salt is the major component in the marine and coastal aerosols (George et al., 2008; Prospero, 2002). Na^+ is used as a tracer to evaluate the contributions of sea salt to aerosols. The equivalent ratio of Cl^- to Na^+ is 1.16 in seawater. We estimated equivalent ratios of Cl^-/Na^+ in each samples and compared with seawater. Figure 3.8 presents scatter plots of Na^+ and Cl^- concentration for different seasons. Throughout the year, only few data points are found to locate below the sea water line, indicating that the loss of Cl was insignificant except for spring samples. Chlorine loss has been observed in many coastal regions and open oceans (Meinert and Winchester, 1977; George et al., 2008; Yao and Zhang, 2012). In some spring samples, estimated chlorine loss was up to 50%, indicating that vigorous reaction occurs between gaseous HNO_3 and H_2SO_4 , and NaCl to emit gaseous HCl (McInnes et al., 1994) in spring.

Ions such as SO_4^{2-} , K^+ , Ca^{2+} , and Mg^{2+} have multiple sources, i.e., oceanic and continental. Additionally, SO_4^{2-} has another oceanic, but nss-source generated by the oxidation of dimethyl sulphide (DMS) that is emitted from the phytoplankton in the sea surface (George et al., 2008; Savoie et al., 1994). Figure 3.9 shows the monthly variation of ss- and nss-species. ss- Mg^{2+} and K^+ dominate over the nss forms. Interestingly, nss- Ca^{2+} dominated over the ss- Ca^{2+} until May with maxima in March and April while after June it was replaced by the ss- Ca^{2+} (Figure 3.9b). Major fraction of Ca^{2+} should be derived from Asian dusts in winter and spring (Kawamura et al., 2004). The percentage of nss- Ca^{2+} to total Ca^{2+} was found highest in winter (62%) to spring (71.5%) and decreases towards summer (31.1%). In spring, the air masses uplift the crustal dust in East Asia and transport over the sampling site. We found strong correlation between nss- Ca^{2+} and TSP ($r=0.81$) in spring, suggesting that crustal dust from East Asia is the main source of TSP. Similar strong correlation was found between nss- Ca^{2+} and TSP in Gosan site, Jeju Island (Kawamura et al., 2004). However, for the rest of the year, we did not find any good correlation between nss- Ca^{2+} and TSP.

Similarly, the contribution of nss- K^+ to total K^+ was found highest in winter (40.6%) to spring (46.2%) with a decrease toward summer (37.1%). K^+ is a tracer of biomass burning (Kundu et al., 2010) whereas EC is a tracer of incomplete combustions of fossil fuel and biomass burning. We found a strong relation between nss- K^+ and EC ($r=0.80$) (Figure 3.10),

indicating that the major fraction of EC is formed by biomass burning. The contribution of nss-Mg²⁺ to total Mg²⁺ increased in winter (30.9%) to spring (35.8%) and decreased in summer (27.4%). Because Mg is also found in the crustal dust (Wang et al., 2010), this study again indicates that our sampling site is strongly influenced by Asian dust in spring. Although all the air masses come from the ocean in summer, the loading of sea salt components maximized in winter and spring and became lowest in summer. In winter and spring when westerlies became strong, continental air masses that stayed over the ocean for few days were mixed with marine aerosols according to the backward trajectory analysis.

3.4.3. Anthropogenic Aerosols and Ionic Composition

nss-SO₄²⁻ in the atmosphere is derived from many sources. It can originate from mineral dusts from the desert/arid region, and combustion of fossil fuels. We found the highest concentration of nss-SO₄²⁻ in winter (av. 1.74 µg m⁻³) followed by spring (1.38 µg m⁻³) and the lowest value in summer (0.51 µg m⁻³). The higher nss-SO₄²⁻ concentration in winter and spring suggest that the air quality of Cape Hedo is strongly influenced by fossil fuel combustions and industrial emissions in East Asia via a long-range atmospheric transport. However, we also suspect ship emissions of nss-SO₄²⁻ in the East China Sea during winter and spring. NO₃⁻ is a tracer of anthropogenic activities and is derived from coal combustions, biomass burning and vehicular emissions (Kundu et al., 2010). We found a positive correlation between NO₃⁻ and biomass burning tracer (nss-K⁺) (r=0.65) in winter, suggesting that NO₃⁻ is associated with biomass burning.

To better understand the sources of nitrogenous components, we calculated NH₄-N/WSTN and NO₃-N/WSTN ratios. We found that NH₄-N/WSTN ratios maximized in winter (0.56) followed by spring (0.42), suggesting that biomass burning is important sources of WSTN in winter. Similarly, NO₃-N/WSTN showed higher ratios in spring (0.51) followed by winter (0.44) and autumn (0.18). Lowest values of NH₄-N/WSTN (0.07) and NO₃-N/WSTN (0.11) were obtained in summer due to less chance for the continental outflow of polluted air masses.

3.4.4. Neutralization Factor and Ionic Composition

The acid neutralization capacity of desired cation is estimated by neutralization factor (NF). NO_3^- and SO_4^{2-} , which are formed by secondary oxidation of NO , NO_2 and SO_2 , are major acid-producing anions, whereas Ca^{2+} , Mg^{2+} , NH_4^+ and K^+ are the cations that neutralize acids. The role of Cl^- in acid production is negligible because Cl^- mainly comes from the ocean as sea salt. We calculated NF and using following formula (Keene et al., 1986).

$$\text{NF} (\text{Ca}^{2+}) = [\text{nss-Ca}^{2+}] / ([\text{NO}_3^-] + [\text{nss-SO}_4^{2-}])$$

$$\text{NF} (\text{Mg}^{2+}) = [\text{nss-Mg}^{2+}] / ([\text{NO}_3^-] + [\text{nss-SO}_4^{2-}])$$

$$\text{NF} (\text{K}^+) = [\text{nss-K}^+] / ([\text{NO}_3^-] + [\text{nss-SO}_4^{2-}])$$

$$\text{NF} (\text{NH}_4^+) = [\text{NH}_4^+] / ([\text{NO}_3^-] + [\text{nss-SO}_4^{2-}])$$

We found that NH_4^+ plays a major role in the neutralization of acidic species. The order of NF is $\text{NH}_4^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$. The NF of NH_4^+ and Ca^{2+} were found highest in winter followed by spring, suggesting that all the acidic species were neutralized with CaCO_3 , MgCO_3 and NH_4^+ . Ca^{2+} and SO_4^{2-} show positive correlation ($r=0.77$), suggesting that these ions mainly exist as CaSO_4 . The mean Ca^{2+} to SO_4^{2-} mass ratio in our samples is 0.53, being similar to the ionic mass ratio of 0.41 in CaSO_4 . NH_4^+ and SO_4^{2-} showed a good correlation ($r=0.87$) with the mean NH_4^+ to SO_4^{2-} ratio of 0.2, which lies in between the NH_4^+ to SO_4^{2-} mass ratios (0.37) and NH_4^+ to HSO_4^- mass ratio (0.18). This result indicates that NH_4^+ and SO_4^{2-} exist in the form of $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 and/or the combination of the two forms. Among these forms, the dominant composition may be NH_4HSO_4 because the measured mass ratios (0.2) is closer to the mass ratio of NH_4HSO_4 rather than that of $(\text{NH}_4)_2\text{SO}_4$.

4. Summary and Conclusions

We conducted one-year observation of chemical compositions in aerosol (TSP) samples collected in Okinawa Island, which is located in an outflow region of Asian dusts. The highest aerosol mass loading and highest concentration of nss-Ca^{2+} in spring are caused by strong westerly winds, which uplift the mineral particles from the arid regions in China and Mongolia

and then transport over the Pacific.

In contrast to East Asia (wintertime maximum), we found higher concentration of OC in spring (av. $2.36 \mu\text{g m}^{-3}$) than winter (av. $1.53 \mu\text{g m}^{-3}$). Higher concentration of OC was obtained during active biota seasons; spring and summer ($1.79 \mu\text{g m}^{-3}$). We also determined WSTN and WSON. Higher concentrations of WSTN were found in winter and higher WSON concentrations were found in summer, suggesting more emissions of water-soluble organic nitrogen from the ocean.

Springtime maxima of OC/EC ratios, MSA^- and correlation coefficients of OC and EC ($r = 0.81$), and MSA^- (0.81) showed an importance of terrestrial and marine biogenic sources as well as anthropogenic sources in spring although the contribution from biogenic source is less significant. Similarly, moderate positive correlation between OC and nss-K^+ was found in both winter ($r = 0.72$) and spring (0.65), suggesting that biomass burning contribution is higher in winter season followed by spring. We found an extremely higher OC/EC ratio and strong correlation between OC and MSA^- (0.71) in summer, further suggesting a strong biogenic emission of OC coupled with photochemical formation of SOC in hot season. The highest SOC concentration in July suggests the oxidation of organic compounds under strong solar radiation. Very high WSOC/OC ratios (0.6) found in winter suggest an important contribution of biomass burning products from the Asian Continent as well as the active oxidation of anthropogenic primary organic compounds emitted from East Asian countries even in cold season during long-range atmospheric transport, followed by the subsequent gas-to-particle conversion.

The high concentrations of NO_3^- and SO_4^{2-} , and enhanced $\text{NH}_4\text{-N/WSTN}$ ratio in winter suggest that Cape Hedo is strongly influenced by vehicular emission, biomass burning, industrial emission and coal combustion in East Asia via a long-range atmospheric transport. We found a strong correlation between the biomass burning tracer (nss-K^-) and EC ($r=0.80$), suggesting an important contribution of incomplete combustion of biomass to EC in the Asian outflow region.

Acknowledgements

This study was in part supported by the Japan Society for the Promotion of Science (Grant-in-Aid Nos. 1920405 and 24221001) and by the Environment Research and Technology Development Fund (B-0903) from the Ministry of the Environment, Japan. We thank S. Yamamoto and T. Arakaki for the help in aerosol sampling at Cape Hedo, Okinawa, Japan, and A. Takami of the National Institute of Environmental Studies, Japan for the courtesy to use the CHAARM site at Cape Hedo. We also thank the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport model and READY website (<http://www.arl.noaa.gov/ready.php>) used in this publication.

References

- Aggarwal, S. G., and Kawamura, K.: Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: Implications for photochemical aging during long-range atmospheric transport, *J. Geophys. Res.*, 113, D14301, doi: 10.1029/2007JD009365, 2008.
- Andreae, M. O., Atlas, E., Cachier, H., Cofer III, W. R., Harris, G. W., Helas, G., Koppmann, R., Lacaux, J. - P., and Ward, D. E.: Trace gas and aerosol emissions from savanna fires, in *Biomass Burning and Global Change*, edited by J. S. Levine, pp. 278–295, MIT Press, Cambridge, Mass, 1996.
- Andreae, M. O., and Merlet, P.: Emission of trace gases and aerosols from biomass burning, *Global Biogeochem. Cycles*, 15(4), 955–966, 2001.
- Arakaki, T., Okada, Y. K., Nakama, Y., Ikota, H., Kinjo, M., Higuchi, T., Uehara, M., and Tanahara, A.: Chemical composition and photochemical formation of hydroxyl radicals in aqueous extracts of aerosol particles collected in Okinawa, Japan, *Atmospheric Environment*, 40, 4764–4774, doi:10.1016/j.atmosenv.2006.04.035, 2006.
- Berg, W. W. Jr., and Winchester, J. W.: Aerosol chemistry of marine atmosphere, in *Chemical Oceanography*, vol. 7, edited by J. P. Riley and R. Chester, pp. 173–231, Academic Press, London, U. K, 1978.
- Buseck, P. R., and Posfai, M.: Airborne minerals and related aerosol particles: Effect on climate and the environment. *Proceedings of the National Academy of Sciences of the United States of America*, 96, 3372-3379, 1999.
- Cao, J.J., Lee, S.C., Ho, K.F., Zhang, X.Y., Zou, S.C., Fung, K., Chow, J.C., and Watson, J.G.: Characteristic of carbonaceous aerosol on Pearl River Delta region, China during 2001 winter period, *Atmospheric Environment* 37, 1451-1460, 2003.
- Cao, J. J., Lee, S. C., Zhang, X. Y., Chow, J. C., An, Z. S., Ho, K. F., Watson, J. G., Fung, K., Wang, Y. Q., Shen, Z. X.: Characterization of airborne carbonate over a site on Asian Dust source regions during 2002 spring and its climatic and environmental significance, *J. Geophys. Res.*, 110, D03203, doi: 10.1029/2004JD005244, 2005.

- Cao, J. J., Lee, S. C., Chow, J. C., Watson, J. G., Ho, K. F., Zhang, R. J., Jin, Z. D., Shen, Z. X., Chen, G. C., Kang, Y. M., Zou, S. C., Zhang, L. Z., Qi, S. H., Dai, M. H., Cheng, Y., and Hu, K.: Spatial and seasonal distributions of carbonaceous aerosols over China, *J. Geophys. Res.*, 112, D22S11, doi: 10.1029/2006JD008205, 2007.
- Cape, J.N., Cornell, S.E., Jickells T.D., and Nemitz, E.: Organic nitrogen in the atmosphere- Where does it come from? A review of sources and methods, *Atmospheric research*, 102, 30-48, 2011.
- Castro, L. M., Pio, C. A., Harrison, R. M., and Smith, D. J. T.: Carbonaceous aerosol in urban and rural European atmosphere: estimation of secondary organic carbon concentrations, *Atmos. Environ.*, 33, 2771–2781, 1999.
- Cooke, W. F., Liousse, C., Cachier, H., and Feichter, J.: Construction of a 1° x 1° fossil fuel emission data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model, *J. Geophys. Res.*, 104, 22137-22162, 1999.
- Draxler, R.R., and Rolph, G.D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model Access via NOAA ARL READY Website, available at: <http://www.arl.noaa.gov/ready/hysplit4.html>, (last access: August 2011), NOAA Air Resources Laboratory, Silver Spring, MD, 2003.
- Ervens, B., Carlton, A. G., Turpin, B. J., Altieri, K. E., Kreidenweis, S. M., and Feingold, G.: Secondary organic aerosol yields from cloud processing of isoprene oxidation products, *Geophys. Res. Lett.*, 35, L02816, doi: 10.1029/2007GL031828, 2008.
- Facchini, M. C., Mircea, M., Fuzzi, S., and Charlson, R. J.: Cloud albedo enhancement by surface active organic solutes in growing droplets, *Nature.*, 401, 257–259, 1999.
- Folinsbee, L.J.: Human Health Effects of Air Pollution, *Environ. Health Perspect.*, 100: 45-56, 1992.
- Fu, P., Kawamura, K., Kobayashi, M., Mochida, M., and Simoneit, B. R. T.: Seasonal variations of sugars in atmospheric particulate matter from Gosan, Jeju Island: Significant contributions of airborne pollen and Asian dust in spring, *Atmos. Environ.*, 55, 234-239, 2012.

- George, K. S., Nair, P. R., Parameswaran, K., Jacob, S., and Abraham, A.: Seasonal trend in chemical composition of aerosols at a tropical coastal site of India, *J. Geophys. Res.*, 113, D16209, doi: 10.1029/2007JD009507, 2008.
- Hagler, G. S. W., Bergin, M. H., Smith, E. A., and Dibb, J. E.: A summer time series of particulate carbon in the air and snow at Summit, Greenland, *J. Geophys. Res.*, 112, D21309, doi:10.1029/2007JD008993, 2007.
- Handa, D., Nakajima, H., Arakaki, T., Kumata, H., Shibata, Y., and Uchida, M.: Radiocarbon analysis of BC and OC in PM10 aerosols at Cape Hedo, Okinawa, Japan, during long-range transport events from East Asian countries, *Nucl. Instrum. Meth., B*, 268, 1125–1128, 2010.
- Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J., Chow, J. C., and Watson, J. G.: Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban atmosphere of China, *J. Geophys. Res.*, 112, D22S27, doi: 10.1029/2006JD008011, 2007.
- Jaffe, D., Prestbo, E., Swartzendruber, P., Penzias, P. W., Kato, S., Takami, A., Hatakeyama, S., and Kajii, Y.: Export of atmospheric mercury from Asia, *Atmos. Environ.*, 39, 3029–3038, 2005.
- Jung, J., Tsatsral, B., Kim, Y. J., and Kawamura, K.: Organic and inorganic aerosol compositions in Ulaanbaatar, Mongolia, during the cold winter of 2007 to 2008: Dicarboxylic acids, ketocarboxylic acids, and α -dicarbonyls, *J. Geophys. Res.*, 115, D22203, doi: 10.1029/2010JD014339, 2010.
- Kawamura, K., and Kaplan, I. R.: Motor exhaust emission as a primary source of dicarboxylic acids in Los Angeles ambient air, *Environ. Sci. Technol.*, 21, 105–110, 1987.
- Kawamura, K., Kasukabe, H., and Barrie, L. A.: Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, *Atmos. Environ.*, 30, 1709–1722, 1996a.
- Kawamura, K., Sempéré, R., Imai, Y., Hayashi, M., and Fujii, Y.: Water soluble dicarboxylic acids and related compounds in the Antarctic aerosols, *J. Geophys. Res.*, 101, 18,721–18,728, 1996b.

- Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanabe, T., and Lee, M.: Organic and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition, in *Geochemical Investigation in Earth and Space Science; A Tribute to Issac R. Kaplan*, The Geochemical Society Special Publication Series, vol. 9, edited by R. J. Hill, pp. 243-265, Elsevier, Amsterdam, Netherlands, 2004.
- Kawamura, K., Kasukabe, H., and Barrie, L. A.: Secondary formation of water-soluble organic acids and α -dicarbonyls and their contribution to total carbon and water-soluble organic carbon: Photochemical ageing of organic aerosols in the Arctic spring, *J. Geophys. Res.*, 115, D21306, doi: 10.1029/2010JD014299, 2010.
- Keene, W. C., Pszenny, A. P., Galloway, J. N., and Hawley, M. E.: Sea-salt corrections and interpretations of constituent ratios in marine precipitation, *J. Geophys. Res.*, 91, 6647-6658, 1986.
- Kim, J.C., Kim, K.J., Kim, D.S., and Han, J.S.: Seasonal variations of monoterpene emissions from coniferous trees of different ages in Korea. *Chemosphere.*, 59, 1685-96, 2005.
- Koch, D.: Transport and direct radiative forcing of carbonaceous and sulfate aerosols in the GISS GCM, *J. Geophys. Res.*, 106, 20,311–20,332, 2001.
- Kundu, S, Kawamura, K., and Lee, M.: Seasonal variations of diacids, ketoacids and α -dicarbonyls in marine aerosols at Gosan, Jeju Island: Implications for their formation and degradation during long-range transport, *J. Geophys. Res.*, 115, D19307, doi: 10.1029/2010JD013973, 2010.
- Lee, J. H., Kim, Y. P., Moon, K.-C., Kim, H.-K., and Lee, C. B.: Fine particle measurements at two background sites in Korea between 1996 and 1997, *Atmos. Environ.*, 35, 635– 643, 2001.
- Limbeck, A., Puxbaum, H., Otter, L., and Scholes, M. C.: Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA), *Atmos. Environ.*, 35(10), 1853-1862, 2001.
- Lin, J. and Tai, H.: Concentrations and Distributions of Carbonaceous Species in Ambient

- Particles in Kaohsiung City, Taiwan. *Atmos. Environ.* 35, 2627-2636, 2001.
- Lun, X., Takami, A., Miyoshi, T., and Hatakeyama, S.: Characteristic of organic aerosol in a remote area of Okinawa Island, *J. Environmental Science.*, 21, 1371-1377, 2009.
- Mayol-Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari, S., Facchini, M. C., Fuzzi, S., and Artaxo, P.: Water-soluble organic compounds in biomass burning aerosols over Amazonia: 2. Apportionment of the chemical composition and importance of the polyacidic fraction, *J. Geophys. Res.*, 107(D20), 8091, doi: 10.1029/2001JD000522, 2002.
- McInnes, L. M., Covert, D. S., Quinn, P. K., and Germani, M. S.: Measurements of chloride depletion and sulphur enrichment in individual sea-salt particles collected remote marine boundary layer, *J. Geophys. Res.*, 99, 8257-8268, 1994.
- Meinert, D. L., and Winchester, J. W.: Chemical relationships in the north Atlantic marine aerosol, *J. Geophys. Res.*, 82(12), 1778-1782, 1977.
- Miyazaki, Y., Kondo, Y., Takegawa, N., Komazaki, Y., Fukuda, M., Kawamura, K., Mochida, M., Okuzawa, K., and Weber, R. J.: Time-resolved measurements of water-soluble organic carbon in Tokyo, *J. Geophys. Res.*, 111, D23206, doi: 10.1029/2006JD007125, 2006.
- Miyazaki, Y., Kondo, Y., Han, S., Koike, M., Kodama, D., Komazaki, Y., Tanimoto, H., and Matsueda, H.: Chemical characteristics of water-soluble organic carbon in the Asian outflow, *J. Geophys. Res.*, 112, D22S30, doi: 10.1029/2007JD009116, 2007.
- Miyazaki, Y., Aggarwal S. C., Singh, K., Gupta, K. P., and Kawamura, K.: Dicarboxylic acids and water-soluble organic carbon in aerosols in New Delhi, India, in winter: Characteristics and formation processes, *J. Geophys. Res.*, 114, D19206, doi: 10.1029/2009JD011790, 2009.
- Miyazaki, Y., Fu, P., Kawamura, K., Mizoguchi, Y., and Yamanoi, K.: Seasonal variations of stable carbon isotopic ratios and biogenic tracer compounds of water-soluble organic aerosols in a deciduous forest, *Atmos. Chem. Phys.*, 12, 1367–1376, doi: 10.5194/acp-12-1367-2012, 2012.

- Mochida M., Nishita-Hara, C., Furutani, H., Miyazaki, Y., Jung, J., Kawamura, K., and Uematsu, M.: Hygroscopicity and cloud condensation nucleus activity of marine aerosol particles over the western North Pacific, *J. Geophys. Res.*, 116, D06204, doi: 10.1029/2010JD014759, 2010.
- Nishikawa, M., Hao, Q., and Morita, M.: Preparation and evaluation of certified reference materials from Asian mineral dust, *Global Environ. Res.* 4, 103-113, 2000.
- Novakov, T., and Penner, J. E.: Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, *Nature.*, 365, 823-826, 1993.
- Pavuluri, C. M., Kawamura, K., Aggarwal, S. G., and Swaminathan, T.: Characteristics, seasonality and sources of carbonaceous and ionic components in the tropical aerosols from Indian region, *Atmos. Chem. Phys.*, 11, 8215-8230, 2011.
- Park, S. S., Kim, Y. J., and Fung, K.: PM_{2.5} carbon measurements in two urban areas: Seoul and Kwangju, Korea, *Atmos. Environ.*, 36, 1287–1297, 2002.
- Prospero, J. M.: The chemical and physical properties of marine aerosols: An introduction, in *Chemistry of Marine Water and Sediments*, edited by A. Gianguzza, E. Pellizzetti, and S. Sammarano, pp. 35-82, Springer-Verlag Berlin, Heidelberg, Germany, 2002.
- Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D.: Aerosols, climate, and the hydrological cycle, *Science.*, 294, 2119–2124, 2001.
- Rudich, Y., Donahue, N. M. and Mentel, T. F.: Aging of organic aerosol: Bridging the gap between laboratory and field studies, *Annual Review of Physical Chemistry*, 58, 321-352, 2007.
- Sempéré, R., and K. Kawamura (2003), Trans-hemispheric contribution of C₂-C₁₀ α, ω -dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions, *Global Biogeochem. Cycles*, 17(2), 1069, doi: 10.1029/2002GB001980.
- Sato, K., Li, H., Tanaka, Y., Ogawa, S., Iwasaki, Y., Takami, A., and Hatakeyama, S.: Long-range transport of particulate polycyclic aromatic hydrocarbons at Cape Hedo remote island site in the East China Sea between 2005 and 2008, *J. Atmos. Chem.*, 61, 243-257,

- 2009.
- Savoie, D. L., Prospero, J. M., Arimoto, R., and Duce, R. A.: Non seasalt sulfate and methanesulfonate at American Samoa, *J. Geophys. Res.*, 99(D2), 3587-3596, 1994.
- Saxena, P., Hildemann, L., McMurry, P., and Seinfeld, J.: Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, 100(D9), 18,755-18,770, 1995.
- Seinfeld, J. H., and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 1326 pp., Jhon Wiley, Hoboken, N. J, 1998.
- Takami, A., Miyoshi, T., Shimono, A., Kaneyasu, N., Kato, S., Kajii, Y., and Hatakeyama, S.: Transport of anthropogenic aerosols from Asia and subsequent chemical toluene, and p-xylene, *J. Phys. Chem. A.*, 105, 7865-7874, 2007.
- Tambunan, P., Baba, S., Kuniyoshi, A., Iwasaki, H., Nakamura, T., Yamasaki, H., and Oku, H.: Isoprene emission from tropical trees in Okinawa Island, Japan, *Chemosphere.*, 65, 2138–2144, 2006.
- Tran, B. N., Lee, P. B., Updyke, M. K., Bones, D. L., Laskin, J., Laskin, A., and Nizkorodov, A. S.: Formation of nitrogen- and sulphur- containing light-absorbing compounds accelerated by evaporation of water from secondary organic aerosols, *J. Geophys. Res.*, 117, D01207, doi: 10.1029/2011JD016944, 2012.
- Turpin, B. J., and Huntzicker, J. J.: Secondary Formation of Organic Aerosol in the Los Angeles Basin: A Descriptive Analysis of Organic and Elemental Carbon Concentrations, *Atmos. Environ.*, 25, 207–215, 1991.
- Turpin, B. J., and Huntzicker, J. J.: Identification of secondary organic aerosol episodes and quantification of primary and secondary organic aerosol concentrations during SCAQS, *Atmos. Environ.*, 29(23), 3527–3544, 1995.
- Turpin, B. J., and Lim, H.-J.: Species contributions to PM_{2.5} mass concentrations: Revisiting common assumptions for estimating organic mass, *Aerosol Sci. Tech.*, 35, 602–610, 2001.
- Turpin, B.J., Huntzicker, J.J., Larson, S.M., Cass, G.R.: Los Angeles Summer Midday Particulate Carbon: Primary and Secondary Aerosol, *Environmental Science and*

- Technology, 25, 1788-1793, 1991.
- Ueda, S., Osada, K., and Takami, A.: Morphological features of soot-containing particles internally mixed with water-soluble materials in continental outflow observed at Cape Hedo, Okinawa, Japan, *J. Geophys. Res.*, 116, D17207, doi: 10.1029/2010JD015565, 2011.
- Verma, R. L., Kondo, Y., Oshima, N., Matsui, H., Kita, K., Sahu, L. K., Kato, S., Kajii, Y., Takami, A., and Miyakawa, T.: Seasonal variations of the transport of black carbon and carbon monoxide from the Asian continent to the western Pacific in the boundary layer, *J. Geophys. Res.*, 116, D21307, doi: 10.1029/2011JD015830, 2011.
- Wedyan, M.A., Preston, M.R.: The coupling of surface seawater organic nitrogen and the marine aerosol as inferred from enantiomer-specific amino acid analysis, *Atmospheric Environment* 42, 8698–8705, 2008.
- Wang, H., Kawamura, K., and Shooter, D.: Carbonaceous and ionic components in wintertime atmospheric aerosols from two New Zealand cities: Implication for solid fuel combustion, *Atmos. Environ.*, 39, 5865-5875, 2005.
- Wang, G. H., Kawamura, K., Lee, S.C., Ho, K. F., and Cao J. J.: Molecular, seasonal and spatial distribution of organic aerosols from fourteen Chinese cities, *Environ. Sci. Technol.*, 40, 4619-4625, 2006.
- Wang, G., Kawamura, K., Xie, M., Hu, S., Gao, S., Cao, J., An, Z., and Wang, Z.: Size-distributions of n-alkanes, PAHs and hopanes and their sources in the urban, mountain and marine atmospheres over East Asia, *Atmos. Chem. Phys.*, 9(22), 8869-8882, 2009.
- Wang, G., Xie, M., Hu, S., Tachibana, E., Kawamura, K.: Dicarboxylic acids, metals and isotopic compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal burning emission and secondary aerosol formation, *Atmos. Chem. Phys.*, 2010.
- Wang, G., Kawamura, K., Hu, S., Xie, M., Zhou, B., Li, J., Cao, J., and An, Z.: Selected water soluble organic compounds found in size-resolved aerosols collected from the urban, mountain, and marine atmospheres over East Asia, *Tellus B*, 63, 371–381, 2011.

- Wang, Z. B., Hu, M., Yue, D. L., He, L. Y., Huang, X. F., Yang, Q., Zheng, J., Zhang, R. Y., and Zhang, Y. H.: New particle formation in the presence of a strong biomass burning episode at a downwind rural site in PRD, China, *Tellus*, 65,19965, doi:10.3402/tellusb.v65i0, 2013a.
- Wang, G., Zhou, B. H., Cheng, C. L., Cao, J. J., Li, J. J., Meng, J., Tao, J., and Fu, P. Q.: Impact of Gobi desert dust on aerosol chemistry of Xi'an, inland China during spring 2009:differences in composition and size distribution between the urban ground surface and the mountain atmosphere, *Atmos. Chem. Phys.*, 2013b.
- Yamamoto, S., and Kawamura, K.: Stable hydrogen isotopic compositions of fossil fuel-derived n-alkanes in the atmospheric aerosols from Okinawa, Japan, *Res. Org. Geochem.*, 27, 81-89, 2011.
- Yao, X., and Zhang, L.: Chemical processes in sea-salt chloride depletion observed at a Canadian rural coastal site, *Atmos. Environ.*, 46, 189–194, doi: 10.1016/j.atmosenv.2011.09.081, 2012.
- Zhang, M., Uno, I., Carmichael, G. R., Akimoto, H., Wang, Z., Tang, Y., Woo, J-H., Streets, D. G., Sachse, G. W., Avery, M. A., Weber, R. J., and Talbot, R. W.: Large-scale structure of trace gas and aerosol distributions over the western Pacific Ocean during the Transport and Chemical Evolution Over the Pacific (TRACE-P) experiment, *J. Geophys. Res.*, 108, 8820, doi: 10.1029/2002JD002946, 2003.

Table 3.1. Seasonal variations of mass concentrations of different organic components in aerosols from Cape Hedo, Okinawa.

Components	Concentration in ($\mu\text{g m}^{-3}$)							
	Winter		Spring		Summer		Autumn	
	Range	AV $\pm$ SD	Range	AV $\pm$ SD	Range	AV $\pm$ SD	Range	
OC	0.83-2.49	1.53 $\pm$ 0.5	1.04-7.12	2.36 $\pm$ 1.71	0.84-3.01	1.79 $\pm$ 0.56	0.76-2.52	1.42 $\pm$ 0.48
EC	0.14-0.59	0.70 $\pm$ 0.5	0.19-0.96	0.41 $\pm$ 0.24	0.07-0.54	0.19 $\pm$ 0.14	0.09-0.38	0.20 $\pm$ 0.09
WSOC	0.45-1.37	0.90 $\pm$ 0.2	0.53-1.88	0.95 $\pm$ 0.40	0.27-1.90	0.52 $\pm$ 0.42	0.29-0.70	0.55 $\pm$ 0.18
WIOC	0.08-1.12	0.63 $\pm$ 0.2	0.51-5.24	1.41 $\pm$ 1.34	0.57-2.29	1.27 $\pm$ 0.41	0.37-1.84	0.89 $\pm$ 0.51
OM	1.66-4.98	3.05 $\pm$ 1.0	2.07-14.2	4.72 $\pm$ 3.42	1.68-6.02	3.59 $\pm$ 1.12	1.52-5.04	2.85 $\pm$ 0.95
WSOM	0.90-2.74	1.80 $\pm$ 0.5	1.06-3.76	1.91 $\pm$ 0.81	0.54-3.80	1.05 $\pm$ 0.85	0.57-1.81	1.12 $\pm$ 0.41
WIOM	0.16-2.24	1.26 $\pm$ 0.5	1.02-10.4	2.82 $\pm$ 2.69	1.14-4.59	2.54 $\pm$ 0.82	0.75-3.69	1.73 $\pm$ 0.81
POC	0.27-1.18	0.72 $\pm$ 0.3	0.38-1.92	0.82 $\pm$ 0.48	0.14-1.08	0.37 $\pm$ 0.28	0.17-0.80	0.42 $\pm$ 0.23
SOC	0.39-1.31	0.81 $\pm$ 0.2	0.65-5.40	1.54 $\pm$ 1.29	0.70-2.18	1.42 $\pm$ 0.37	0.46-2.08	1.01 $\pm$ 0.42

Table 3.2. Seasonal variations of ionic species in aerosols from Cape Hedo, Okinawa.

Ions	Concentration ($\mu\text{g m}^{-3}$)							
	Winter		Spring		Summer		Autumn	
	Range	AV $\pm$ SD	Range	AV $\pm$ SD	Range	AV $\pm$ SD	Range	AV $\pm$ SD
Anions								
F ⁻	0.00-0.01	BDL $\pm$ BDL	0.00-0.01	BDL $\pm$ BDL	0.00-0.01	BDL $\pm$ BDL	0.00-0.01	BDL $\pm$ BDL
MSA ⁻	0.01-0.05	0.03 $\pm$ 0.01	0.01-0.05	0.04 $\pm$ 0.02	0.01-0.05	0.02 $\pm$ 0.01	0.01-0.05	0.02 $\pm$ 0.02
Cl ⁻	4.63-26.2	13.9 $\pm$ 6.18	4.63-26.2	12.7 $\pm$ 9.89	3.31-12.1	6.95 $\pm$ 2.84	2.84-26.2	10.8 $\pm$ 8.13
NO ₂ ⁻	0.00-0.00	0.00 $\pm$ 0.00	0.00-0.00	0.00 $\pm$ 0.00	0.00-0.00	0.00 $\pm$ 0.00	0.00-0.00	0.00 $\pm$ 0.00
Br ⁻	0.00-0.01	0.00 $\pm$ 0.00	0.00-0.01	0.00 $\pm$ 0.00	0.00-0.02	0.01 $\pm$ BDL	0.00-0.02	0.01 $\pm$ BDL
NO ₃ ⁻	0.86-3.90	2.11 $\pm$ 0.93	0.86-3.90	1.95 $\pm$ 1.42	0.17-3.84	0.79 $\pm$ 0.97	0.17-3.90	1.81 $\pm$ 1.35
PO ₄ ³⁻	0.00-0.00	0.00 $\pm$ 0.00	0.00-0.01	BDL $\pm$ BDL	0.00-0.01	BDL $\pm$ BDL	0.00-0.01	BDL $\pm$ BDL
SO ₄ ²⁻	2.34-5.04	3.63 $\pm$ 0.82	0.01-5.04	2.37 $\pm$ 2.04	0.46-5.96	1.29 $\pm$ 1.47	0.01-5.96	2.54 $\pm$ 1.96
Total	7.84-35.2	19.7 $\pm$ 7.94	0.01-25.6	8.32 $\pm$ 7.15	1.67-12.0	4.14 $\pm$ 2.89	1.23-15.0	6.90 $\pm$ 4.08
Cations								
Na ⁺	4.64-12.0	7.57 $\pm$ 2.40	0.01-12.0	5.34 $\pm$ 4.68	2.26-6.35	3.58 $\pm$ 1.30	0.01-12.0	5.19 $\pm$ 3.85
NH ₄ ⁺	0.23-1.51	0.79 $\pm$ 0.41	0.20-1.51	0.74 $\pm$ 0.48	0.00-0.15	0.02 $\pm$ 0.05	0.00-1.51	0.51 $\pm$ 0.53
K ⁺	0.20-0.68	0.44 $\pm$ 0.16	0.01-0.68	0.31 $\pm$ 0.23	0.12-0.43	0.21 $\pm$ 0.09	0.01-0.68	0.30 $\pm$ 0.22
Ca ²⁺	0.30-1.35	0.70 $\pm$ 0.28	0.00-1.35	0.62 $\pm$ 0.49	0.09-0.37	0.18 $\pm$ 0.09	0.00-1.35	0.48 $\pm$ 0.45
Mg ²⁺	0.48-1.48	0.92 $\pm$ 0.32	0.00-1.48	0.60 $\pm$ 0.48	0.24-0.66	0.41 $\pm$ 0.14	0.00-1.48	0.60 $\pm$ 0.48
Total	5.85-17.0	10.4 $\pm$ 3.57	10.3-44.7	20.4 $\pm$ 10.7	6.26-18.2	10.1 $\pm$ 3.82	3.72-35.8	17.7 $\pm$ 9.17

Note: BDL means Below Detection Limit ($0.001 \mu\text{g m}^{-3}$).

Table 3.3. OC and EC concentrations and OC to EC mass ratios in atmospheric aerosols from different locations in East Asia.

Location	Period	Size	Concentrations ($\mu\text{g m}^{-3}$)		OC/EC	References
			OC	EC		
Mongolia	11/ 2007 to 1/ 2008	PM2.5	31.8	6.7	4.7	Jung et al., 2010
Beijing	Winter	PM2.5	27.2	7.1	3.7	Cao et al., 2007
Beijing	Summer	PM2.5	17.2	4.6	4.4	Cao et al., 2007
Jinchang	Winter	PM2.5	23	5	4.5	Cao et al., 2007
Jinchang	Summer	PM2.5	8.1	1.6	5.9	Cao et al., 2007
Gangzhou	Winter	PM2.5	41.1	14.5	2.8	Cao et al., 2007
Gangzhou	Summer	PM2.5	10.6	3.2	3.6	Cao et al., 2007
Hong Kong	Winter	PM2.5	11.2	5.8	2	Cao et al., 2007
Hong Kong	Summer	PM10	7.3	3.6	2.1	Cao et al., 2007
Hong Kong, PU, China	Nov-Feb, 2000-2001	PM2.5	12.0	6.86	>2	Ho et al., 2003
Hong Kong, KT, China	Nov-Feb, 2000-2001	PM2.5	10.1	5.05	>2	Ho et al., 2003
Hong Kong, HT, China	Nov-Feb, 2000-2001	PM2.5	5.52	1.36	>3	Ho et al., 2003
PRD regions., China	1-2/2002	PM2.5	14.7	6.1	2.4	Cao et al., 2003
Taiwan	11/1998-4/1999	PM10	14.5	6.1	2.4	Lin and Tai, 2001
Seoul, Korea	11/27-12/09/99	PM2.5	15.2	7.3	2.2	Park et al., 2002
Gosan (Jeju Island)	Dec, 1996	PM2.5	4.41	0.43	10	Lee et al., 2001
Gosan (Jeju Island)	Mar, 1996	PM2.5	2.97	0.32	9.3	Lee et al., 2001
Gosan (Jeju Island)	Jan-1997	PM2.5	3.31	0.23	14	Lee et al., 2001
Gosan (Jeju Island)	Sep, 1997	PM2.5	3.56	0.42	8.5	Lee et al., 2001
Gosan (Jeju Island)	Dec, 1997	PM2.5	2.6	0.34	7.7	Lee et al., 2001
Cape Hedo, Okinawa	Oct. 2009 to Oct. 2010	TSP	1.78	0.28	7.7	This Study

Table 3.4. Correlation coefficients (r) of major ions in winter aerosols from Cape Hedo, Okinawa.

	Na ⁺	NH ₄ ⁺	nss K ⁺	ss K ⁺	nssCa ²⁺	ssCa ²⁺	nssMg ²⁺	ssMg ²⁺	Cl ⁻	NO ₃ ⁻	nssSO ₄ ²⁻	ssSO ₄ ²⁻
Na ⁺	1											
NH ₄ ⁺	0.54	1										
nssK ⁺	0.63	0.94	1									
ssK ⁺	1.00	0.54	0.63	1								
nssCa ²⁺	0.16	0.26	0.30	0.16	1							
ssCa ²⁺	1.00	0.54	0.63	1.00	0.16	1						
nssMg ²⁺	0.92	0.64	0.73	0.92	0.37	0.92	1					
ssMg ²⁺	1.00	0.54	0.63	1.00	0.16	1.00	0.92	1				
Cl ⁻	0.97	0.44	0.55	0.97	0.22	0.97	0.91	0.97	1			
NO ₃ ⁻	0.48	0.85	0.83	0.48	0.42	0.48	0.62	0.49	0.35	1		
nssSO ₄ ²⁻	-0.48	0.02	-0.05	-0.48	-0.34	-0.49	-0.54	-0.49	-0.62	0.11	1	
ssSO ₄ ²⁻	0.86	0.80	0.80	0.86	0.35	0.86	0.87	0.86	0.76	0.77	-0.30	1

t-test is <0.01 for the correction where r is ≥0.71

t-test is <0.05 for the correction where r is ≥0.54 to 0.70

Table 3.5. Correlation coefficients (r) of major ions in spring aerosols from Cape Hedo, Okinawa.

	Na ⁺	NH ₄ ⁺	nss K ⁺	ss K ⁺	nssCa ²⁺	ssCa ²⁺	nssMg ²⁺	ssMg ²⁺	Cl ⁻	NO ₃ ⁻	nssSO ₄ ²⁻	ssSO ₄ ²⁻
Na ⁺	1											
NH ₄ ⁺	-0.35	1										
nssK ⁺	0.53	-0.16	1									
ssK ⁺	1.00	-0.35	0.53	1								
nssCa ²⁺	0.28	-0.38	0.76	0.28	1							
ssCa ²⁺	1.00	-0.35	0.53	1.00	0.28	1						
nssMg ²⁺	0.65	-0.26	0.87	0.65	0.79	0.65	1					
ssMg ²⁺	1.00	-0.35	0.53	1.00	0.28	1.00	0.65	1				
Cl ⁻	0.91	-0.24	0.57	0.91	0.35	0.91	0.63	0.91	1			
NO ₃ ⁻	0.47	-0.47	0.43	0.48	0.22	0.48	0.27	0.48	0.51	1		
nssSO ₄ ²⁻	-0.33	-0.05	0.40	-0.33	0.70	-0.33	0.36	-0.33	-0.18	-0.26	1	
ssSO ₄ ²⁻	0.70	-0.14	0.85	0.70	0.53	0.70	0.71	0.70	0.81	0.69	0.05	1

t-test is <0.01 for the correction where r is ≥0.71

t-test is <0.05 for the correction where r is ≥0.54 to 0.70

Table 3.6. Correlation coefficients (r) of major ions in summer aerosols from Cape Hedo, Okinawa.

	Na ⁺	NH ₄ ⁺	nss K ⁺	ss K ⁺	nssCa ²⁺	ssCa ²⁺	nssMg ²⁺	ssMg ²⁺	Cl ⁻	NO ₃ ⁻	nssSO ₄ ²⁻	ssSO ₄ ²⁻
Na ⁺	1											
NH ₄ ⁺	0.23	1										
nssK ⁺	-0.09	0.02	1									
ssK ⁺	1.00	0.23	-0.09	1								
nssCa ²⁺	-0.03	-0.07	0.90	-0.03	1							
ssCa ²⁺	1.00	0.23	-0.09	1.00	-0.04	1						
nssMg ²⁺	0.29	-0.06	0.86	0.29	0.79	0.29	1					
ssMg ²⁺	1.00	0.23	-0.09	1.00	-0.04	1.00	0.29	1				
Cl ⁻	0.97	0.27	-0.17	0.97	-0.18	0.97	0.23	0.97	1			
NO ₃ ⁻	-0.20	0.07	0.93	-0.20	0.93	-0.21	0.77	-0.21	-0.32	1		
nssSO ₄ ²⁻	-0.28	-0.14	0.94	-0.28	0.93	-0.28	0.73	-0.28	-0.39	0.94	1	
ssSO ₄ ²⁻	0.79	0.05	0.32	0.79	0.47	0.79	0.56	0.79	0.65	0.27	0.23	1

t-test is <0.01 for the correction where r is ≥0.71

t-test is <0.05 for the correction where r is ≥0.54 to 0.70

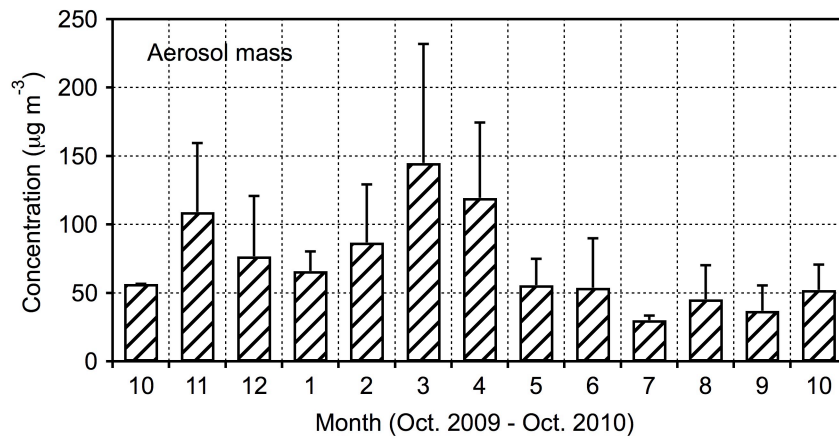


Figure 3.1. Average monthly variation of aerosol mass loading in ambient aerosols collected in Cape Hedo, Okinawa.

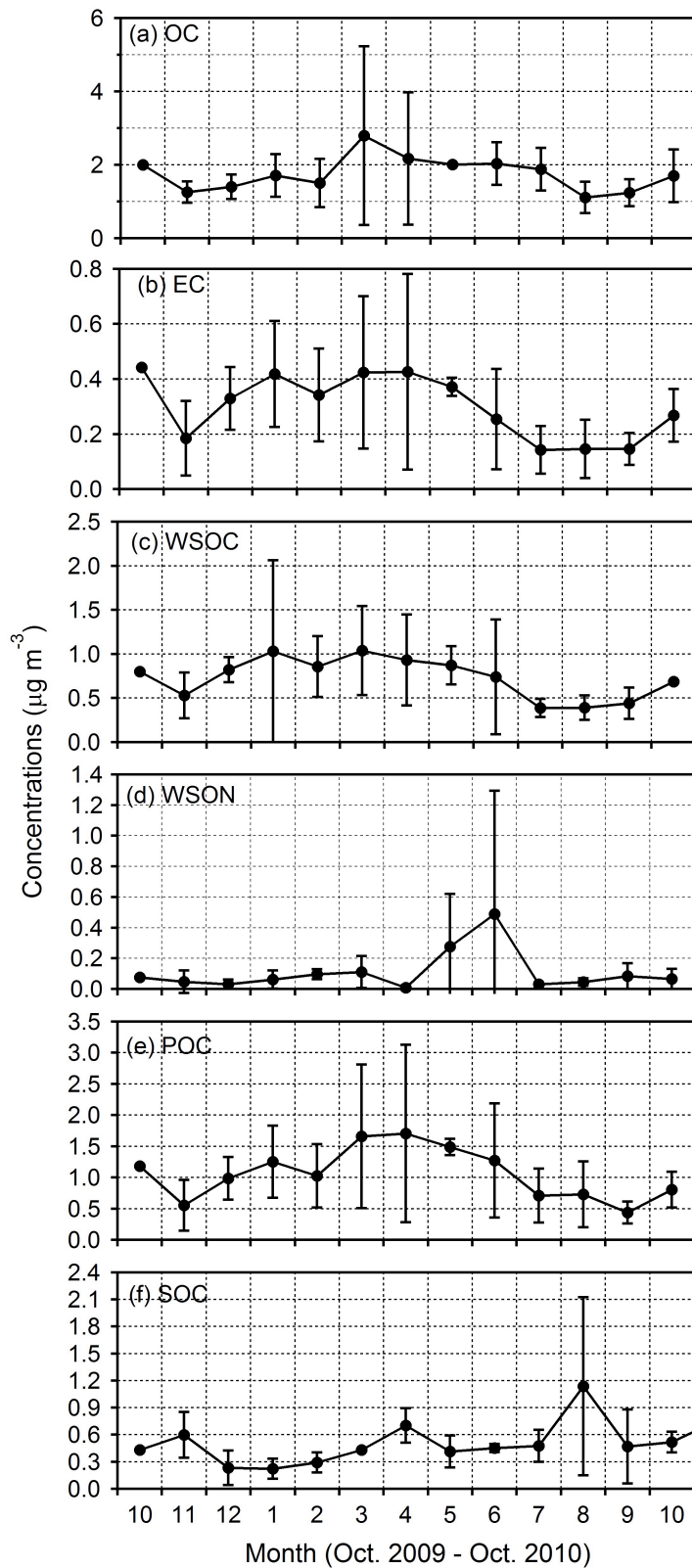


Figure 3.2. Seasonal variation in concentrations of (a) organic carbon (OC), (b) elemental carbon (EC), (c) water soluble organic carbon (WSOC), (d) water soluble organic nitrogen (WSON), (e) primary organic carbon (POC), and (f) secondary organic carbon (SOC) in ambient aerosols collected in Cape Hedo, Okinawa.

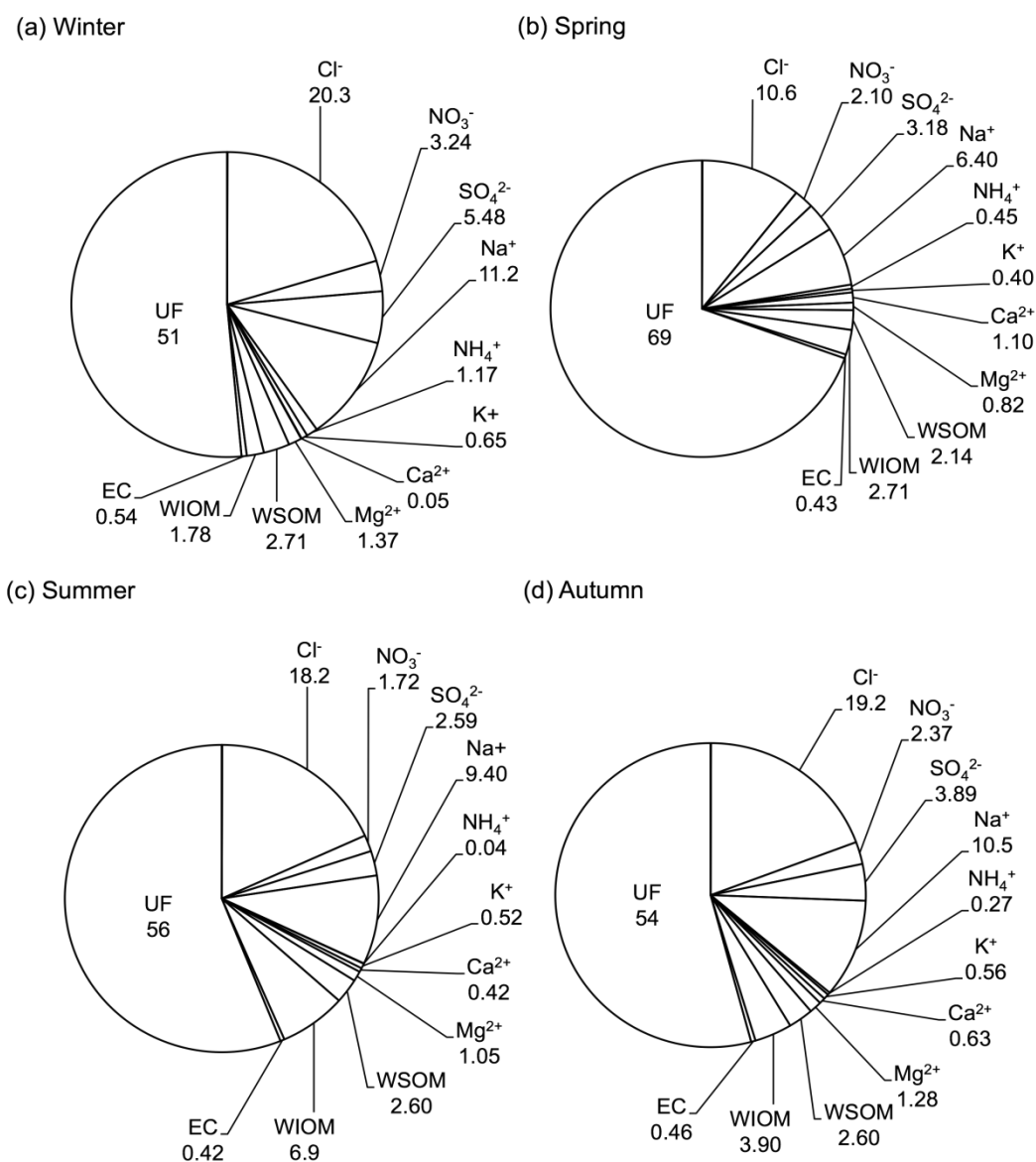


Figure 3.3. Average relative abundances (%) of water-soluble organic matter (WSOM), water insoluble organic matter (WIOM), elemental carbon (EC), and major ions in ambient aerosols collected in Cape Hedo, Okinawa. UF is unanalysed fraction

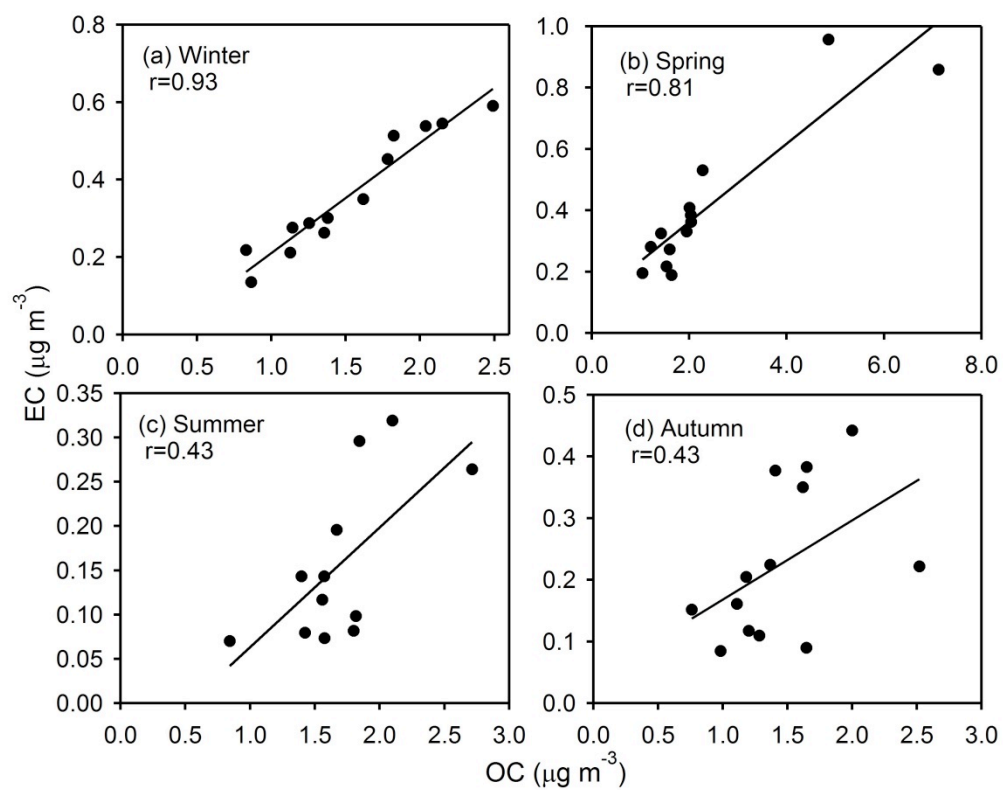


Figure 3.4. Correlation analysis between elemental carbon (EC) and organic carbon (OC) in ambient aerosol samples collected from Cape Hedo Okinawa.

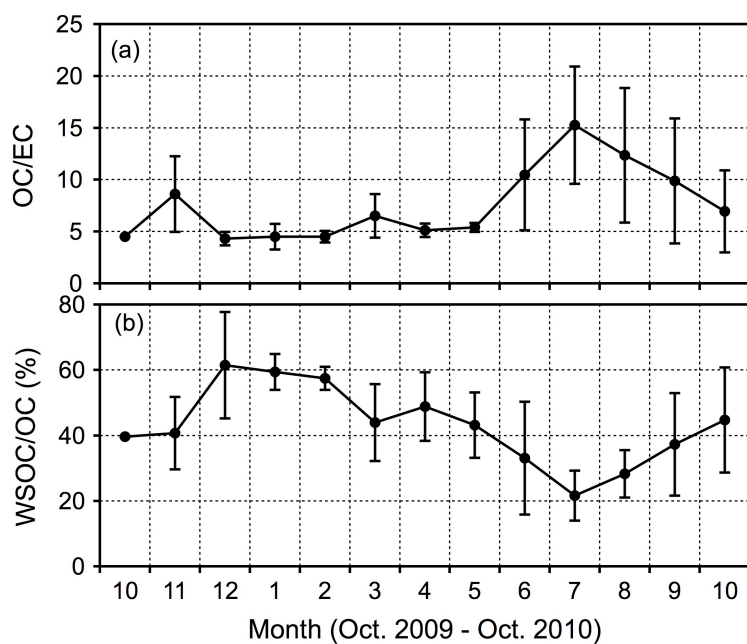


Figure 3.5. Monthly average variations of concentration ratios of (a) organic carbon (OC) to elemental carbon (EC), and (b) water soluble organic carbon (WSOC) to organic carbon (OC) in ambient aerosols collected from Cape Hedo Okinawa during October 2009 to October 2010.

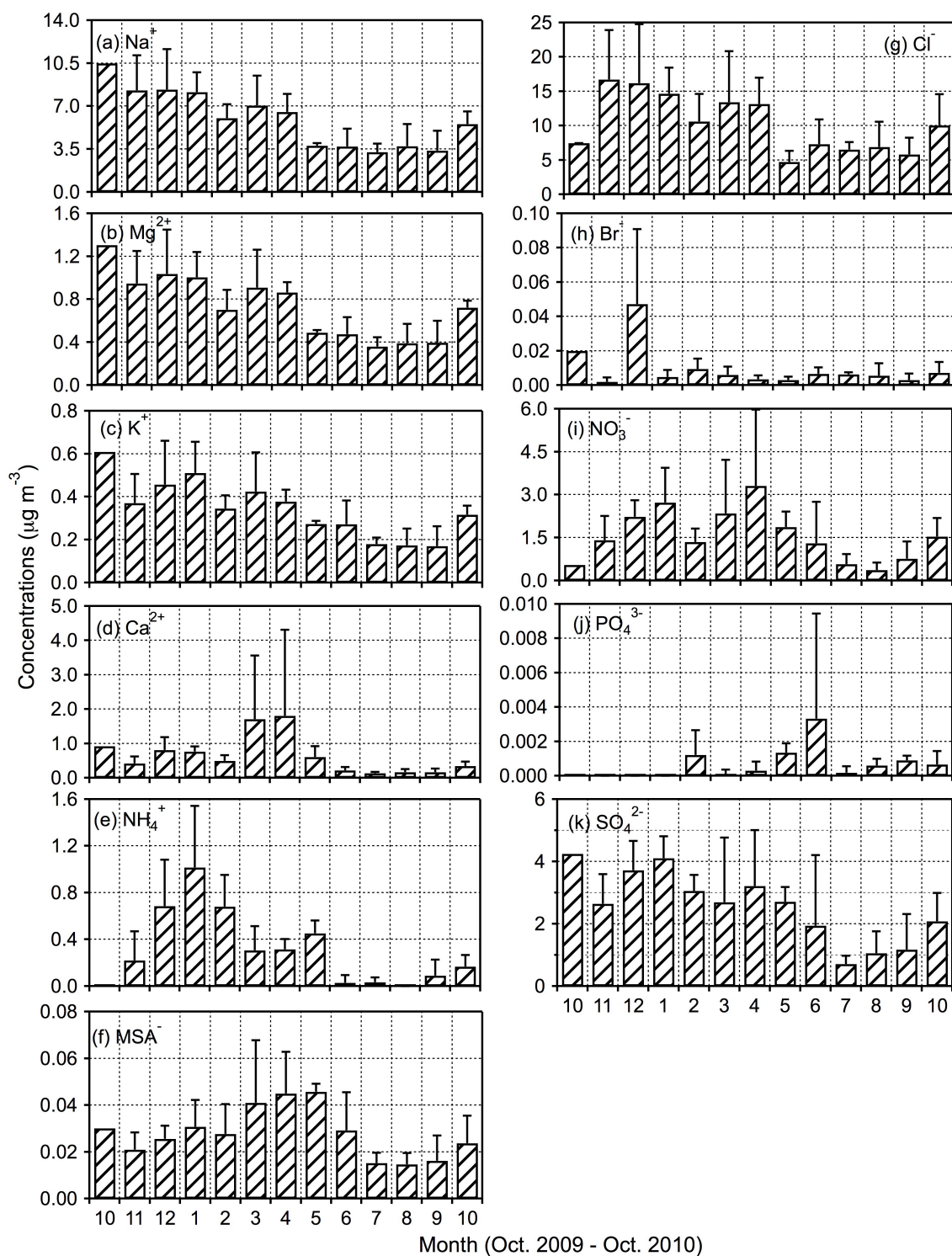


Figure 3.6. Monthly average variations in concentrations of major ions (a) Na^+ , (b) Mg^{2+} , (c) K^+ , (d) Ca^{2+} , (e) NH_4^+ , (f) MSA^- , (g) Cl^- , (h) Br^- , (i) NO_3^- , (j) PO_4^{3-} , and (k) SO_4^{2-} in the ambient aerosols collected from Cape Hedo, Okinawa.

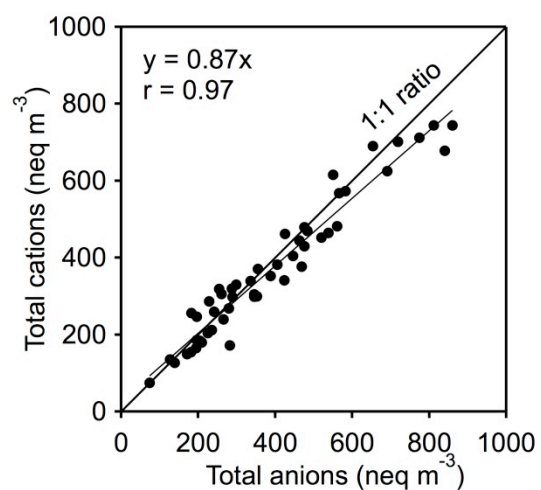


Figure 3.7. Linear regression plots between sum of cation equivalents (neq) and anion equivalents (neq) in ambient aerosol samples collected from Cape Hedo, Okinawa during October 2009 to October 2010.

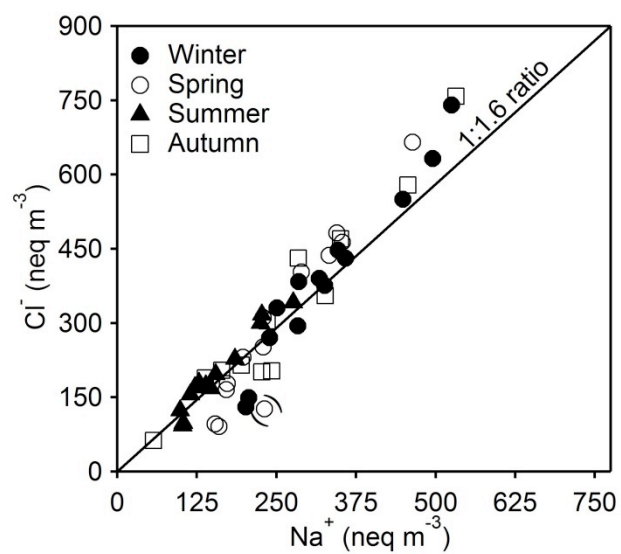


Figure 3.8. Scatter plot showing variation of Na^+ and Cl^- with respect to sea water line in ambient aerosols collected from Cape Hedo, Okinawa. The point within the bracket shows the maximum chlorine loss.

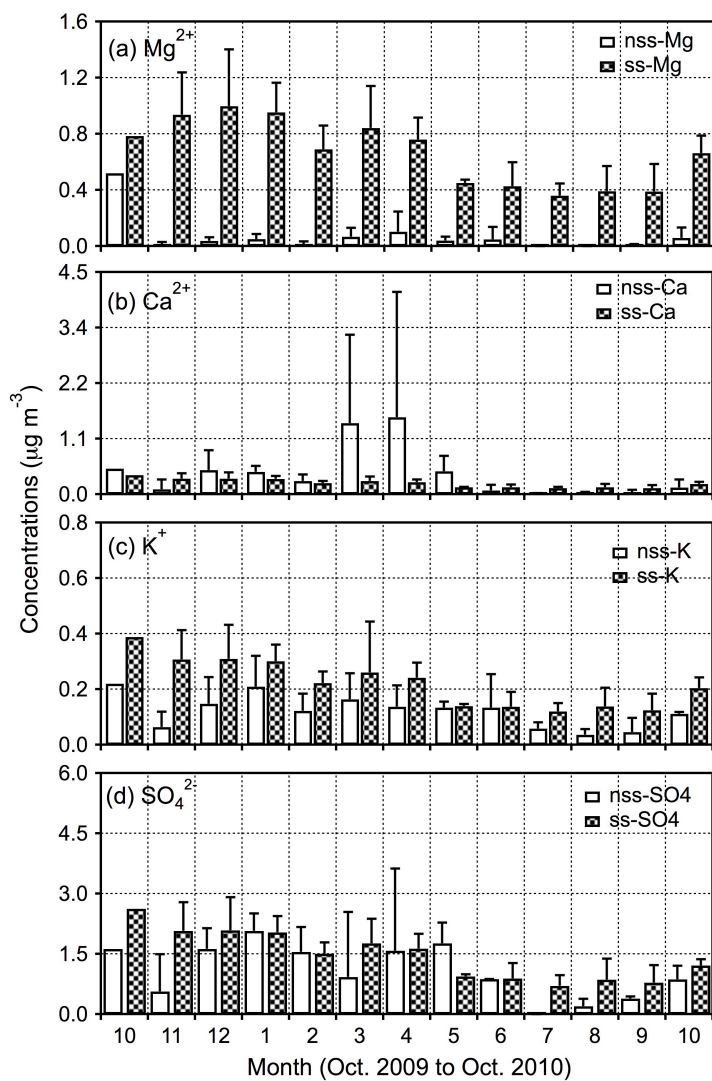


Figure 3.9. Estimated mass concentration of sea salt (ss) and non-sea salt (nss) component of (a) Mg^{2+} , (b) Ca^{2+} , (c) K^{+} , and (d) SO_4^{2-} in ambient aerosols collected from Cape Hedo, Okinawa.

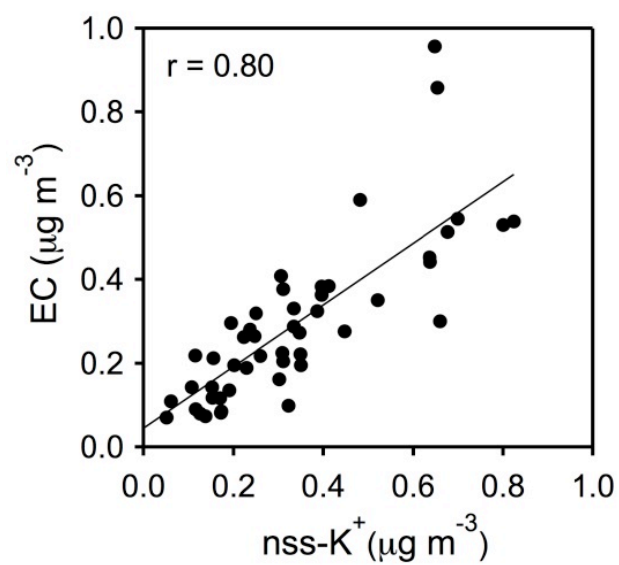


Figure 3.10. Correlation analysis between nss-K and EC in ambient aerosols collected from Cape Hedo, Okinawa.

Chapter 4: Seasonal Variations of Stable Carbon and Nitrogen Isotopic Compositions of Ambient Aerosol Samples Collected at Cape Hedo, Subtropical Okinawa Island, an Outflow Region of Asian Dusts

4.1. Introduction

Stable carbon and nitrogen isotope ratios have been used to identify the sources and transformation processes of aerosol particles in the atmosphere [Cachier et al., 1986; Cornell et al., 1995; Kawamura et al., 2004; Narukawa et al., 1999]. Recently, Miyazaki et al. [2012] discussed the source of water-soluble organic carbon (WSOC) using $\delta^{13}\text{C}$ ratios. Sugawara et al. [1996] found a natural gas leakage using $\delta^{13}\text{C}$ ratios of methane from oil well and gas pipeline by aircraft measurement. In East Asia, fossil fuel consumption increased significantly due to growing economies. Depending upon the source and chemical processes, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values have different values. Organic aerosols are formed from primary and secondary emissions in the atmosphere. Secondary organic aerosols (SOA) are formed by the oxidation of volatile organic compounds (VOC) through a long-range atmospheric transport. During oxidation processes, isotopic fractionation occurs leaving the lighter isotopes in the product and heavier isotopes in the reactants due to the kinetic isotope effect (KIE) [Fisseha et al., 2009]. Thus, organic compounds produced by the oxidation processes show lower isotope ratios [Fisseha et al., 2009] and the remaining precursors are enriched with heavier isotopes [Anderson et al., 2004].

Here, we report the stable carbon and nitrogen isotope ratios of the marine aerosols (TSP samples) collected for one year at Cape Hedo, Okinawa Island: an outflow region of Asian dusts. We also discuss seasonal changes of the isotope ratios in terms of source and source regions, and atmospheric processes during long-range atmospheric transport.

4.2. Experimental

4.2.1 Site Description and Aerosol Sampling

Samples collection was performed on the rooftop of the Cape Hedo Atmosphere and Aerosol Measurement Station (CHAAMS, 26.87°N, 128.26°E). CHAAMS is located at the northwestern edge of Okinawa Island, Japan (see Figure 2.1), which is within the outflow region of East Asia. Because of its location, CHAAMS has been used as a supersite of the Atmospheric Brown Clouds (ABC) project by the United Nations Environment Programme (UNEP) for studying atmospheric aerosols [Kunwar and Kawamura, 2013; Takami et al., 2007]. The surroundings of Cape Hedo are covered with subtropical rain forest and thus there are no major industries near the station [Yamamoto and Kawamura, 2011]. It is influenced by East Asian monsoon in winter to spring whereas the monsoon from the Pacific Ocean affects the region in summer to fall [Sato et al., 2009]. Therefore, continental air masses arrive over the sampling site in winter to spring. This is confirmed by air mass trajectory analyses [Kunwar and Kawamura, 2013].

Aerosol (TSP) samples (n=50) were collected on weekly basis using a pre-combusted quartz fiber filter and high-volume air sampler [Kunwar and Kawamura, 2013]. Filter samples were placed in a preheated glass jar with a Teflon-lined screw cap, shipped from Okinawa to Sapporo and stored in a freezer room at -20°C until analysis.

4.2.2. Measurements of TC and TN, and their Stable Isotopes

To measure total carbon (TC) and nitrogen (TN), we combusted a small filter disc (3.14 cm²) placed in a tin cup at 1400°C using elemental analyzer (EA) (Carlo Ebra, EA 1500). All the nitrogen species are converted to NO and further reduced to N₂ in a reduction column. Carbonaceous species are oxidized to carbon dioxide (CO₂). N₂ and CO₂ are separated on a packed GC column in EA and measured with a thermal conductivity detector [Pavuluri et al 2010; Kawamura et al., 2004]. Portions of CO₂ and N₂ gases were transferred to EA/isotope ratio mass spectrometer (irMS) via an interface (ConFlo II) for isotope ratio measurement. The $\delta^{13}\text{C}$ values of TC and $\delta^{15}\text{N}$ of TN are calculated using the following equation:

$$\delta^{13}\text{C} (\text{‰}) = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}/({}^{13}\text{C}/{}^{12}\text{C})_{\text{standard}} - 1] \times 1000 \quad (1)$$

$$\delta^{15}\text{N} (\text{‰}) = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}}/({}^{15}\text{N}/{}^{14}\text{N})_{\text{standard}} - 1] \times 1000 \quad (2)$$

The composition of sample is expressed with respect to nitrogen gas in the atmospheric N₂ ($\delta^{15}\text{N}$ value of atmospheric nitrogen is 0‰). The two nitrogen isotopes show different properties with regard to their kinetics and thus, depends upon the nature of their respective formation and that of their precursors, the isotopic composition of the particular species will be different. Heaton. [1986] and references therein, isotopic fractionation process can be explained in terms of isotopic enrichment factor (ϵ), where,

$$\epsilon_{\text{product-reactant}} (\text{‰}) = [\{ (15\text{N}/14\text{N})_{\text{product}} / (15\text{N}/14\text{N})_{\text{reactant}} \} - 1] \times 1000$$

Organic nitrogen (ON) is calculated by using following equation:

$$\text{ON} = \text{TN} - 14 \times ([\text{NO}_3^-]/62 + [\text{NH}_4^+]/18) \quad (3)$$

NO_3^- and NH_4^+ are the major ions in our sampling site whereas NO_2^- is not detectable.

4.2.3. Measurements of WSOC, WSTN, Major Ions and OC/EC

To measure water-soluble organic carbon (WSOC) and water-soluble total nitrogen (WSTN), known area of filter was cut and extracted with organic-free pure water. After ultrasonication for 15 minutes, extracts were passed through a syringe filter (Millex-GV, 0.45 μm , Millipore) and the WSOC and WSTN concentrations were measured using a total carbon and nitrogen analyzer (Shimadzu TOC-V_{CSH}). The filter extracts were acidified with 1.2 M HCl and purged with pure air before the analysis to remove dissolved inorganic carbon and volatile organics. The reproducibility for triplicate analysis of laboratory standards was within 5% [Miyazaki et al., 2011].

To measure cations and anions, an aliquot of sample filter disc (20 mm diameter) was extracted with organic-free pure water under ultrasonication. After filtration by using a membrane disc filter (Millex-GV, 0.45 μm , Millipore), extracts were injected to an ion chromatograph (IC) (761 Compact IC, Metrohm, Switzerland) to measure major ions. The data sets were reported in Kunwar and Kawamura (2013). The analytical errors in duplicate analysis of the authentic standards were within 5%. We also measured OC/EC using a Sunset Laboratory carbon analyzer.

4.3. Results and Discussion

4.3.1. Seasonal variations of TC, TN, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$

Concentrations of TC ranged from 1.0 -7.30 $\mu\text{g m}^{-3}$ (av. $2.1\pm 1.0 \mu\text{g m}^{-3}$). Monthly averaged concentrations of TC are shown in Figure 4.1a. The average TC concentrations with standard deviation were 2.01 ± 0.60 (range: 1.17-3.15 $\mu\text{g m}^{-3}$) in winter, $2.70\pm 1.67 \mu\text{g m}^{-3}$ (1.24-7.3 $\mu\text{g m}^{-3}$) in spring, $2.09\pm 0.63 \mu\text{g m}^{-3}$ (1.10-3.77 $\mu\text{g m}^{-3}$) in summer and $1.68\pm 0.47 \mu\text{g m}^{-3}$ (1.04-2.61 $\mu\text{g m}^{-3}$) in autumn. The highest TC concentration was observed during spring followed by summer, suggesting that our sampling site was influenced by both polluted air masses and biogenic sources during spring because spring is growing season when biogenic activities are higher. The summertime TC concentration suggests that Okinawa is strongly influenced from biogenic source because more than 90% of air masses come from the ocean [Kunwar and Kawamura, 2013].

To better understand the sources of organic carbon, we calculated TC/EC ratios. The TC/EC ratio shows the higher value (14.6) during summer, suggesting the major fraction of TC come from biogenic sources probably from oceanic phytoplankton and other biota. TC concentration in Cape Hedo is lower than the previous studies from many Chinese cities [Ho et al., 2006; Wang et al., 2010], Gosan [Jung et al., 2011; Kawamura et al., 2004; Kundu et al., 2010], Chennai [Pavuluri et al., 2010] and Tokyo [Kawamura and Ikushima, 1993]. However, TC content from Okinawa is higher than the high-Arctic aerosols [Narukawa et al., 2008], marine aerosols from the Arctic Ocean (Kawamura et al., 2012). However, average TC concentration in western North to equatorial Pacific Ocean showed 5.5 times lower than TC concentration from Cape Hedo, Okinawa [Kawamura and Sakaguchi, 1999].

Average annual TN concentration with standard deviation was $0.77\pm 0.65 \mu\text{g m}^{-3}$ (range: 0.15-3.30 $\mu\text{g m}^{-3}$). The annual average TN concentration from Cape Hedo is 3.2 times lower than that ($2.5 \mu\text{g m}^{-3}$) of one-year observation from Gosan [Kundu et al., 2010] and 4.1 times lower than that ($3.1 \mu\text{g m}^{-3}$) from the same Gosan site during spring [Kawamura et al., 2004]. In contrast, average TN concentration of Cape Hedo is 6.4 times higher than those from the north to equatorial Pacific Ocean [Kawamura and Sakaguchi, 1999]. The seasonally

averaged TN concentrations with standard deviation were $1.19 \pm 0.58 \mu\text{g m}^{-3}$ (range: $0.49\text{--}2.4 \mu\text{g m}^{-3}$) in winter, $0.93 \pm 0.50 \mu\text{g m}^{-3}$ ($0.42\text{--}2.31 \mu\text{g m}^{-3}$) in spring, $0.50 \pm 0.64 \mu\text{g m}^{-3}$ ($0.15\text{--}3.30 \mu\text{g m}^{-3}$) in summer and $0.43 \pm 0.19 \mu\text{g m}^{-3}$ ($0.22\text{--}0.96 \mu\text{g m}^{-3}$) in autumn. The highest concentration of TN was found in winter followed by spring (Figure 4.1b), suggesting that the source of TN is associated with polluted continental air masses from East Asia. The average C/N ratio during whole campaign was 5.3 ± 3.4 . The highest C/N ratio was observed in summer (7.11) whereas the lowest one was observed in winter (1.9). Particulate carbon is more important than the particulate nitrogen due to the biogenic emissions in summer. $\delta^{13}\text{C}$ of TC range from -24.2 to -21.6‰ (av. $-22.5 \pm 0.62\text{‰}$) in winter, -23.5 to -18.2‰ ($-22.1 \pm 1.3\text{‰}$) in spring, -23.9 to -21.6‰ ($-22.9 \pm 0.69\text{‰}$) in summer and -22.9 to -14.6‰ ($-20.7 \pm 2.15\text{‰}$) in autumn. Figure 4.1c showed the monthly variation of $\delta^{13}\text{C}$. As mentioned in the experimental section, most of the air parcels come from the north and south part of China during winter and spring. Thus, it is very reasonable to compare our data with the data from Chinese cities and Gosan site [Jung et al., 2011; Kawamura et al., 2004; Kundu et al., 2010], especially Gosan is located in between China and Okinawa. The average $\delta^{13}\text{C}$ value in the northern part of China during winter is -24.4‰ [Cao et al., 2011], which is lower than that (-23.4‰) of Gosan aerosols [Kawamura et al., 2004]. The $\delta^{13}\text{C}$ value of Gosan aerosols is still lower than Okinawa aerosols (-22.1‰), suggesting an isotopic enrichment of ^{13}C in aerosols that occurs by the photochemical aging of aerosols during long-range atmospheric transport.

The higher $\delta^{13}\text{C}$ value of TC (-22.1‰) from Cape Hedo than the Chinese cities [Cao et al., 2011] is probably due to the oxidation of organic aerosols during long-range atmospheric transport. During the oxidation process, OH or O_3 react with lighter carbon in aerosols. Hence, heavier carbon is enriched in the remaining aerosols. The enrichment of $\delta^{13}\text{C}$ is the indication of atmospheric aging [Aggarwal et al., 2013; Pavuluri et al., 2011; Wang et al., 2010]. During winter, $\delta^{13}\text{C}$ showed narrow range (-24.2 to -21.6‰) than spring (-23.5 to -18.2‰), suggesting that various sources and/or more aged aerosols may contribute the higher values in spring via long-range atmospheric transport. The higher value (-18‰) in spring may be caused by a significant oxidation of organic aerosols or the association with dusts and soil that may contain

carbonates. Carbonate carbon in Asian dust could contribute to the higher values [Kawamura, 2004]. Lopez-Veneroni et al. [2010] also shows the similar value of $\delta^{13}\text{C}$ for the TC, which is associated with dusts and soil. The average value of Cape Hedo aerosols in winter (-22.5‰) is higher than those of winter aerosols from 14 Chinese cities [Cao et al., 2011], suggesting the outflow of Asian aerosols is important in Cape Hedo by a long-range atmospheric transport of organic aerosols, which are subjected to oxidation to result in higher isotope ratios.

To confirm whether $\delta^{13}\text{C}$ value is associated with dust or not, we performed correlation analyses between nss-Ca and TC in spring. We found strong a correlation between nss-Ca and TC ($r^2 = 0.67$), suggesting the influence from dust because nss-Ca specially originates from dust. Interestingly, we did not get any good correlation between nss-Ca/TC and $\delta^{13}\text{C}$. This may suggest that during long-range transport bulk carbon associated with dust is intermixed with the carbon from various sources as it passes over the continent, coast and ocean. In contrast, Aggarwal et al. (2013) found a good correlation between nss-Ca/TC and $\delta^{13}\text{C}$ for Delhi aerosols.

As explained in experimental section, most of the summer aerosols come from the ocean. Here, we found very narrow range for $\delta^{13}\text{C}$ (-21.6 to -23.9‰). This value is comparable with those (-23.3 to -20‰) from the marine aerosols reported by Ceburnis et al. [2011]. However, we get lower $\delta^{13}\text{C}$ value in our sampling site, which may be due to the emissions of BVOCs. Marine plants get higher $\delta^{13}\text{C}$ value compare to terrestrial plants because of limited supply of inorganic carbon in water during the peak of biological activities in marine environment. Loh et al. [2004] showed that protein like fraction, carbohydrates and dissolved organic carbon in ocean water ranged from -21.1 to -20.7‰. Fry and Parker [1987] showed $\delta^{13}\text{C}$ values for the marine phytoplankton (-18 to -24‰) and marine macro algae (-8 to -27‰), suggesting that summer time aerosols are influenced from phytoplankton and macro algae in the ocean.

The $\delta^{15}\text{N}$ ranged from +8.03 to +22.6 ‰ (+12.7±2.6‰) (n = 50). This value is comparable with Gosan aerosols [Kundu et al., 2010]. The $\delta^{15}\text{N}$ value ranged from +10.4 to +15.4‰ (+13.6±1.7‰) in winter, +8.36 to +22.6‰ (+14.0±3.7‰) in spring, +9.69 to +13.2‰

($+11.1 \pm 1.1\%$) in summer and $+8.04$ to $+16.1\%$ ($+11.9 \pm 2.2\%$) in autumn. Both lower and higher range was observed in spring, further suggesting that various sources of nitrogenous compounds are possible in spring than other seasons. The average $\delta^{15}\text{N}$ value of TN for biomass burning aerosol was $+23.5\%$ ($+23.5$ to $+25.7\%$) [Kundu et al., 2010] whereas the average value was $+15\%$ ($+6.8$ to $+26.2\%$) in the marine aerosols from Jeju Island in the East China Sea (Kundu et al., 2010). The $\delta^{15}\text{N}$ from Cape Hedo is similar to the Gosan site and the average $\delta^{15}\text{N}$ is very similar to those ($+10.6\%$) reported in the atmospheric aerosol samples collected from Piracicaba regions in Brazil where major sources of aerosols are unburned vegetation tissues [Martinelli et al., 2002].

Figure 4.2a and 4.2b shows the monthly average variations of TC/TSP (%) and TN/TSP (%), respectively. TC/TSP ratio is higher during summer followed by winter, suggesting that higher loading of particulate carbon in summer and winter whereas the lowest ratio was observed during spring. TN/TSP shows the higher ratio in winter followed by spring, suggesting the higher loading of nitrogen content in winter and spring.

4.3.2. Sources of TC and TN and Variations of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$

We found the strong correlation between TC and TN in spring (Figure 4.3), suggesting that they have similar sources or similar formation processes. Weak positive correlation between TC and TN in winter suggests that some fractions of TC and TN have similar sources. The high TC/EC ratio during four seasons in Okinawa may suggest that they are formed from secondary oxidation of organic compounds [Kunwar and Kawamura, 2013]. To better understand the variation of $\delta^{13}\text{C}$ (primary or secondary), we performed correlation analysis of the WSOC/TC vs $\delta^{13}\text{C}$ because WSOC is formed by secondary oxidation of precursor organics. However, we did not find any significant correlation in four seasons. This is in contrast to the study in Mumbai, India, where a positive correlation was found between WSOC/TC and $\delta^{13}\text{C}$ [Aggarwal et al., 2013]. Thus, there may exist unknown processes for the various sources of $\delta^{13}\text{C}$ in Cape Hedo aerosols. Organic nitrogen is important component, but its source and formation mechanisms are less understood although the sources of organic

nitrogen are considered to be from algal blooms, bacteria [Facchini et al., 2008; Muller et al., 200], degraded protein [Kuznetsova et al., 2005], livestock/animal husbandry, fertilizers, biomass burning [Mace et al., 2003b]. Iinuma et al. [2007] and Nojima et al. [1983] reported that nitrophenols are originated from biomass burning and vehicular exhaust.

Organic nitrogen (ON) showed the highest concentration in winter ($0.38 \mu\text{g m}^{-3}$) followed by summer ($0.35 \mu\text{g m}^{-3}$) and spring ($0.28 \mu\text{g m}^{-3}$) whereas lowest concentration was observed in autumn ($0.12 \mu\text{g m}^{-3}$). The highest concentration of ON in winter suggests that ON is influenced from polluted air masses. We found lower concentration of WSON in winter and higher value in summer [Kunwar and Kawamura, 2013]. To identify the sources of ON and WSON in summer, we performed correlation analysis between ON and Na^+ ; the latter is a tracer of primary oceanic emission. However, we did not get a statistically important correlation, suggesting that ON and also WSON are probably formed from secondary oxidation of organic aerosols emitted by marine biogenic sources. Although ON and WSON concentrations were rarely reported in Chinese aerosols, we compare our WSON data with available data from Chinese cities. Wang et al. (2010) reported that the concentration of WSON is 4.2 times higher in winter ($22 \mu\text{g m}^{-3}$) than in spring ($5.2 \mu\text{g m}^{-3}$) in Chinese aerosols but in our sampling site winter and springtime WSON concentrations are almost same, suggesting that there are additional biogenic sources in spring. WSON/WSTN ratios showed the higher value in summer (0.35) followed by autumn (0.24) and spring (0.14) whereas the lowest value was observed in winter (0.07). These results suggest that water-soluble ON is more importantly produced in summer.

4.3.3. Contribution of NO_3^- and NH_4^+ to TN

Relations of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ against to TN are shown in Figure 4.4. The regression lines show that the main nitrogen species is NO_3^- . NO_3^- contributed about 45% of TN whereas NH_4^+ contributed only 18% of TN. Similarly, ON account for 37% of TN (Figure 4.5). The higher contribution of NO_3 to TN supports that our sampling site is significantly influenced by vehicular emissions and biomass burnings in East Asia through a long-range atmospheric

transport. The highest contribution of NO_3^- to TN was found in spring (51.3%) followed by winter (36.6%) and the lowest value was observed in summer (34%). In contrast, the average contribution of NH_4^+ to TN was highest in winter (29.1%) followed by spring (22.7%) whereas the lowest value was found in summer (3%). Both NO_3^- -N and NH_4^+ -N show good correlations ($r^2=0.70$ and 0.64) with TN and , suggesting that both are originated from the same sources.

The $[\text{SO}_4^{2-}]/[\text{NH}_4^+]$ ratio can be used as an indicator for the atmospheric processing of aerosols [Aggarwal et al., 2013; Pavuluri et al., 2010]. During winter and spring, SO_4^{2-} to NH_4^+ ratio (0.55 in winter and 0.35 in spring) is similar to those of Chennai aerosols and Mumbai aerosols where atmospheric oxidation is significant. As suggested by Aggarwal et al. [2013] and Pavuluri et al. (2010), the enrichment of ^{15}N in aerosol is due to following two reactions;



As shown in equation 1, the conversion of gaseous NH_3 to particle phase (NH_4^+) favors under the conditions of low pH. It is very meaningful to see the pH of the extract of Okinawa samples. Measured average pH of water extracts of winter samples (5.3) is lower than spring (5.6), suggesting that conversion of gaseous NH_3 to particle ammonium is important in winter. The low pH in winter and spring aerosols further supports the gas-to-particle conversion of nitrogenous components.

4.4. Summary and Conclusions

Stable carbon and nitrogen isotope ratios were determined for TC and TN in aerosols (TSP) samples from Okinawa, the outflow region of East Asian aerosols. We found higher values for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ during spring and lower values during summer. Higher $\delta^{13}\text{C}$ in spring suggests that springtime aerosols were associated with dusts and soils. No correlation between $\text{nss-Ca}/\text{TC}$ and $\delta^{13}\text{C}$ suggest that unknown processes of various sources of $\delta^{13}\text{C}$. The higher range of $\delta^{15}\text{N}$ in spring suggests the presence of various sources of nitrogen. The average $\delta^{15}\text{N}$ during winter and spring are similar whereas $\delta^{15}\text{N}$ during summer is lower than winter and spring, suggesting that the influenced from clean air masses during summer. The lower TC/TN

ratios in winter than summer suggest that TN is more emitted in the source regions during winter. Except for autumn, total carbon and nitrogen have common sources. The higher TC/EC ratios during summer are due to the biogenic emission from the ocean. Contribution of NO_3^- to TN is higher than that of NH_4^+ , suggesting the vehicular emission is the most important source of nitrogenous aerosols in Okinawa through a long-range atmospheric transport. Higher concentration of ON in wintertime is due to the presence of water insoluble organic nitrogen in winter. The higher WSON/WSTN ratios during summer suggest the more production of WSON during summer.

References

- Aggarwal, S. G., Kawamura, K., Umarji, S. G., Tachibana, E., Patil, R. S., Gupta, P. K., 2013. Organic and inorganic markers and stable C-, N-isotopic compositions of tropical coastal aerosols from megacity Mumbai: sources of organic aerosols and atmospheric processing, *Atmos. Chem. Phys.*, 13, 4667-4680.
- Anderson, R. S., Iannone, R., Thompson, A. E., Rudolph, J., Huang, L., 2004. Carbon kinetic isotope effects in the gas phase reactions of aromatic hydrocarbons with the OH radical at 296±4K, *Geophys. Res. Lett.* 31, Art. No. L15108.
- Cachier, H., Buat-Me'nard, M. P., Fontugne, M., Chesselet, R., 1986. Long-range transport of continentally-derived particulate carbon in the marine atmosphere: Evidence from stable carbon isotope studies, *Tellus, Ser. B*, 38, 161– 177.
- Cao, J., Chow, J. C., Tao, J., Lee, S-C., Waston, J.G, Ho, K. F., Wang , G., Zhu, C.S., Han, Y. M., 2011. Stable carbon isotopes in aerosols from Chinese cities: Influence of fossil fuels, *Atmos. Environ.*, 45, 1359-1363.
- Ceburnis, D., Garbaras, A., Szidat, S., Rinaldi, M., Fahrni, S., Perron, N., Wacker, L., Leinert, S., Remeikis, V., Faccini, M. C., Prevot, A. S. H., Jennings, S. G., Ramonet, M., O'Dowd, C. D., 2011. Quantification of carbonaceous matter origin in submicron marine aerosol by ¹³C and ¹⁴C isotope analysis, *Atmos. Chem. Phys.*, 11, 8593–8606.
- Cornell, S., Rendell, A., Jickells, T., 1995. Atmospheric inputs of dissolved organic nitrogen to the oceans. *Nature*, 376,243-246.
- Facchini, M. C., Decesari, S., Rinaldi, M., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Moretti, F., Tagliavini, E., Ceburnis, D., O'Dowd, C. D., 2008. Important source of marine secondary organic aerosol from biogenic amines, *Environ. Sci. Technol.*, 42, 9116–9121.
- Fisseha. R, Spahn, H., Wegener, R., Hohaus, T., Brasse, G., Wissel, H., Tillmann, R., Wahner, A., 2009. Stable carbon isotope composition of secondary organic aerosol from β -pinene oxidation. *Journal of Geophysical Research*, 114, D02304, doi:10.1029/2008JD011326.

- Fry, B., Parker, P. L., 1979. Animal diet in Texas seagrass meadows: $\delta^{13}\text{C}$ evidence for the importance of benthic plants, *Estuarine and coastal Marine Science*, 8, 499-509.
- Ho, K. F., Lee, S.C., Cao, J. J., Li, Y. S., Chow, J. C., Watson, J. G., Fung, K., 2006. Variability of organic and elemental carbon, water soluble organic carbon, and isotopes in Hong Kong, *Atmos. Chem. Phys.*, 6, 4569– 4576.
- Iinuma, Y., Brüggemann, Gnauk, T., Müller, K., Andreae, M. O., Helas, G., Parmar, R., Herrmann, H., 2007. Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat, *Journal of Geophysical Research*, 112, D08209, doi:10.1029/2006JD007120.
- Jung, J., Kawamura, K., 2011. Springtime carbon episodes at Gosan background site revealed by total carbon, stable carbon isotopic composition, and thermal characteristics of carbonaceous particles. *Atmospheric Chemistry and Physics* 11, 10911–10928.
- Kawamura, K., Ikushima, K., 1993. Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.*, 27, 2227-2235.
- Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanabe, T., Lee, M., 2004. Organic and inorganic compositions of marine aerosols from East Asia: seasonal variations of water-soluble dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition. In: Hill, R.J., et al. (Eds.), *Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan*. The Geochemical Society, Publication No. 9, pp. 243–265.
- Kawamura, K., Ono, K., Tachibana, E., Charrie, B., Sempere, R., 2012. Distributions of low molecular weight dicarboxylic acids, ketoacids and α -dicarbonyls in the marine aerosols collected over the Arctic Ocean during late summer, *Biogeoscience*, 9, 4725-4737.
- Kawamura, K., Sakaguchi, F., 1999, Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropic, *J. Geophys. Res.*, 104, 3501-3509.

- Kawamura, K., Watanabe, T., 2004. Determination of stable carbon isotopic compositions of low molecular weight dicarboxylic acids and ketocarboxylic acids in atmospheric aerosol and snow samples, *Analytical Chemistry*, 76, 5762–5768.
- Kundu, S., Kawamura, K., Lee, M., 2010. Seasonal variation of the concentrations of nitrogenous species and their nitrogen isotopic ratios in aerosols at Gosan, Jeju Island: Implications for atmospheric processing and source changes of aerosols. *Journal of Geophysical Research*, 115, D20305, doi:10.1029/2009JD013323.
- Kunwar, B., Kawamura, K., 2013. One-year observations of carbonaceous and nitrogenous components and major ions in the aerosols from subtropical Okinawa Island, an outflow region of Asian dusts. *Atmos. Chem. Phys. Discuss*, 13, 22059-22106, doi: 10.5194/acpd-13-22059-2013.
- Kuznetsova, M., Lee, C., Aller, J., 2005. Characterization of the proteinaceous matter in marine, *Marine Chem*, 96, 359–377.
- Loh, A. N., Bauer, J. E., Druffel, E. R. M., 2004. Variable ageing and storage of dissolved organic component in the open ocean, *Nature*, 430, 877-881.
- López - Veneroni, D. (2009), The stable carbon isotope composition of PM_{2.5} and PM₁₀ in Mexico City Metropolitan area air, *Atmos. Environ.*, 43, 4491–4502, doi:10.1016/j.atmosenv.2009.06.036.
- Mace, K. A., Artaxo, P., Duce, R. A., 2003. Water- soluble organic nitrogen in Amazon Basin aerosols during the dry (biomass burning) and wet seasons, *Journal of Geophysical Research*, 108, doi:10.1029/2003JD003557.
- Martinelli, L. A., Camargo, P. B., Lara, L. B. L. S., Victoria, R. L., Artaxo, P., 2002. Stable carbon and nitrogen isotopic composition of bulk aerosol particles in a C₄ plant landscape of southeast Brazil, 36, 2427-2432.
- Miyazaki, Y., Fu, P., Kawamura, K., Mizoguchi, Y., Yamanoi, K., 2012. Seasonal variations of stable carbon isotopic composition and biogenic tracer compounds of water soluble organic aerosols in deciduous forest, *Atmos. Chem. Phys.*, 12, 1367-1376.

- Miyazaki, Y., Fu, P., Kawamura, K., Mizoguchi, Y., Yamanoi, K., 2011. Seasonal variations of stable carbon isotopic ratios and biogenic tracer compounds of water-soluble organic aerosols in a deciduous forest, *Atmos. Chem. Phys. Discuss.*, 11, 30773–30795, doi:10.5194/acpd-11-30773.
- Muller, C., Iinuma, Y., Karstensen, J., van Pinxteren, D., Lehmann, S., Gnauk, T., Herrmann, H., 2009. Seasonal variation of aliphatic amines in marine sub-micrometer particles at the Cape Verde islands, 2009. *Atmos. Chem. Phys.*, 9, 9587–9597, doi:10.5194/acp-9-9587.
- Narukawa, M., Kawamura, K., Li, S-M., Bottenheim, J. W., 2008. Stable carbon isotopic ratios and ionic composition of the high-Arctic aerosols: An increase in $\delta^{13}\text{C}$ values from winter to spring, *J. of Geophys. Res.*, 113, D02312, doi:10.1029/2007JD008755.
- Narukawa, M., Kawamura, K., Takeuchi, N., Nakajima, T, 1999. Distribution of dicarboxylic acids and carbon isotopic composition in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.*, 26, 3101-3104.
- Nojima, K., Kawaguchi, A., Ohya, T., Kanno, S., Hirobe, M., 1983. Studies on photochemical reaction of air pollutants. 10. Identification of nitrophenols in suspended particulates, *Chem. Pharm. Bull*, 31, 1047-1051.
- Pavuluri, C. M., Kawamura, K., Swaminathan, T., Tachibana, E., 2011. Stable carbon isotopic compositions of total carbon, dicarboxylic acids and glyoxylic acid in the tropical Indian aerosols: Implications for sources and photochemical processing of organic aerosols, *J. of Geophys. Res.-atmos*, 116, D18307. doi:10.1029/2011JD015617.
- Sato, K., H. Li., Tanaka, Y., Ogawa, S., Iwasaki, Y., Takami, A., Hatakeyama, S., 2009. Long-range transport of particulate polycyclic aromatic hydrocarbons at Cape Hedo remote island site in the East China Sea between 2005 and 2008, *J. Atmos. Chem.*, 61, 243-257.
- Sugawara, S., Nakazawa, T., Inoue, G., Machida, T., Mukai, H., Vinnichenko, N. K., and Khattatov, V. U., 1996. Aircraft measurements of the stable carbon isotopic ratio of atmospheric methane over Siberia, *GLOBAL BIOGEOCHEMICAL CYCLES*, Vol. 10, No. 2, Pages 223-231, June 1996.

- Takami, A., Miyoshi, T., Shimono, A., Kaneyasu, N., Kato, S., Kajii, Y., Hatakeyama, S., 2007. Transport of anthropogenic aerosols from Asia and subsequent chemical toluene, and p-xylene, *J. Phys. Chem. A.*, 105, 7865-7874.
- Wang, G., Xie, M., Hu, S., Gao, S., Tachibana, E., Kawamura, K., 2010. Dicarboxylic acids, metals and isotopic compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal burning emission and secondary aerosol formation, *Atmos. Chem. Phys.*, 10, 6087-6096.
- Wang, G., Zhou, B. H., Cheng, C.L., Cao, J.J., Li, J. J., Meng, J. J., Tao, J., Zhang, R. J., Fu, P. Q., 2013. Impact of Gobi desert on aerosol chemistry of Xi'an, inland China during spring 2009: differences in composition and size distribution between the urban ground surface and mountain atmosphere, 2013. *Atmos. Chem. Phys.*, 13, 819-835.
- Yamamoto, S., Kawamura, K., 2011. Stable hydrogen isotopic compositions of fossil fuel-derived n-alkanes in the atmospheric aerosols from Okinawa, Japan, *Res. Org. Geochem.*, 27, 81-89.

Table 4.1. Seasonal variations of mass concentrations and stable isotope ratios in aerosols from Cape Hedo, Okinawa

Species	Winter	Spring	Summer	Autumn
	Ave±STD	Ave±STD	Ave±STD	Ave±STD
Total carbon (TC)	2.01 ±0.60	2.77±0.68	2.09±0.60	1.68±0.61
Total nitrogen (TN)	1.19±0.58	0.93±0.50	0.50±0.64	0.43±0.19
TC/Aerosol mass (%)	4.05±2.14	3.77±2.48	7.15±2.63	4.57±3.23
TN/Aerosol mass (%)	1.52±0.95	1.04±0.85	0.82±0.31	0.86±0.51
C/N ratios	2.36±0.76	4.05±1.01	9.50±3.46	5.40±2.50
$\delta^{13}\text{C}$	-22.5±0.62	-22.1±1.3	-22.9±0.69	-20.7±2.15
$\delta^{15}\text{N}$	+13.6± 1.72	+14±3.73	+11.1±1.19	+11.9±2.24

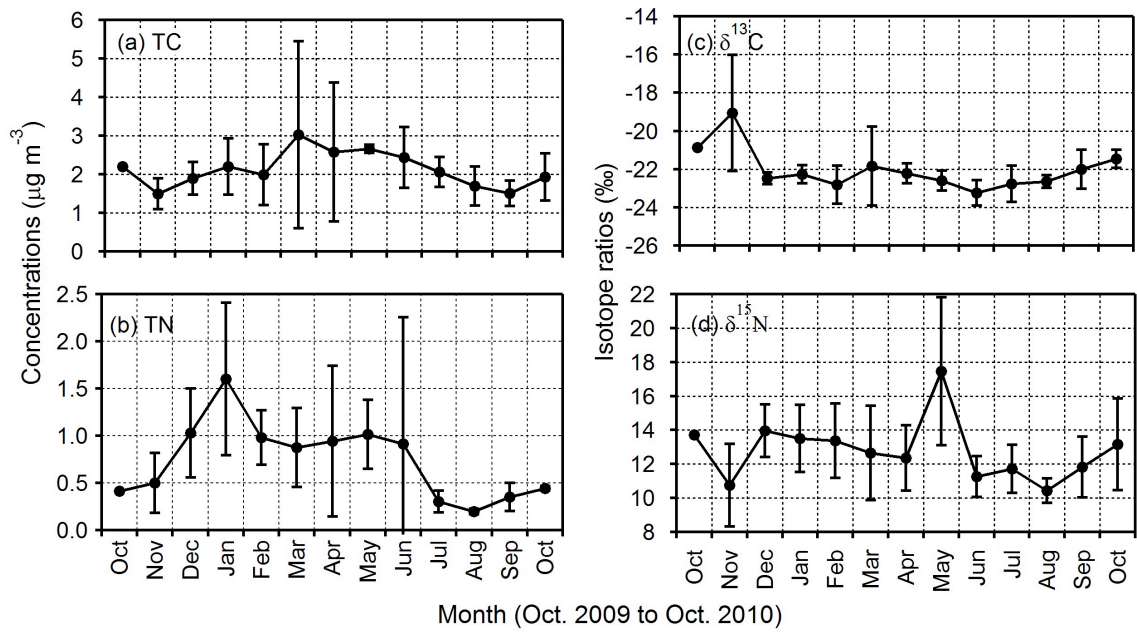


Figure 4.1. Average monthly variations of (a) TC, (b) TN, (c) $\delta^{13}\text{C}$ and (d) $\delta^{15}\text{N}$ in ambient aerosols collected from Cape Hedo, Okinawa.

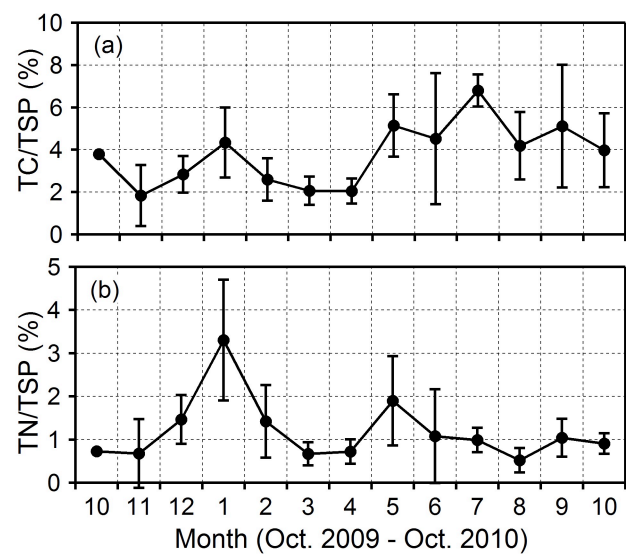


Figure 4.2. Average monthly variations of TC/TSP (%) and TN/TSP (%) in ambient aerosols collected from Cape Hedo, Okinawa.

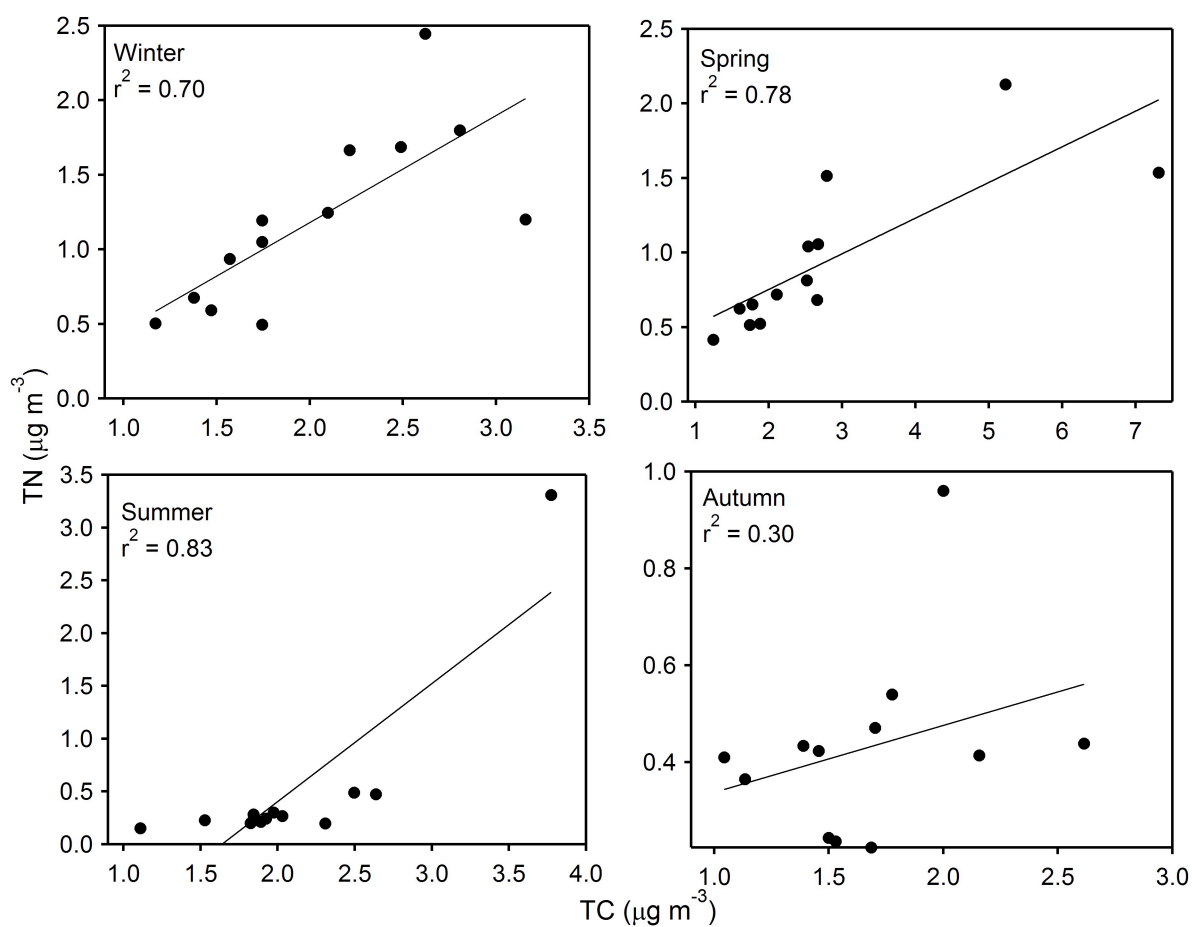


Figure 4.3. Correlation analysis between total nitrogen (TN) and total carbon (TC) in aerosol samples collected from Cape Hedo Okinawa.

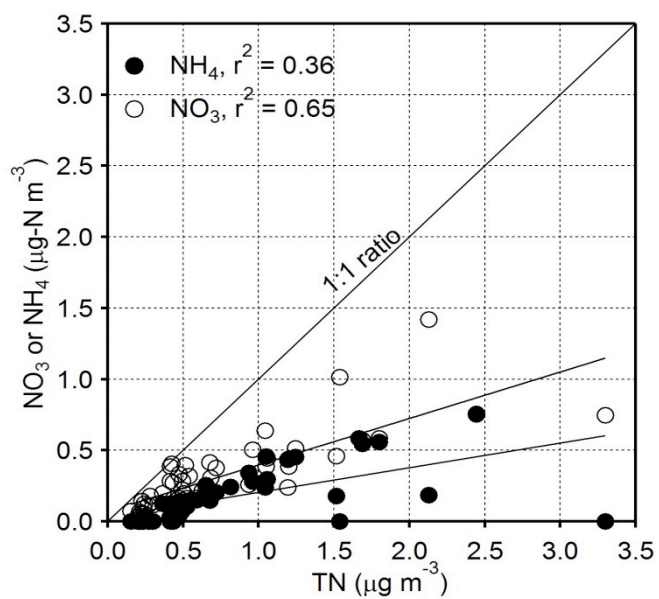


Figure 4.4. Scatter plot between NO₃-N or NH₄-N versus TN in aerosols collected in Cape Hedo Okinawa. The points in the bracket represent the outliers.

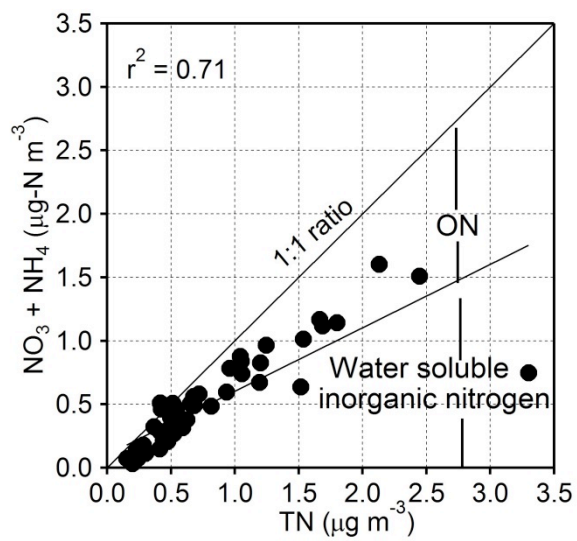


Figure 4.5. Scatter plot between $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ versus TN in ambient aerosols collected in Cape Hedo, Okinawa. The point in the bracket represents the outliers.

Chapter 5: Summary and Conclusions

A homologous series of α , ω -dicarboxylic acids (C_2 - C_{12}), ketocarboxylic acids (ωC_2 - ωC_9 and Pyr), aromatic diacids (phthalic, isophthalic, and terephthalic acids), and α -dicarbonyls (glyoxal and methylglyoxal), as well as fatty acids, were studied in aerosol samples collected in Okinawa Island in 2009 to 2010 to better understand their seasonal distributions. The results are discussed in terms of photochemical processing of organic aerosols and also biogenic versus anthropogenic sources. Oxalic acid (C_2) was found as the most abundant diacid species followed by malonic (C_3) and succinic (C_4) acid in all seasons. The seasonal variation of C_2 , C_3 and C_4 showed winter to spring maxima. The summertime maximum ratios of C_3/C_4 and fumaric to maleic acid were due to photochemical processing of diacids during warmer season. Enhanced phthalic to C_9 (Ph/ C_9) and C_6/C_9 ratios were observed in winter due to an important anthropogenic emissions followed by long-range atmospheric transport from East Asian megacities. The declined Ph/ C_9 and C_6/C_9 ratios and increased $C_{18:1}$ concentration in summer demonstrates a significant contribution of oceanic organic matter to the Okinawa aerosols in warm season. The increased C_3/C_4 ratio and strong correlations of C_2 to its precursors indicate that photochemical processing of organic aerosols is significant in summer.

Averaged total diacid-C/TC ratio (5.4%) in the Okinawa aerosols was found to be much higher than the values (<2%) reported in urban aerosols from Japan and China, but lower than that (8.8%) reported in the remote marine aerosols from the western Pacific including tropics. These comparisons explain that Okinawa aerosols are photochemically much more aged than urban aerosols, but less aged than the remote marine aerosols in the open ocean. Total diacids accounted for on average 5.8% of OC and 8.2% of WSOC in the aerosols from Okinawa. The relatively high ratios demonstrate that the organic aerosols from the western Pacific Rim are enriched with water-soluble organic acids as a result of photochemical aging during long-range atmospheric transport in the outflow region of East Asia. Finally, although the aerosol concentrations of diacids from Okinawa were several times lower than those from Gosan site, Jeju Island, South Korea, detailed analyses of molecular

compositions (e.g., C_3/C_4 ratios) demonstrated that the Okinawa aerosols are photochemically more aged than the Gosan aerosols due to the longer distance from the source regions in East Asia and higher ambient temperature and solar radiation because Okinawa is located in subtropical region. In contrast to East Asia (wintertime maximum), we found higher concentration of OC in spring (av. $2.36 \mu\text{g m}^{-3}$) than winter (av. $1.53 \mu\text{g m}^{-3}$). Higher concentration of OC was obtained during active biota seasons; spring and summer ($1.79 \mu\text{g m}^{-3}$). We also determined WSON. Higher concentrations of WSON were found summer, suggesting more emissions of water-soluble organic nitrogen from the ocean. The seasonal variations of oxalic, malonic and succinic acids are similar with those of EC and WSOC, suggesting that the low molecular weight diacids, WSOC and EC have similar source or similar formation pathway.

Springtime maxima of OC/EC ratios, MSA^- and correlation coefficients of OC and EC ($r = 0.81$), and MSA^- (0.81) showed that the importance of terrestrial and marine biogenic sources as well as anthropogenic sources in spring although the contribution from biogenic source is less significant. Similarly, moderate positive correlation between OC and nss-K^+ was found in both winter ($r = 0.72$) and spring (0.65), suggesting that biomass burning contribution is higher in winter and spring. We found an extremely higher OC/EC ratio and strong correlation between OC and MSA^- (0.71) in summer, further suggesting a strong biogenic emission of OC followed by photochemical formation of SOC in hot season as well as emission of BVOCs. Very high WSOC/OC ratios (0.6) in winter suggest the oxidation of anthropogenic primary organic compounds emitted in East Asian countries is still active even in cold season during long-range atmospheric transport, followed by the subsequent gas-to-particle conversion.

The high concentrations of NO_3^- , SO_4^{2-} , $\text{NH}_4\text{-N/WSTN}$ ratio in winter suggest that Cape Hedo is strongly influenced by vehicular emission, biomass burning, industrial emission and coal combustion in East Asia. We found a strong correlation between the biomass burning tracer (nss-K^-) and EC ($r=0.80$), suggesting that major fraction of EC is formed from the incomplete combustion of biomass.

Stable carbon and nitrogen isotope ratios were determined for TC and TN in aerosols (TSP) samples from the Cape Hedo, Okinawa. We found higher values for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ during spring and lower values during summer. Higher $\delta^{13}\text{C}$ in spring suggests that springtime aerosols were associated with dusts and soils. No correlation between nss-Ca/TC and $\delta^{13}\text{C}$ suggest that unknown processes of various sources of $\delta^{13}\text{C}$ such as biomass burning, coal combustion, and vehicular emission. The higher range of $\delta^{15}\text{N}$ in spring suggests the presence of various sources of nitrogen such as vehicular emission, biofuel burning emission and soil dust emission. The average $\delta^{15}\text{N}$ during winter and spring are similar whereas $\delta^{15}\text{N}$ during summer is lower than winter and spring, suggesting that the influenced from clean air masses during summer. The lower TC/TN ratios in winter than summer suggest that TN is more emitted in the source regions during winter. The higher TC/EC ratios during summer are due to the biogenic emission from the ocean. Contribution of NO_3^- to TN is higher than that of NH_4^+ , suggesting the vehicular emission is the most important source of nitrogenous aerosols in Okinawa through a long-range atmospheric transport. Higher concentration of ON in wintertime is due to the presence of water insoluble organic nitrogen in winter. The higher WSON/WSTN ratios during summer suggest the more production of WSON during summer.