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**Geochemical study on low molecular weight dicarboxylic acids
and related compounds in the marine aerosols from the Pacific
Ocean**

by

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Abstract

To better understand the sources and atmospheric processing of organic aerosols in the remote marine atmosphere, aerosol (TSP) samples were collected over the western North Pacific (13°14'N-53°37'N and 140°46'E-179°54'W) during May-July 2010, central Pacific (1°59'N-35°N and 171°54'E-90°58'W) during September-October 1999, and North-South Pacific (3°05'N-34°02'N, 6°59'S-25°46'S and 144°52'E-173°55'W) during February-April 1994 and were studied for dicarboxylic acids (C₂-C₁₁), ω -oxoacids, pyruvic acid and α -dicarbonyls as well as organic and elemental carbon and water-soluble organic carbon. Over the western North Pacific, diacids are most abundant followed by ω -oxoacids and α -dicarbonyls. Although the molecular compositions of diacids are generally characterized by the predominance of oxalic (C₂) acid, I found a depletion of C₂ in four samples, which were collected in the high latitudes (48°N-54°N) of the western North Pacific where succinic (C₄) acid is dominant. I consider that photochemical degradation of unsaturated fatty acids emitted from the ocean surface produced C₄ over the high latitudinal western North Pacific, where *Chlorophyll-a* maximized during the cruise. Moreover, seven samples collected in mid and high latitudes of the western North Pacific show predominance of malonic (C₃) acid over C₄, suggesting photochemical degradation of C₄ to C₃. Spatial distributions of diacids, ω -oxoacids and α -dicarbonyls together with total carbon were characterized by their higher abundances in the coastal western North Pacific followed by high and low latitudinal regions, signifying that continental aerosols are transported long distances to the remote marine atmosphere. However, in the central Pacific aerosols collected between Japan to Mexico, I found a predominance of oxalic (C₂) acid followed by malonic (C₃) and succinic (C₄) acid, where oxalic acid comprises 74% of total diacids. Abundances of oxalic acid showed 3 times higher values in the upwelling zone of the central Pacific than those of the non-upwelling zone. Positive relation ($r^2=0.79$) between oxalic acid and oxidation products (ω C₂+Gly+Pyr)

of biological volatile organic compounds (BVOCs) suggests that secondary production of oxalic acid occurs in aqueous aerosol phase via the oxidation of marine derived BVOCs in the upwelling central Pacific. Atmospheric abundances of short chain (C_2 - C_4) diacids during the North-South Pacific cruise, showed 4 times higher values in the North Pacific than in the South Pacific. During this cruise, abundances of C_2 in the western North Pacific illustrated 5 to 10 time higher values than in the central North and South Pacific, respectively. However, the aerosol samples that were collected in the western North Pacific, demonstrated that glyoxylic (ωC_2) acid and methylglyoxal (MeGly) were dominant with C_2 . I found a strong correlation between C_2 and ωC_2 ($r^2=0.89$) and C_2 and MeGly ($r^2=0.96$) in the same samples that were collected in the western North Pacific but their correlations are significantly weak for the rest of the samples. These results together with 7-day back-ward air masses trajectory indicate that ωC_2 and MeGly are both photochemical oxidation products of aromatic hydrocarbons in polluted-continental air masses, which are then serve as precursor of C_2 during long-range atmospheric transport.

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Chapter 1: Introduction

1.1. Atmospheric aerosols

The word aerosol is defined as solid or liquid particles suspended in gas, and it includes a wide range of phenomena such as dust, fume, smoke, mist, fog, haze and smog (Seinfeld and Pandis, 1998). Atmospheric aerosols are generally considered as particles having range in size from few nanometers (nm) to 10 micrometers (μm) in diameter. These particles either directly emitted into the atmosphere or formed there through oxidation of precursor gases, such as sulphur dioxide, nitrogen oxides and volatile organic compounds (VOCs), where the resulting oxidation products further nucleate to form new particles or condense on pre-existing ones (Finlayson-Pitts and Pitts, 1997; Seinfeld and Pandis, 1998). Sources of particles in the atmosphere incorporate natural and anthropogenic activities. The natural source includes wind borne dust, sea spray, volcanic emissions and forest fires, while emissions of particles attributes to anthropogenic activities including fossil fuel combustion, industrial processing, transportation and construction activities. On a global scale, natural aerosols sources are 4-5 times higher than anthropogenic sources, but regional variations in anthropogenic pollution may change this ratio significantly in certain areas, particularly in the highly industrialized Northern Hemisphere (Seinfeld and Pandis, 1998).

1.2. Primary and secondary organic aerosol components

Depending on the origin of organic aerosol, aerosols components can be classified as primary and secondary organic aerosol. Primary organic aerosol (POA) components are directly emitted in the condensed phase or as semi-volatile vapors, which are condensable under atmospheric conditions. The main sources of POA particles are natural and anthropogenic biomass burning including forest fires, slashing and burning, domestic heating, fossil-fuel combustion and wind-driven or traffic-related suspension of soil and road dusts, sea spray and spray from other surface waters with dissolved organic compounds (Pöschl et al., 2005). Secondary organic aerosol (SOA) components are formed by chemical reaction

and gas-to-particle conversion of volatile organic compounds (VOCs) in the atmosphere, which may proceed through different pathways:

- a) New particle formation: formation of semi-volatile organic compounds (SVOCs) by gas-phase reactions and participation of SVOCs in nucleation and growth of new aerosol particles.
- b) Gas-particle partitioning: formation of SVOCs by gas phase reactions and uptake (adsorption and absorption) by pre-existing aerosol or cloud particles.
- c) Heterogeneous or multiphase reaction: formation of low volatility and non-volatile organic compounds (LVOCs, NVOCs) by chemical reaction of VOCs or SVOCs at the surface or in the bulk of aerosol or cloud particles.

1.3. Aerosol chemical composition

Atmospheric aerosols are generally composed of variable amounts of sulphate, ammonium, nitrate, sodium, chloride, trace metals, crustal elements, water and carbonaceous material. The sulphate components are derived predominantly from the atmospheric oxidation of anthropogenic and natural sulphur-containing compounds such as sulphur dioxide (SO_2) and dimethyl sulphide (DMS) (Calvo et al., 2013). NO_3^- and NH_4^+ are the main nitrogenous compounds in atmospheric particulate matter. The most important precursor gases emitted by natural and anthropogenic sources are NO, NO_2 , N_2O and NH_3 and nitric acid is the main product generated by oxidation in the atmosphere (Mészáros, 1999). The anthropogenic production of secondary nitrate precursor gases occurs in the generation of power (gas, fuel-oil and coal combustion) and in other combustion processes involving high temperatures, such as those occurring in the motors of vehicles and in biomass burning (Pinder et al., 2012). Diacids including oxalic, malonic, maleic and phthalic acids can contribute to aerosol nucleation process by binding to sulphuric acid and ammonia (Xu and Zhang, 2012), formation of new particles and nanoparticles in the atmosphere are enhanced with the presence of these organic acids (Zhang et al., 2004; Wang et al., 2010).

The carbonaceous fraction of the aerosols consists of both elemental and organic carbon. Elemental carbon (EC) is emitted directly into the atmosphere, predominantly from combustion processes. The particles containing organic carbon (OC) can be emitted directly into the atmosphere (i.e. from primary sources such as biomass and fossil fuels combustion) but in remote oceanic regions source of OC is associated with biological activity (O'Dowd et al., 2008), they can also be introduced by secondary organic aerosol (SOA) formation. SOA may represent up to 90% of OC in urban areas and 14% in remote marine atmosphere (Fu et al., 2013). It has been demonstrated that a significant fraction of OC is formed by water-soluble compounds (WSOC) (Novakov and Penner, 1993), and these particles may be found in the atmospheric aqueous phase (Sellegri, 2002). Water soluble organic aerosols play an important role in climate forcing (Novakov and Penner, 1993) and CCN activity (Saxena et al., 1995).

Marine aerosol is the most important aerosol fraction worldwide (White, 2008). Dimethylsulfide (DMS), which is emitted into the atmosphere through phytoplankton activities, is one of the most significant precursors of atmospheric sulphate in oceanic regions (Yang et al., 2011). Marine salt aerosol is formed mainly by sodium and chloride, with smaller amounts of other components such as sulphate, potassium, magnesium and calcium. Ocean is the main source of sea salt aerosol in coastal areas (Claeys et al., 2010), which are emitted to the atmosphere by bubble bursting processes and are depend on the wind speed. Secondary organic aerosol (SOA) can form in the marine boundary layer through a number of different processes. Biogenic volatile organic compounds (BVOCs), emitted by the sea surface and their oxidation products can be involved in new particle formation through nucleation (Rinaldi et al., 2010). BVOCs and related oxidation products can also condense on pre-existing particles and droplets, contributing to the particle mass. One of the important

SOA components in marine aerosol is ocean-emitted isoprene, which can change the properties of clouds over the marine atmosphere during bloom (Meskhidze and Nenes, 2006).

1.4. Atmospheric impacts of aerosols

1.4.1. Aerosols and radiative forcing

Aerosols absorb solar radiation in the atmosphere, together with the reflection of solar radiation to space, which leads to a large reduction in the solar radiation absorbed by the earth's surface and carbonaceous aerosols are identified as playing a major role in this process. The changes arising from the aerosol scattering and absorption of radiation are referred to as the direct radiative forcing. The increase in aerosols in the atmosphere may cause an increase in the droplet number concentration and finally leads to an increase in the reflection to space of solar radiation from clouds, leading to a climate cooling (IPCC, 2001). This is called the first indirect radiative forcing. If the condensed moisture inside the cloud is not altered by the increase in aerosols, it decrease droplet radius due to increment of number concentration resulting in a decrease in the precipitation efficiency (IPCC, 2001; Haywood and Boucher, 2000; Ramaswamy et al., 2001). This direct microphysical process effect leads to suppression of precipitation in polluted clouds, which may leads to an increase in cloud life time and in turn the amount of clouds. The increase in cloudiness will lead to a further increase in the reflection of solar radiation, giving rise to the so-called second indirect radiative forcing.

1.4.2. Effects of aerosols on clouds formation

The Twomey effect refers to the enhanced reflection of solar radiation due to the more but smaller cloud droplets in a cloud whose liquid water content remains constant (Twomey, 1959). The more but smaller droplets reduce the precipitation efficiency and therefore enhance the cloud life time and hence the cloud reflectivity, which is referred to as cloud life time (Albrecht, 1989). Absorption of solar radiation by aerosols leads to heating of

the air, which can result in an evaporation of cloud droplets. The IPCC aviation report has identified that the effect of aircraft on upper tropospheric cirrus clouds as a potentially important to climate forcing. One aspect may be describe as the “direct” effect due to the formation of contrails as a result of supersaturated air from the aircraft and the “indirect” effect is due to the impact of an increase in freezing nuclei (FN) in the upper tropospheric regions due to particulates from aircraft emissions. These FN act as nuclei for ice crystals which form cirrus clouds. An increase in the number of ice crystals in cirrus clouds would also exert a Twomey effect in the same way as for water clouds. Moreover, a change in the ice water content of cirrus clouds may exert a radiative effect in the infrared.

1.4.3. Effects of aerosols on precipitation

Excess emissions of aerosols in the atmosphere due to human activities, which is increasing cloud optical depth and reducing solar radiation at the surface. Such a reduction has been observed in the industrial regions of the northern Hemisphere (Gilen et al., 1998; Liepert, 2002; Stanhill and Cohen, 2001). On a regional scale, smoke from sugarcane and forest fires has reduced cloud droplet size and therefore trends to inhibit precipitation (Warner and Twomey, 1967; Warner, 1968; Eagan et al., 1974). Heavy smoke from the Amazon Basin has been observed to increase cloud droplet sizes (Reid et al., 1999; Andreae et al., 2004). Andreae et al. (2004) also suggest that this delayed the onset of precipitation from 1.5 km above cloud base in pristine clouds to more than 5 km in polluted clouds and more than 7 km in pyro clouds. They also proposed that elevating the onset of precipitation released latent heat higher in the atmosphere and allowed invigoration of the updrafts, causing intense thunderstorm and large hail. Finally, these processes might affect the water cycle, pollution burden of the atmosphere and the dynamics of the atmosphere.

1.4.4. Aerosols effects on the vertical stability of the atmosphere

Changes in the atmospheric lapse rate modify the long wave emission, affect the water vapor feedback and cloud formation (Hu, 1996). Both of the observations and model studies has shown that an increase in the lapse rate enhances water vapor feedback (Sinha, 1995). Model simulation by Feichter et al. (2004) has shown that aerosols cooling extend up to the tropopause with a maximum in the boundary layer of the northern mid and high latitudes and in the tropics aerosol cooling maximized in the upper troposphere. The overall effect of the aerosol cooling near the surface in the polluted regions of the Northern Hemisphere that stabilizes the lower atmosphere whereas near the surface changes in temperature are smaller in the tropics and the mid latitudes of the southern Hemisphere. Destabilization of the atmosphere above the boundary as a result of black carbon heating above the boundary layer was obtained in a climate model study by Menon et al. (2002b) based on GCM driven by the observed aerosol optical depth over India and China. They assumed that when aerosols were absorbed, the atmospheric stability above the boundary layers were reduced, resulting in enhanced vertical motion. This affected the large-scale circulation and produced precipitation pattern in China, which are associated with extreme floods and drought that China has experienced in recent years.

1.5. Purpose of the study

The western North Pacific is influenced by Asian continental and anthropogenic outflows during the study. These continental air masses bring anthropogenic gaseous species, particulate matters, dust particles, ozone (O₃), volatile organic compounds (VOCs) and NO_x from East Asia towards coastal western North Pacific during atmospheric transport particularly in winter and spring (Miyazaki et al., 2010; Naja and Akimoto, 2004; Huebert et al., 2003). In contrast, during summer, vast areas of the western North Pacific influenced by frequent intrusion of air from the south and southeast due to the persistent high-pressure

system in the Pacific (Miyazaki et al., 2010) and in every spring, it experienced with huge of phytoplankton bloom (Kasai et al., 1998). The central and eastern equatorial Pacific is characterized by cold tongue of up-welled water, which contains huge concentrations of macronutrients (N, P, Si) and high dissolved inorganic carbon (Chavez and Barber, 1987; Toggweiler and Carson, 1995). The vastness of the upwelling region makes the eastern equatorial Pacific as one of the most productive oceanic ecosystem, which is accounted for ~18% of the global new production (Chavez and Toggweiler, 1995) and largest source of oceanic CO₂ to the atmosphere which is equivalent to ~10% of the total anthropogenic flux (Marland et al., 2000). In this study, we have a chance to catch East Asian polluted and aged aerosols which have transported long distances over the coastal regions of Japanese Islands, and even marine fresh aerosol from the pelagic ocean of central Pacific. In general, concentration of diacids and related compounds showed several times higher values in the coastal western North Pacific than remote oceanic regions. The main objectives of this study are to understand the molecular compositions, abundances and spatial distributions of diacids and related compounds together with carbonaceous components in the marine aerosols from the different oceanic regions of the Pacific. Here we discuss the sources of diacids and their photochemical transformation during long-range atmospheric transport. In addition, we evaluate the contributions of diacids to WSOC and TC and discuss the sources and photochemical alteration of water-soluble organics in remote marine atmosphere.

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Chapter 2: Experimental methods

2.1. Experimental procedures for diacids and related compounds

Water-soluble diacids, ω -oxoacids, pyruvic acid and α -dicarbonyls were determined using the improved method of Kawamura and Ikushima (1993) and Kawamura (1993). In brief, aliquots of filter samples were extracted with organic-free ultra pure water ($5\text{ ml} \times 3$, $>18\text{ M}\Omega$) under ultrasonic agitation for the isolation of diacids and other water-soluble organic compounds. The extracts were passed through a glass column (Pasteur pipet) packed with quartz wool for removing filter debris and particles. The extracts were adjusted to pH=8.5-9.0 using 0.05 M KOH and then concentrated to almost dryness using a rotary evaporator ($\sim 40^\circ\text{C}$) under vacuum. After the dryness, concentrates were derivatized with 14% borontrifluoride in n-butanol at 100°C for 1 hour. The derived dibutyl esters and dibutoxy acetals were extracted with $\sim 5\text{ ml}$ of n-hexane after adding $\sim 5\text{ ml}$ pure water. The hexane layer was concentrated to about $50\text{ }\mu\text{l}$ using a rotary evaporator, transferred to a glass vial (1.5 ml), consequently dried by N_2 blow down and dissolved in $100\text{ }\mu\text{l}$ of n-hexane.

The derivatives ($2\text{ }\mu\text{l}$) were injected into a capillary gas chromatograph (GC) system (Agilent 6890) equipped with a split/splitless injector, fused silica capillary column (HP-5, $25\text{ m} \times 0.2\text{ mm id} \times 0.5\text{ }\mu\text{m}$ film thickness) and flame ionization detector (FID). Identification of esters and acetals were performed by the comparison of GC retention times and mass spectra with those of authentic standards. Mass spectral analysis was conducted with a GC/mass spectrometry system (Agilent MS) and the quantification of compounds was performed by GC/FID. Similar procedure was also conducted for recovery and blank experiments. I got 85% recovery for oxalic acid and more than 90% for malonic, succinic and adipic acids. Triplicate analyses of the sample showed that analytical errors are less than 10% for major diacids. Field blanks showed very small peaks of oxalic, pyruvic and phthalic acids on the

GC chromatograms, which are less than 4% of the real samples. The reported concentrations for the samples were corrected for the field blanks.

2.2. Experimental procedures for water-soluble organic carbon (WSOC), water-soluble total nitrogen (WSTN), organic and elemental carbon

Water-soluble organic carbon (WSOC) and total nitrogen (WSTN) were measured using a Shimadzu total carbon/nitrogen analyzer (TOC-V_{CSH}) (Miyazaki et al., 2011). First, a filter disc of 3.14 cm² was extracted with organic-free ultra pure water under ultrasonication for 15 minutes. The extracts were then passed through a syringe filter (Millex-GV, 0.45 µm, Millipore). For the removal of inorganic carbon and volatile organics, the extracts were acidified with 1.2 M HCl and purged with a pure air. The analytical errors of WSOC and WSTN during triplicate analyses were within 5%. WSOC and WSTN concentrations reported here are corrected for the field blanks.

Concentrations of organic carbon (OC) and elemental (EC) were measured using a Sunset Laboratory carbon (OC/EC) analyzer following Interagency Monitoring Protected Visual Environments (IMPROVE) thermal/optical evolution protocol (Wang et al., 2005). The presence of carbonate carbon may be negligible because 5-day air mass back trajectories do not reach the arid regions in China where carbonates such as CaCO₃ are emitted as discussed later. Total carbon (TC) was calculated as TC=OC+EC. A filter disc of 1.4 cm² punch was put in quartz boat placed in the thermal desorption chamber and applied to stepwise heating in a helium flow, and then helium gas was switched to He/O₂. Finally, evolved CO₂ during the oxidation at each temperature step was measured with non-dispersive infrared (NDIR) detector. For the setting up of the OC/EC split point and OC correction, a transmittance of light (red 660 nm) was applied through the filter punch. The analytical error

in duplicate analysis for OC and EC of the filter sample were within 10% and the reported concentrations are corrected for the field blanks.

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Chapter 3: Spatial distributions of dicarboxylic acids, ω -oxoacids, pyruvic acid and α -dicarbonyls in the remote marine aerosols over the western North Pacific

3.1. Introduction

Low molecular weight (LMW) carboxylic acids are water-soluble and thus their presence in aerosols enhances the hygroscopic properties of atmospheric particles (Kawamura et al., 2010a). They can account for 0.3-4.5% of total carbon (TC) in urban aerosols and more than 10% of TC or water-soluble organic carbon (WSOC) in remote marine aerosols (Ho et al., 2007; Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999; Kawamura and Yasui, 2005; Kerminen et al., 2000; Wang et al., 2006). Most of organic aerosol studies in remote marine areas have been conducted in terms of long-range atmospheric transport of lipid class compounds (Gagosian et al., 1987; Kawamura et al., 2004; Peltzer and Gagosian, 1989; Sicre et al., 1990) and photochemical processing of water-soluble organic compounds such as diacids (Kawamura et al., 1996a; Kawamura and Gagosian, 1987; Kawamura and Usukura, 1993; Stephanou, 1992).

Diacids and related compounds play an important role in the radiative forcing of the earth by scattering light and have potential contribution to cloud condensation nuclei (CCN) because of their high water solubility and hygroscopic properties (Kawamura and Usukura, 1993; Kerminen et al., 1999; Saxena et al., 1995). However, little is known about their spatial distributions in the remote marine atmosphere (Sempéré and Kawamura, 2003), although water-soluble dicarboxylic acids are important constituents of organic aerosols in the remote marine atmosphere (Bikkina et al., 2014; Kawamura and Sakaguchi, 1999).

LMW α , ω -dicarboxylic acids and related compounds, i.e., ω -oxocarboxylic acids and α -dicarbonyls are the most abundant water-soluble organic compound classes (Sempéré

and Kawamura, 2003). These compounds are significantly produced in polluted areas by the incomplete combustion of fossil fuels (Kawamura and Kaplan, 1987; Kerminen et al., 2000; Sempéré and Kawamura, 2003), meat cooking (Rogge et al., 1991; Schauer et al., 1999), biomass burning (Gao et al., 2003; Kundu et al., 2010a; Mayol-Bracero et al., 2002; Yamasoe et al., 2000) and from biogenic emissions of unsaturated fatty acids and isoprene (Bikkina et al., 2014; Kawamura and Gagosian, 1990). LMW diacids are also produced through ozonolysis and photooxidation of various organic compounds (Bandow et al., 1985; Grosjean et al., 1978; Hatakeyama et al., 1987; Kawamura and Gagosian, 1987; Kawamura and Ikushima, 1993; Norton et al., 1983; Schuetzle et al., 1975) and have been reported at significant concentrations in the urban, semi-urban, rural and even in the remote marine atmosphere (Kawamura and Sakaguchi, 1999; Kawamura and Usukura, 1993; Limbeck et al., 2001; Sempéré and Kawamura, 1996; Wang et al., 2002) and in the Arctic atmosphere (Kawamura et al., 2010a, 1996b, 1995a; Li and Winchester, 1993). They are also abundant in ice core samples (Kawamura et al., 2001a; Kawamura and Yasui, 1991; Legrand and De Angelis, 1996).

The western North Pacific is an ideal area to study those water-soluble organics for their long-range atmospheric transport, photochemical production and transformation, the contributions from anthropogenic and biogenic sources, and their global background concentration levels. Moreover, the western North Pacific is a transitional spot for the mixing of both continental and marine aerosols as influenced by the different continental air masses transported from China, Korea, Japan, and Siberia. In this study, we collected remote marine aerosol samples over the western North Pacific during May-July, 2010 for the determination of water-soluble dicarboxylic, ω -oxocarboxylic acids, pyruvic acid and α -dicarbonyls as well as organic carbon, elemental carbon, water-soluble organic carbon and total nitrogen. Here, we report the molecular compositions of diacids and related

compounds, their spatial distributions together with aerosol mass, aerosol carbon and nitrogen concentrations in the western North Pacific aerosols and contributions of water-soluble dicarboxylic acids to aerosol TC. We also discuss the sources of diacids and their photochemical transformation during long-range atmospheric transport.

3.2. Aerosol sampling

Remote marine aerosol samples were collected in the western North Pacific (13°14'N-53°37'N and 140°46'E-179°54'W) from the upper deck of the T/V *Oshoro Maru* cruise using pre-combusted (450°C) quartz fiber filters (Pallflex 2500QAT-UP, 20 × 25 cm) and high volume air sampler during May-July, 2010. The sampler was controlled with a wind sector ($\pm 60^\circ$) and wind speed ($\geq 5 \text{ m s}^{-1}$) system to avoid potential contamination from the ship exhausts (Kawamura and Sakaguchi, 1999). Sampling time was about 48 hours. The cruise track is shown in Fig. 3.1. After sample collection, the sample filter was stored in a clean glass jar with a Teflon-lined screw cap at -20°C prior to analysis. Total aerosol mass was calculated by weighing the filter before and after sample collection. Blank filters were exposed to the marine air in the sample shelter for a few seconds and then recovered.

3.3. Backward air mass trajectory analysis

To find out the source regions of air masses in the western North Pacific (13°14'N-53°37'N and 140°46'E-179°54'W), 5-day backward trajectory analysis at 500 m above the ground was performed for every day during the sampling period of 9 May, 2010 to 28 July, 2010 using a Hybrid Single-Particle Lagrangian Trajectory (HYSPLIT) model NOAA Air Resources Laboratory. Fig. 3.8 shows backward air masses trajectories for low, mid and high latitudinal regions of the western North Pacific Ocean. The coastal western North Pacific is influenced by the continental air masses from Japanese Islands, China and Korea. In contrast,

low and high latitudinal regions of the western North Pacific were strongly covered by oceanic air masses.

3.4. Results and discussion

3.4.1. Aerosol mass, total carbon and water-soluble total nitrogen contents

Aerosol mass concentrations ranged from 11 to 232 $\mu\text{g m}^{-3}$ (av. 44 $\mu\text{g m}^{-3}$, median 32 $\mu\text{g m}^{-3}$) over the western North Pacific. These values are comparable to those of previous studies from the western Pacific (11-68 $\mu\text{g m}^{-3}$) (Sempéré and Kawamura, 2003), the western to central Pacific (19-404 $\mu\text{g m}^{-3}$, av. 48 $\mu\text{g m}^{-3}$) (Kawamura and Sakaguchi, 1999) and urban Tokyo, Japan (54-220 $\mu\text{g m}^{-3}$, av. 48 $\mu\text{g m}^{-3}$) (Kawamura and Ikushima, 1993). During the study period, higher aerosol mass concentrations were observed in mid latitudinal regions of the western North Pacific near the Japanese Islands, suggesting that their sources are mainly of continental origin.

Concentrations of TC in the western North Pacific aerosol samples ranged from 0.10 to 2.71 $\mu\text{g m}^{-3}$ (av. 0.67 $\mu\text{g m}^{-3}$, median 0.44 $\mu\text{g m}^{-3}$). These TC contents are similar or little higher than those reported from the western North and central Pacific Ocean (av. 0.38 $\mu\text{g m}^{-3}$) (Kawamura and Sakaguchi, 1999) and the Arctic (av. 0.36 $\mu\text{g m}^{-3}$) (Kawamura et al., 2010a), but are significantly lower (approximately 28 times) than those (av. 19 $\mu\text{g m}^{-3}$) reported in the urban Tokyo aerosols (Kawamura et al., 1995b). Spatial distributions of TC showed higher levels in the coastal western North Pacific, supporting a significant atmospheric transport of continent-derived organics over the western North Pacific.

The carbonaceous fraction (TC%) of the aerosols ranged from 0.3 to 5.7% (av. 2.1%, median 1.4%) with higher values in mid latitudes of the western North Pacific. This result suggests an atmospheric input of continental aerosols over the western North Pacific Rim near the Asian Continent. Interestingly, TC/aerosol mass ratios in the present western North

Pacific aerosols are ~3 times higher than those (av. 0.75%) reported over the western North to central Pacific (Kawamura and Sakaguchi, 1999), but much lower than those (8-39%, av. 20%) reported for urban aerosols from Tokyo (Kawamura and Ikushima, 1993). These comparisons suggest that TC% are higher near the outflow regions of Asian dusts and their precursors and in high latitudes of the western North Pacific with higher biological productivity. It is also likely that marine organic aerosols in the remote ocean (e.g., the central Pacific) may be diluted by inorganic materials such as sea salt.

Aerosol WSTN contents ranged from 0.02 to 0.90 $\mu\text{g m}^{-3}$ (av. 0.20 $\mu\text{g m}^{-3}$, median 0.10 $\mu\text{g m}^{-3}$) in the western North Pacific aerosols. These values are ca. 3 times lower than those (0.07-3.02 $\mu\text{g m}^{-3}$, av. 0.58 $\mu\text{g m}^{-3}$) reported for Okinawa Island in the western North Pacific rim (Kunwar and Kawamura, 2014). WSTN show spatial distribution pattern similar to TC, whose concentrations are rather constant over the western North Pacific, except for mid latitudinal segment of the western North Pacific rim. WSTN account for 0.1 to 1.6% (av. 0.4%, median 0.2%) of the marine aerosol masses from the western North Pacific. These values are generally lower than those (1.9-15%) reported for total nitrogen from urban Tokyo (Kawamura and Ikushima, 1993), the Arctic (0.48-2.4%, av. 1.6%) (Kawamura et al., 2010a), but similar to those from the Pacific (0.05-1.3%, av. 0.27%) (Kawamura and Sakaguchi, 1999).

3.4.2. Latitudinal variations of WSOC/OC and WSOC/TC ratios

Jung et al. (2010) proposed that WSOC to OC ratio is useful to discuss a potential source of carbonaceous aerosols. High WSOC/OC ratios (av. 47%) were reported for the long-range transported aerosols (Saarikoski et al., 2008). The enhanced WSOC/OC ratios (81%) were also reported for Greenland summit aerosols (Hagler et al., 2007). Moreover, elevated WSOC/OC ratios can be used as an indicator for aged aerosols (Ho et al., 2006).

WSOC/OC ratios from our study show almost 2 orders of magnitudes higher values in mid latitudes of the western North Pacific (Fig. 3.2a) than those of low and high latitudes, indicating an enhanced photochemical oxidation of anthropogenic organic compounds during long-range atmospheric transport and/or gas-to-particle conversion of anthropogenic semi-volatile organic compounds via photochemical oxidation. Five-day backward air mass trajectories also reveal that mid latitudinal regions of the western North Pacific is significantly influenced by long-range transported air masses from the Asian Continent (Fig. 3.8).

Contribution of WSOC to TC varied from 6 to 58% (av. 32%, median 28%). These values are equivalent to those reported in Tokyo urban aerosols (28-55%, av. 37%) (Sempéré and Kawamura, 1994) and those from the marine aerosols in the western Pacific (29-53%, av. 40%) (Sempéré and Kawamura, 2003). As shown in Fig. 3.2b, WSOC/TC ratios in the mid latitudinal western North Pacific than the low (subtropical) and high latitudinal western North Pacific, suggesting more photochemical production of WSOC in the mid latitudinal western North Pacific with more influence from the Asian Continent (see Fig. 3.8).

3.4.3. Molecular composition and concentrations of diacids, ω -oxoacids, pyruvic acid and α -dicarbonyls

A homologous series of low molecular weight dicarboxylic acids (C_2 - C_{11}), ω -oxoacids, pyruvic acid and α -dicarbonyls were detected in the marine aerosols from the western North Pacific. Table 3.2 summarizes their concentration ranges, median and average concentrations as well as their relative abundances in each compound class. Generally, oxalic acid (C_2) was found as the most abundant diacid species followed by malonic (C_3) and succinic (C_4) acid (Fig. 3.3a), being consistent with previous aerosol studies from East Asia (Ho et al., 2007; Kawamura and Ikushima, 1993; Kawamura and Kaplan, 1987; Kundu et al., 2010c; Miyazaki et al., 2007; Tran et al., 2000; Yao et al., 2002), the remote Pacific

(Kawamura and Sakaguchi, 1999; Kerminen et al., 2000; Mochida et al., 2003a, 2003b) and the Arctic Ocean (Kawamura et al., 2012).

However, in few samples collected in higher latitudes of the western North Pacific near the Aleutian trench, we found a predominance of succinic (C_4) acid followed by oxalic (C_2) and malonic (C_3) acid (Fig. 3.3b). Similar phenomenon has been reported in the marine aerosols collected over the Arctic Ocean during late summer (Kawamura et al., 2012), where photochemical degradation of oxalic acid may occur in aqueous phase of aerosols due to the presence of Fe (Kawamura et al., 2010a). Pavuluri and Kawamura (2012) reported that oxalic acid decomposes in the presence of Fe under the UV irradiation in the laboratory experiment, but it is stable in the absence of Fe. Malonic acid could also decompose in the presence of Fe (III), however, the decomposition rate of its Fe-complex is ca. 20 times lower than that of oxalic acid (Faust and Zepp, 1993). The decomposition of oxalic and malonic acid may be accelerated under foggy conditions together with solar irradiation (Kawamura et al., 2012).

In addition, some samples collected from high and mid latitudes of the western North Pacific show the predominance of malonic acid followed by succinic and oxalic acid (Fig. 3.3c). Such molecular compositions could be explained by the depletion of oxalic acid (Kawamura et al., 2010a) and oxidation of succinic acid to malonic acid (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999). It is of interest to note that azelaic acid (C_9) is relatively abundant in the marine aerosols in which C_3 or C_4 is dominant (Fig. 3.3b, c). Because C_9 is derived from photo-oxidation of unsaturated fatty acids (Kawamura and Gagosian, 1987), sea-to-air emission of unsaturated fatty acids may be significant in those oceanic regions. Interestingly, 4-Oxobutanoic acid (ωC_4), which is a oxidation product of unsaturated fatty acid like oleic acid ($C_{18:1}$) showed 10 times higher values in high latitudes than low latitudes and 2 times higher values than those of mid latitudinal regions of the western North pacific. Moreover, a good correlation ($r^2=0.67$) between ωC_4 and C_4 were

observed in high latitudes of the western North Pacific, confirming that high abundances of C₄ in higher latitudes are associated with phytoplankton activity. As discussed later, I found higher *Chlorophyll-a* concentrations in high latitudes of the western North Pacific.

Concentrations of total dicarboxylic acids (13.4 to 177 ng m⁻³) are several times lower than those reported in the continental aerosols from Tokyo (Kawamura and Yasui, 2005), Sapporo (Aggarwal et al., 2008) and Chinese megacities (Ho et al., 2007), but are comparable to those for the marine aerosols from the northern North Pacific (Kawamura and Usukura, 1993), the Pacific Ocean including tropics (Kawamura and Sakaguchi, 1999) and the western Pacific (Wang et al., 2006). Glyoxylic (ω C₂) acid was the dominant ω -oxoacid species, comprising 45.2% of the total ω -oxoacids detected, followed by 7-oxoheptanoic acid (av. 15.8%). These results indicate that in the western North Pacific atmosphere both anthropogenic and biogenic emissions are significant source of diacids and ω -oxoacids. Among α -dicarbonyls, glyoxal was generally more abundant than methylglyoxal (Table 3.2). This result may suggest that anthropogenic (e.g., benzene and toluene) emissions are more important than biogenic emissions (e.g., isoprene) because glyoxal is often more abundant than methylglyoxal in Chinese aerosols (Ho et al., 2007). However, in high latitudinal western North Pacific aerosols, methylglyoxal is more abundant than glyoxal (Fig. 3.3b), suggesting an importance of isoprene emission from the ocean and subsequent oxidation to result in methylglyoxal (Bikkina et al., 2014). Interestingly, five-day backward air mass trajectories showed that continental influence is not significant over higher latitudes of the western North Pacific (Fig. 3.8).

3.4.4. Distributions of diacids, ω -oxoacids, α -dicarbonyls and their contributions (%) to aerosol total carbon over the western North Pacific

Spatial distribution of diacids over the western North Pacific is presented in Fig. 3.4a. Over the coastal western North Pacific, diacids concentrations showed 4 times higher values

than low latitudes and 2 times higher values than those of the high latitudinal regions of the western North Pacific. It is interesting to note that concentrations of both ω -oxoacids and α -dicarbonyls exhibit spatial distribution patterns similar to diacids (the results are not presented as a figure). The decrease in the concentrations of diacids and related compounds from mid latitudes towards high and low latitudes of the western North Pacific indicates that Asian continental aerosols are transported long distances to the remote marine atmosphere. Lower concentrations of diacids, ω -oxoacids, pyruvic acid and α -dicarbonyls over the open ocean than the coastal regions may be caused by atmospheric dilution of continentally derived organics during long-range transport. These distribution patterns may also support that both dry and wet depositions of aerosol particles can scavenge diacids and other organics from the atmosphere (Fu et al., 2013; Kawamura and Sakaguchi, 1999).

Fig. 3.4b shows the spatial distribution of relative abundances of diacid-C in aerosol total carbon (TC). Total diacids accounted for 1.9-31% of TC (av. 7.4%, median 5.8%). These values are comparative to those (1.1-15.8%, av. 8.8%, median 8.4%) reported for the marine aerosols collected from the Pacific Ocean including tropics (Kawamura and Sakaguchi, 1999), but are approximately 3 times higher than those (1.1-4.9%, av. 3.2%) from the western Pacific at 35°N to 40°S (Sempéré and Kawamura, 2003). Further, they are ~ 8 times higher than those (0.18-1.8%, av. 0.95%) obtained in continental aerosols from Tokyo (Kawamura and Ikushima, 1993). Higher diacid-C/TC ratios detected in the remote marine aerosols may be due to the intensive photochemical conversion of continental and marine derived organics to diacids under suitable atmospheric conditions. It is important to note that ozone and its precursors (e.g., NO_x and VOCs) are transported to the northern North Pacific near the Japanese Islands (Hoell et al., 1996; Naja and Akimoto, 2004). Spatial distributions of diacid-C/TC ratios showed 3 times higher values in the mid-high latitudes than those of low latitudes of the western North Pacific (Fig. 3.4b). It is of interest to note that diacid-C/TC

ratios increased from spring to summer and decreased towards winter in Gosan site, Jeju Island in the East China Sea (Kawamura et al., 2004).

The highest diacid-C/TC ratio (31%) was found in higher latitudes of the western North Pacific around 50°N (Fig. 3.4b), where succinic (C₄) acid became the dominant diacid species and its contribution to aerosol TC maximized (4.3%) during sampling period (the result is not shown as a figure). The samples from higher latitudes of the western North Pacific were collected during summer but aerosol samples from mid and high latitudinal segment of the western North and subtropical Pacific were collected during spring. We also found high *Chlorophyll-a* concentrations (0.2-10 mg m⁻³) in higher latitudes during the cruise in July 5-July 24, 2010 (Fig. 3.7). Thus, I suspect that the sea-to-air emission of biogenic unsaturated fatty acids, which are enriched in the sea surface micro layer (Garrett, 1967), was intensified in higher latitudes of the western North Pacific due to the high biological activity of the ocean followed by the subsequent atmospheric oxidation to result in C₄ diacid. It is also of interest to note that azelaic acid (C₉ diacid), which is a specific oxidation product of unsaturated fatty acids (Kawamura and Gagosian, 1987), was abundantly detected in the same aerosol sample (see Fig. 3.3b).

On the other hand, shorter chain diacids (C₂-C₄) accounted for 81% of total diacids in the western North Pacific aerosols. Fig. 3.5a-3.5c represent latitudinal distributions of relative abundances of oxalic, malonic and succinic acid-C in aerosol TC over the western North Pacific. We found an increasing trend of C₃ and C₄ diacid-C/TC over high latitudinal western North Pacific from lower to higher latitudes (Fig. 3.5b, c). Their relative abundances are higher in high latitudes than the mid and low latitudinal region of the western North Pacific. However, oxalic acid-C/TC ratio did not show higher values in the higher latitudes (Fig. 3.5a). Long chain diacids (C₅-C₉) also show latitudinal distributions similar to C₃ and C₄ diacids, but trends are less clear for C₁₀-C₁₁ diacids (results are not shown here as a figure). These

results indicate that both short (C₃-C₄) and long (C₅-C₉) chain diacids may be preferentially produced by photo-oxidation of unsaturated fatty acids under favorable atmospheric conditions over the high latitudinal western North Pacific, where *Chlorophyll-a* contents are high (Fig. 3.7) and the sea-to-air emissions of phytoplankton-derived unsaturated fatty acids may be significant whereas continental influences are insignificant due to the air mass trajectory analyses (Fig. 3.8).

3.4.5. Latitudinal variations in the concentration ratios of diacids and related compounds

Laboratory studies show that glyoxal and methylglyoxal are produced from the photochemical oxidation of aromatic hydrocarbons like benzene and toluene (Bandow et al., 1985). They are also produced by photochemical oxidation of isoprene and other VOCs (Carlton et al., 2006, 2009). Glyoxylic acid (ω C₂) may be produced by atmospheric oxidation of glyoxal (Gly) (Kawamura, 1993). Kawamura et al. (1996a) proposed that ω C₂ and pyruvic (Pyr) acid are intermediate in the photochemical oxidation of anthropogenic and natural organic compounds to the production of oxalic acid. Gly, ω C₂ and Pyr may be photochemically oxidized to oxalic (C₂) acid (Kundu et al., 2010c). In aerosol phase, photooxidation of Pyr produces C₂ and ω C₂ (Carlton et al., 2007). C₂ is also produced by the oxidation of Gly via the formation of ω C₂ (Warneck, 2003). As shown in Fig. 3.6a-3.6c, concentration ratios of C₂/ ω C₂, C₂/Pyr and C₂/Gly are higher in the low latitudinal regions than the mid and high latitudinal regions of the western North Pacific, suggesting that in the subtropical Pacific photochemical conversion of ω C₂, Pyr and Gly to C₂ is more significant.

Kawamura and Sakaguchi (1999) anticipated that oxalic and malonic acids are likely produced in the marine atmosphere by photooxidation of succinic acid via intermediates such as hydroxysuccinic (malic) acid and ketomalonic acid. Laboratory oxidation of isoprene with ozone also produces malonic, succinic and malic acids (Nguyen et al., 2010). Fig. 3.6d-3.6f

represent the latitudinal distributions of oxalic (C_2), malonic (C_3) and malic (hC_4) acids relative to succinic (C_4) acid. The results show that their concentration ratios became higher in the subtropical regions followed by mid and high latitudinal regions of the western North Pacific, indicating that considerable photochemical transformation of organic compounds occurs in the subtropical Pacific.

The C_3/C_4 ratios have been successfully used to distinguish the relative importance of their primary and secondary sources. Kawamura and Ikushima (1993) proposed that succinic (C_4) acid can be degraded to malonic (C_3) acid via abstraction of hydrogen by OH radicals and subsequent decarboxylation. The C_3/C_4 ratios in the western North Pacific aerosols varied from 0.8-5.8 (av. 1.9, median 1.4). These values are lower than and/or similar to those (0.9-5.8, av. 2.3) reported for marine aerosols collected during a round the world cruise (Fu et al., 2013), in Gosan, Jeju Island (av. 1.6) (Kundu et al., 2010c) and Chichijima Island in the western Pacific (av. 2.2) (Mochida et al., 2003a), but higher than urban aerosols from Chinese cities (0.6-1.1, av. 0.74) (Ho et al., 2007), Tokyo (0.56-2.9, av. 1.6) (Kawamura and Ikushima, 1993) and Los Angeles (0.31-1.4) (Kawamura and Kaplan, 1987). Higher C_3/C_4 ratios in marine aerosols than in urban/continental aerosols suggest that malonic (C_3) acid is photochemically produced from succinic (C_4) acid during long-range transport of continentally derived organics to the remote marine atmosphere.

Unsaturated diacids such as maleic (M) and fumaric (F) acids are thought to be photo-oxidation products of aromatic hydrocarbons including benzene and toluene (Wang et al., 2006) and M may be isomerized to F under the solar radiation (Kawamura and Ikushima, 1993). However, M/F ratios in the present study (av. 0.9) is similar to those (av. 0.9) reported in the western North Pacific aerosols (Fu et al., 2013), Arctic aerosols (0.5-1.0) (Kawamura et al., 1996a), but lower than those reported in the urban aerosols from Hong Kong (0.9-1.9) (Li and Yu, 2010), Sapporo (av. 2.0) (Aggarwal and Kawamura, 2008), Chinese megacities

(av. 2.2) (Ho et al., 2007) and Tokyo aerosols (av. 1.5) (Kawamura and Ikushima, 1993). Lower M/F ratios observed in our remote marine aerosol samples further indicate that isomerization of M to F occurs in the marine atmosphere during long-range transport (Fu et al., 2013). Fig. 3.6g shows the latitudinal changes in M/F ratios of the western North Pacific aerosols. M/F ratios are almost 2 times lower in lower latitudinal regions than mid latitudes and approximately 4 times lower than those of higher latitudes. This trend may be due to an enhanced isomerization reaction in low latitudes under intensified solar radiation and ambient temperature. Moreover, a negative correlation between M/F ratios and ambient air temperatures were observed during the cruise. Their concentration ratios show a decreasing trend with increasing temperatures. These results confirms that isomerization of maleic acid to fumaric acid have been intensified in the lower latitudes of the western North Pacific due to high ambient air temperature and strong solar irradiation.

Phthalic (Ph) and adipic (C_6) acids are the oxidation products of anthropogenic precursors such as naphthalene and cyclic hexane, respectively (Hatakeyama et al., 1987; Jang and McDaw, 1997; Kawamura and Kaplan, 1987; Kawamura and Sakaguchi, 1999; Wang et al., 2006). On the contrary, azelaic (C_9) acid is produced by the oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987; Rogge et al., 1991). Therefore, Ph/ C_9 and C_6/C_9 ratios can be used to estimate the contributions from anthropogenic or biogenic precursors. The higher ratios indicate more emissions from anthropogenic sources. Fig. 3.6h-i show the latitudinal variations in Ph/ C_9 and C_6/C_9 concentration ratios in the western North Pacific aerosols. Estimated Ph/ C_9 ratios showed 4-6 times higher values in the mid latitudes than those of lower and higher latitudinal regions of the western North Pacific. Similarly, C_6/C_9 ratios showed 3-5 times higher values near the coastal western North Pacific than those of low and high latitudes. Ph/ C_9 and C_6/C_9 ratios peaked around at 41°N, where the continental outflow of polluted air masses from Japanese

Islands is important (see Fig. 3.8). These results indicate that in mid latitudes of the western North Pacific anthropogenic emissions are more significant than the marine biogenic emissions near the Japanese Islands.

Interestingly, higher level of diacids, ω -oxoacids, pyruvic acid, α -dicarbonyls, total carbon (TC) and water soluble total nitrogen (WSTN) were detected near the Japanese Islands in the western North Pacific during the study. These findings may suggest that atmospheric concentrations of the organics over the western North Pacific have been influenced by the outflow of continental air masses, and the relative strength of their marine sources may be significantly weak in this region. As shown in Fig. 3.8, five-day backward air mass trajectories also demonstrate that outflows of continental air masses strongly affect the air quality over the western North Pacific near the Japanese Islands.

3.4.6. Principal component analysis of diacids

In order to discuss the sources and transformation process of dicarboxylic acids in the remote marine atmosphere, diacid data from the western North Pacific aerosol samples ($n=29$) were subjected to principal component analysis (PCA) with varimax rotation. Table 3.3 provides correlations (r) of each diacids with each component. Components 1 (Anthropogenic emission), 2 (biogenic emission) and 3 (photochemical oxidation) accounted for 56%, 18% and 10% of variance in the data sets, respectively.

Shorter chain diacids such as oxalic (C_2) acid, adipic (C_6) acid, and unsaturated diacids, i.e., maleic (M), methylmaleic (mM), phthalic (Ph) and terephthalic (tPh) show good correlations with component 1. Oxalic (C_2) acid may be emitted directly to the atmosphere from automobiles and fossil fuel combustion (Kawamura et al., 1996a). Adipic acid is a specific tracer of anthropogenic emissions, which is emitting as oxidation product of cyclic olefins (Hatakeyama et al., 1987; Kawamura et al., 1996a). Maleic acid has been reported as

photooxidation products of aromatic hydrocarbons (Bandow et al., 1985) and reported in urban aerosols (Kawamura and Ikushima, 1993). mM is the oxidation product of aromatic hydrocarbons such as toluene and may be photochemically converted to oxalic (C_2) acid (Kawamura et al., 1996a). Burning of municipal solid wastes and plastic polymers are the emission sources of t-Ph (Kawamura and Pavuluri, 2010b; Simoneit et al., 2005).

Succinic (C_4), glutaric (C_5), pimelic (C_7), and azelaic (C_9) acids showed good correlations with component 2. In the remote marine atmosphere, succinic acid and other long chain diacids (C_5 - C_{11}) are produced by the photooxidation of unsaturated fatty acids from their biological sources (Kawamura and Gagosian, 1987) and are further oxidized to oxalic acid under favorable solar irradiation (Kawamura and Sakaguchi, 1999). Succinic (C_4) acid may be emitted from photochemical oxidation of oxoacid such as ωC_4 (Kawamura et al., 1996a) whereas pimelic (C_7) acid can be photochemically produced from unsaturated fatty acids and their oxidation intermediates (Kawamura and Sakaguchi, 1999).

Malonic (C_3) acid and fumaric (F) acid showed good correlation with component 3. C_3 is produced from succinic acid via malic (hC_4) acid through photochemical oxidation (Kawamura et al., 1996a). Maleic anhydride has been reported as the photo-oxidation product of aromatic hydrocarbons such as benzene and toluene (Bandow et al., 19985) and further isomerizes to fumaric (F) acid in the presence of sunlight (Kawamura and Ikushima, 1993; Kundu et al., 2010c).

3.5. Conclusions

Diacids and related compounds (ω -oxoacids, pyruvic acid and α -dicarbonyls) have been determined in remote marine aerosol samples collected over the western North Pacific, together with organic carbon (OC), water-soluble organic carbon (WSOC), total carbon (TC) and water-soluble total nitrogen (WSTN). Molecular distributions of water-soluble dicarboxylic acids generally showed a predominance of oxalic (C_2) acid, followed by malonic (C_3) and succinic (C_4) acids. However, one-third of the samples showed the predominance of C_3 or C_4 diacid, especially, in high latitudinal regions of the western North Pacific where phytoplankton activities were higher during the cruise.

Spatial distributions of diacids and related compounds showed higher levels in mid latitudes followed by high and low latitudes of the western North Pacific, suggesting that diacids and their precursors are of continental origin and transported long distances over the remote western North Pacific. Short chain (C_2 - C_4) diacids account for 0.7-17% of total aerosol carbon (0.1 - $2.7 \mu\text{g m}^{-3}$) with higher values in high latitudinal western North Pacific, where *Chlorophyll-a* showed higher concentrations (0.2 - 10 mg m^{-3}) during the sampling period. These results demonstrate that short chain diacids are largely produced in higher latitudes of the western North Pacific by the photochemical oxidation of unsaturated fatty acids and isoprene produced by marine phytoplankton. C_2/C_4 and C_3/C_4 concentration ratios were enhanced in the low latitudinal regions than the mid and high latitudinal regions of the western North Pacific, indicating that the photochemical conversion of both marine and continentally derived organic compounds is more significant in the subtropical Pacific.

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Table 3.1. Aerosol mass, concentrations of various organic components in the western North Pacific aerosol samples and their concentration ratios.

Components	Minimum	Maximum	Average	Median
Aerosol mass ($\mu\text{g m}^{-3}$)	11	232	44	32
TC ($\mu\text{g m}^{-3}$)	0.1	2.7	0.7	0.4
WSTN ($\mu\text{g m}^{-3}$)	0.02	1.0	0.2	0.1
WSOC ($\mu\text{g m}^{-3}$)	0.02	1.5	0.3	0.1
OC ($\mu\text{g m}^{-3}$)	0.1	2.6	0.6	0.4
WSOC/TC (%)	6	58	32	28
WSOC/OC (%)	7	73	40	30
WSTN/aerosol mass (%)	0.1	1.6	0.4	0.2
TC/aerosol mass (%)	0.3	5.7	2.1	1.4

Table 3.2. Concentrations (ng m⁻³) of dicarboxylic acids, ω-oxoacids, pyruvic acid and α-dicarbonyls in the marine aerosol samples from the western North Pacific (n=29).

Compounds	Minimum	Maximum	Average	Median	Average relative abundances (%)
Saturated straight chain diacids					
Oxalic, C ₂	5.5	80.9	25.3	18.9	40.0
Malonic, C ₃	2.6	37.4	14.7	11.0	23.0
Succinic, C ₄	0.9	36.8	11.6	10.3	18.3
Glutaric, C ₅	0.2	19.9	3.8	2.4	6.0
Adipic, C ₆	0.1	2.8	1.0	0.6	1.6
Pimelic, C ₇	BDL ^a	3.5	0.6	0.3	0.9
Suberic, C ₈	BDL ^a	1.0	0.2	0.2	0.2
Azelaic, C ₉	0.1	0.9	0.5	0.5	0.8
Sebacic, C ₁₀	BDL ^a	2.3	0.2	0.1	0.3
Undecanoic, C ₁₁	BDL ^a	2.9	0.2	0.1	0.3
Unsaturated diacids					
Fumaric, F	0.01	1.9	0.3	0.1	0.5
Maleic, M	0.05	2.8	0.4	0.2	0.7
Methylmaleic, mM	0.02	1.0	0.2	0.1	0.2
Phthalic, Ph	0.1	3.4	1.1	0.6	1.7
Isophthalic, iPh	BDL ^a	0.4	0.1	0.05	0.1
Terephthalic, tPh	0.02	1.0	0.3	0.2	0.4
Branched chain diacids					
Methylmalonic, iC ₄	0.05	0.9	0.3	0.3	0.5
Methylsuccinic, iC ₅	BDL ^a	1.9	0.5	0.3	0.8
2-Methylglutaric, iC ₆	BDL ^a	0.2	0.1	0.04	0.1
Multifunctional diacids					
Hydroxysuccinic, hC ₄	0.01	0.7	0.2	0.1	0.2
Ketomalonic, kC ₃	0.02	1.0	0.3	0.2	0.4
Ketopimelic, kC ₇	0.01	5.0	1.0	0.6	1.5
Total diacids	13.4	177	63.5	51	-
ω-oxoacids					
Glyoxylic, ωC ₂	0.2	9.5	2.0	1.4	45.2
3-Oxopropanoic, ωC ₃	0.02	0.7	0.2	0.1	4.0
4-Oxobutanoic, ωC ₄	BDL ^a	2.8	0.6	0.3	13.1
5-Oxopentanoic, ωC ₅	BDL ^a	1.0	0.2	0.1	4.7
7-Oxoheptanoic, ωC ₇	BDL ^a	3.0	0.7	0.4	15.8
8-Oxo-octanoic, ωC ₈	BDL ^a	3.4	0.6	0.3	13.8
9-Oxononanoic, ωC ₉	BDL ^a	1.0	0.2	0.1	3.4
Total ω-oxoacids	0.7	18.7	4.4	3.3	-
Pyruvic acid, Pyr	0.04	6.1	0.6	0.3	14.4
α-Dicarbonyls					
Glyoxal, Gly	BDL ^a	6.9	0.6	0.2	75.0
Methylglyoxal, MeGly	0.02	0.8	0.2	0.2	25.0
Total α-dicarbonyls	0.02	7.0	0.8	0.5	-

^aBDL, below detection limit (0.005 ng m⁻³).

Table 3.3. Principal component analysis with Varimax-Kaiser normalization for the selected dicarboxylic acids and related compounds from the western North Pacific aerosol samples collected May-July, 2010

Compounds	Component 1	Component 2	Component 3
Oxalic (C ₂)	0.7	-0.07	0.6
Malonic (C ₃)	0.4	0.5	0.7
Succinic (C ₄)	0.3	0.7	0.6
Glutaric (C ₅)	-0.1	0.9	0.4
Adipic(C ₆)	0.8	0.5	0.3
Pimelic (C ₇)	0.1	0.8	0.4
Azelaic (C ₉)	0.3	0.9	-0.2
Maleic (M)	0.9	0.1	0.3
Fumaric (F)	0.2	0.2	0.9
Methylmaleic (mM)	0.9	0.2	0.1
Phthalic (Ph)	0.7	0.3	-0.2
Terephthalic (tPh)	0.8	0.1	0.4
Variance (%)	56	18	10

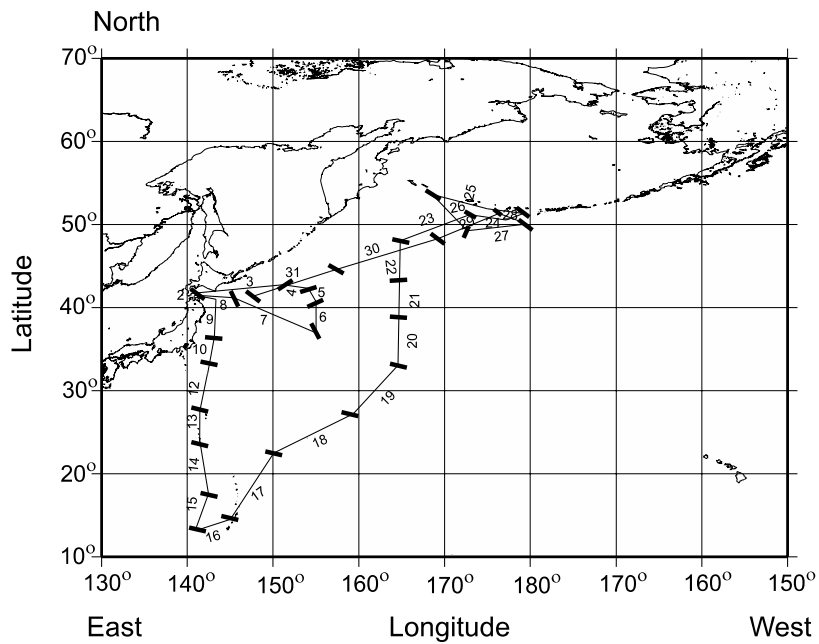


Fig. 3.1. Cruise track of T/V *Oshoro Maru* 2010. The numbers and thick black marks are shown in the map represent sample identification numbers and sampling locations, respectively.

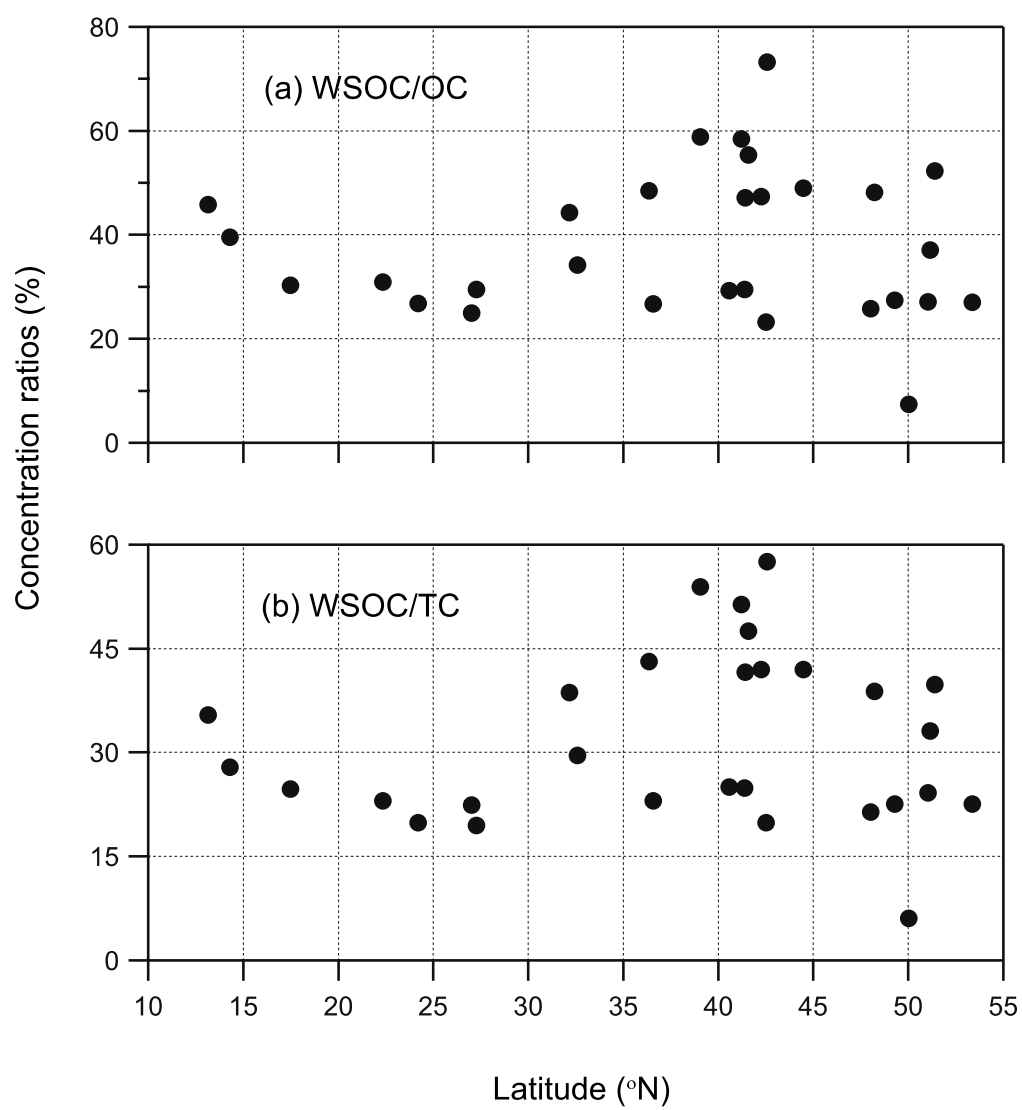


Fig. 3.2. Latitudinal variations in the concentration ratios of (a) WSOC/OC and WSOC/TC in the marine aerosols from the western North Pacific.

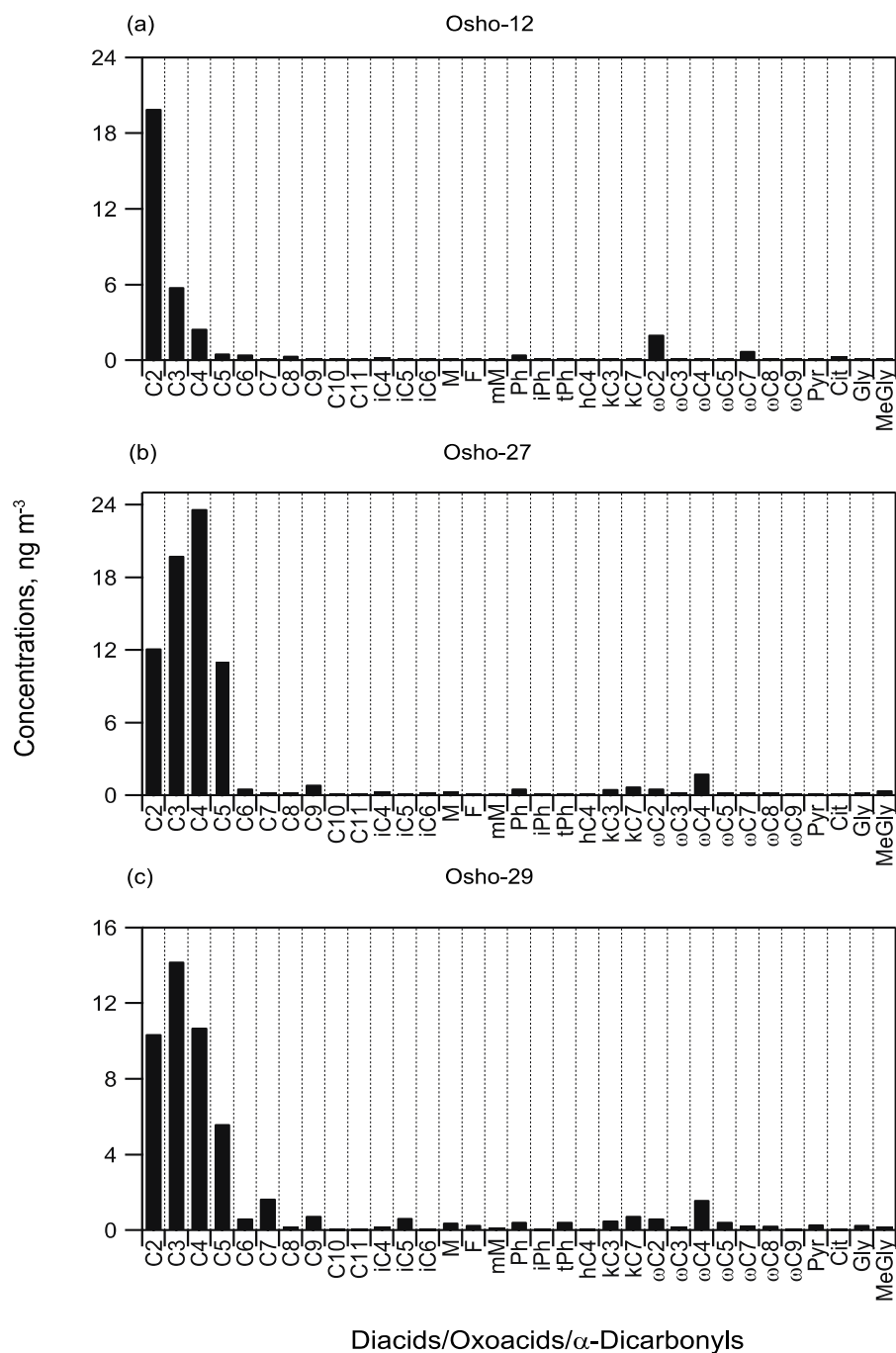


Fig. 3.3. Molecular composition of low molecular weight dicarboxylic acids (C₂-C₁₁), ω-oxoacids, α-dicarbonyls and pyruvic acid in selected marine aerosols from the western North Pacific. For details of the samples Osho-12, 27, and 29, see Fig. 1. For the abbreviations of the compounds, see Table 2.

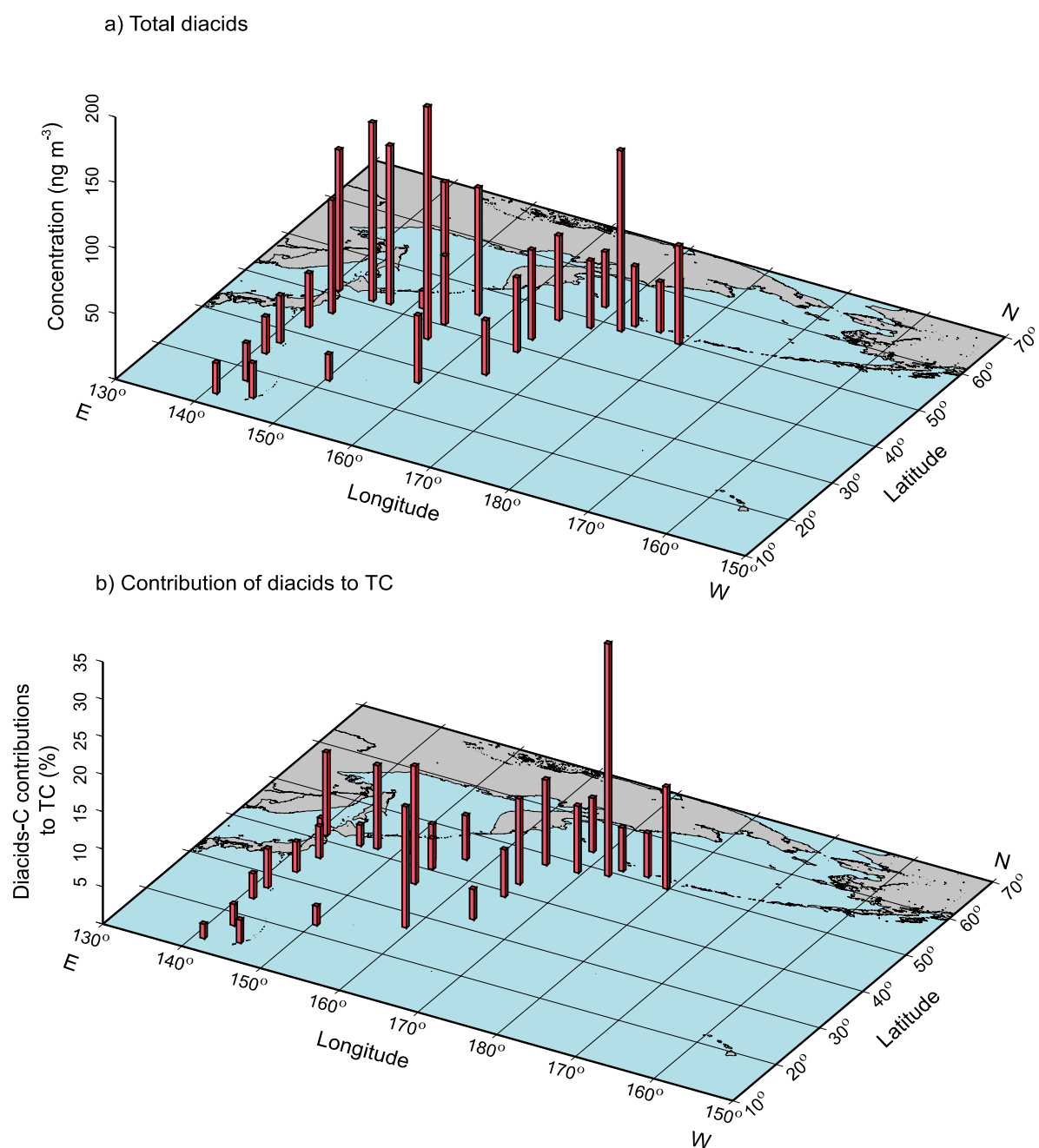


Fig. 3.4. Spatial distributions of (a) dicarboxylic acids and (b) contribution of diacid-C in total aerosol carbon for the remote marine aerosols from the western North Pacific.

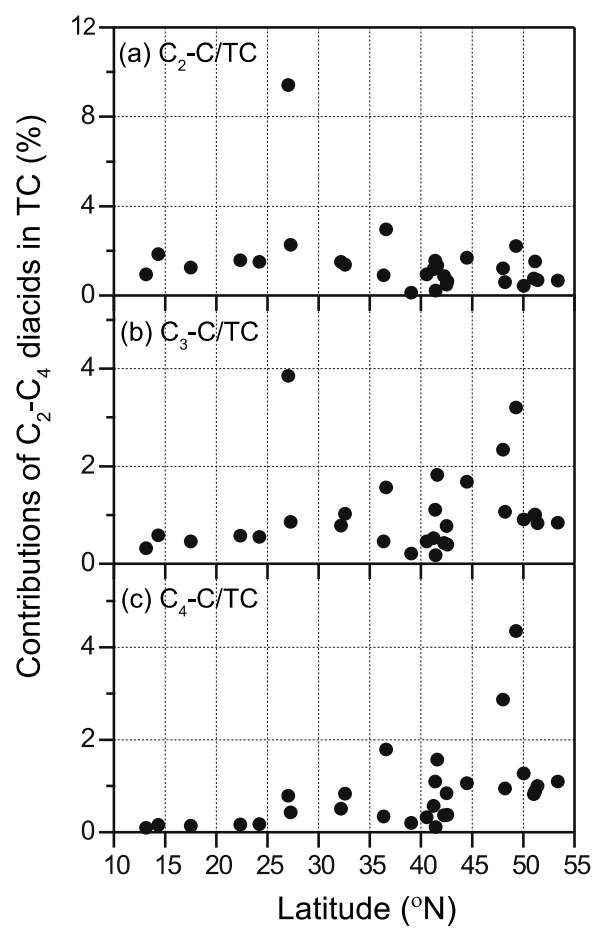


Fig. 3.5. Latitudinal distributions of (a) oxalic (C₂), (b) malonic (C₃) and (c) succinic (C₄) acids carbon in total aerosol carbon (TC) in the marine aerosols from the western North Pacific.

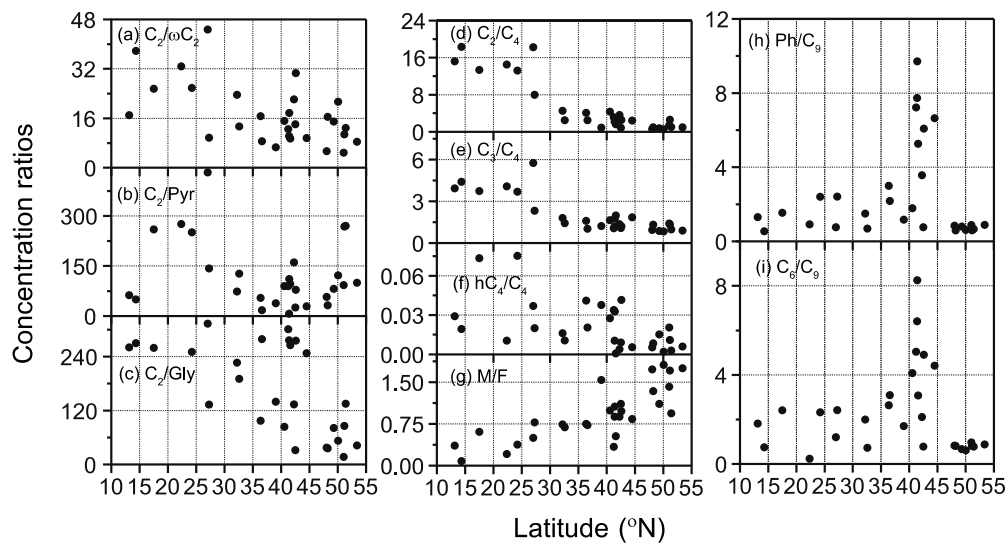


Fig. 3.6. Latitudinal distributions of (a) $C_2/\omega C_2$, (b) C_2/Pyr , (c) C_2/Gly , (d) C_2/C_4 , (e) C_3/C_4 , (f) hC_4/C_4 , (g) M/F , (h) Ph/C_9 , (i) C_6/C_9 concentration ratios for the remote marine aerosols from the western North Pacific.

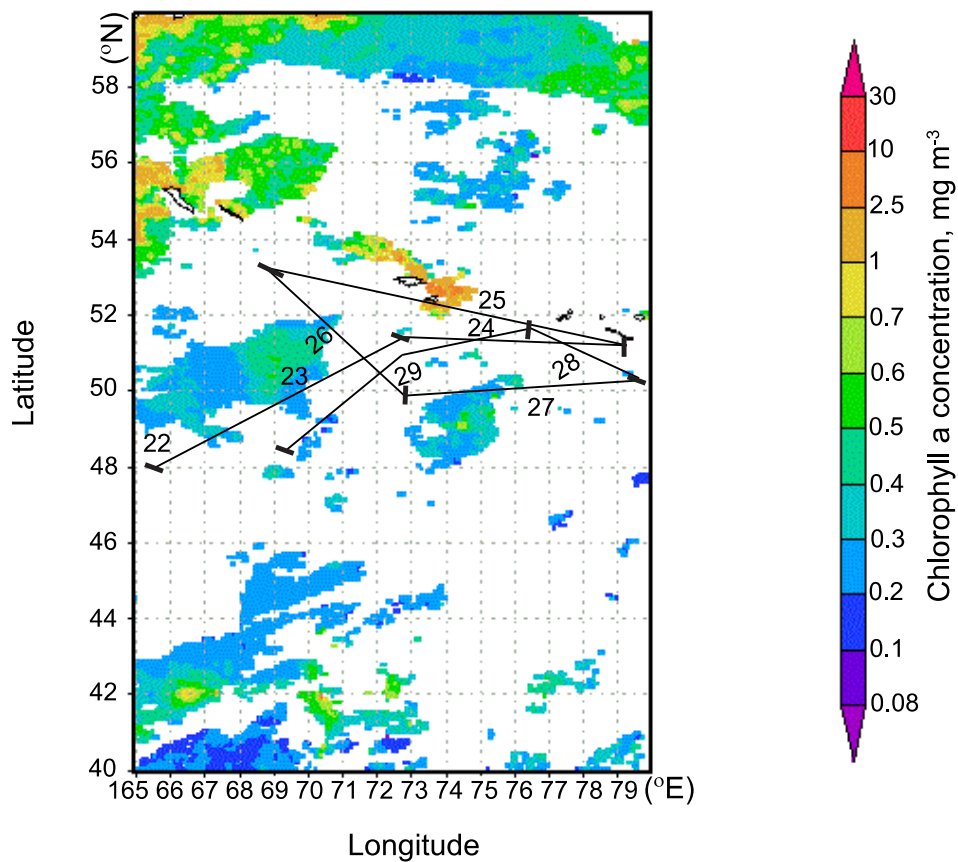


Fig. 3.7. *Chlorophyll-a* concentration (mg m^{-3}) in the surface ocean during July 2010 when the aerosol samples were collected in the central northern North Pacific (48.02°N - 53.37°N and 165°E - 179.5°W). The black line, thick black marks and numbers are shown in the figure represent cruise track, sample locations and sample identification numbers, respectively. This figure was prepared with Giovanni online data system, NASA GES DISC.

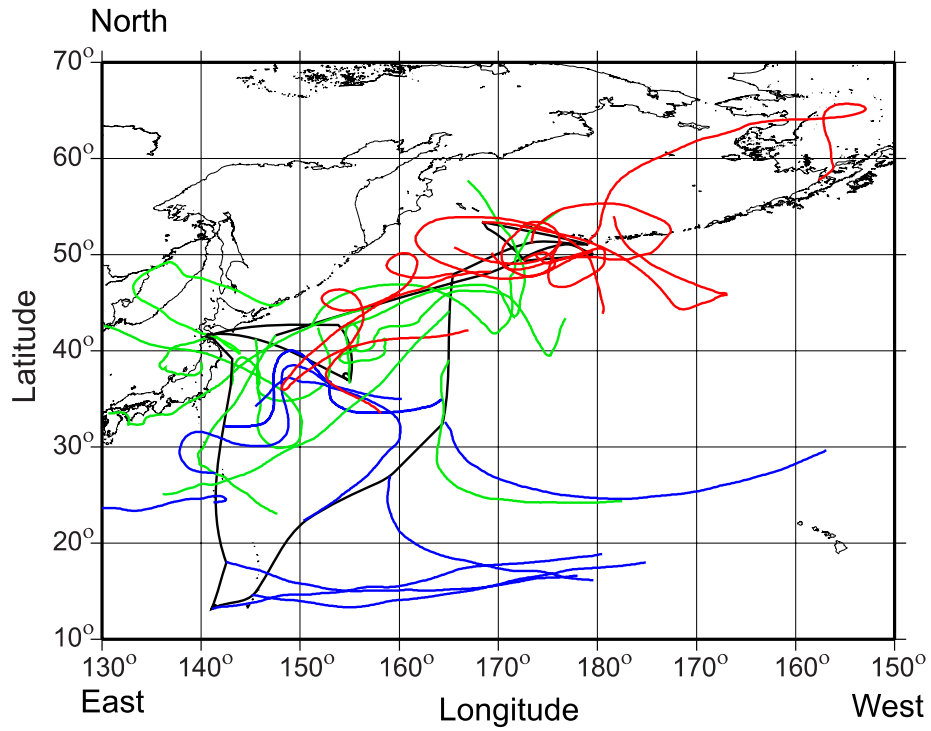


Fig. 3.8. Five day backward air masses trajectories at 500 m above ground were drawn with NOAA HYSPLIT model. Black line indicates cruise track. For details of the cruise track see fig. 1. The lines having green, blue and red color represent backward air masses trajectories for the mid, low and high latitudinal western North Pacific Ocean, respectively.

Chapter: 4 Longitudinal distributions of dicarboxylic acids, ω -oxoacids, pyruvic acid, α -dicarbonyls and fatty acids in the marine aerosols from the central Pacific including equatorial upwelling

4.1. Introduction

Primary marine organic aerosols are emitted into the atmosphere through bubble bursting process (Lewis and Schwartz, 2004) through mobilization of organic surfactants via sea spray formation. In contrast, secondary marine organic aerosols are produced by the oxidation of biogenic volatile organic compounds (BVOCs) emitted from the ocean surces (Lapina et al., 2011; Rinaldi et al., 2010). Low molecular weight (LMW) dicarboxylic acids and related polar compounds are one of the most abundant compound classes in marine organic aerosols (Fu et al., 2013, Cristina et al., 2008). They are highly water-soluble in nature and are present in the fine particles. The water-soluble organic aerosol species may act as an important source of cloud condensation nuclei (CCN), affecting cloud microphysics and consequently climate (Ayers and Gras, 1991; Liss and Lovelock, 2007).

LMW α , ω -dicarboxylic acids and related compounds, i.e., ω -oxocarboxylic acids (C_2 - C_9) and α -dicarbonyls (C_2 - C_3), are abundantly present in the urban (Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994; Yao et al., 2002; Kitanovski et al., 2011), semi-urban areas (Khwaja, 1995), rural (Limbeck et al., 2001), and remote marine atmosphere (Stephanou, 1992; Kawamura and Usukura, 1993; Sempéré and Kawamura, 1996; Kawamura and Sakaguchi, 1999; Mochida et al., 2003a,b). They are also reported in the aerosols from the Arctic and Antarctic regions (Kawamura et al., 1996a,b, 2005; Narukawa et al., 2002, 2003) as well as polar ice cores (Kawamura and Yasui, 1991; Legrand and De Angelis, 1996; Kawamura et al., 2001a). Their molecular distributions are in general

characterized by the predominance of oxalic acid (C₂) followed by malonic (C₃) or succinic (C₄) acid and glyoxylic acid (ωC₂) (e.g., Kawamura et al., 1996a).

LMW dicarboxylic acids and related compounds are primarily produced by incomplete combustion of fossil fuels (Kawamura and Kaplan, 1987; Kerminen et al., 2000), biomass burning (Narukawa et al., 1999; Kundu et al., 2010), and meat cooking operation (Rogge et al., 1991; Schauer et al., 2002). Natural marine sources such as direct emission of biogenic unsaturated fatty acids from the ocean followed by photochemical oxidation further produce LMW dicarboxylic acids (Kawamura and Gagosian, 1987; Kawamura and Gagosian, 1990; Stephanou, 1992; Kawamura and Sakaguchi, 1999; Rinaldi et al., 2011). In the remote marine atmosphere, low molecular weight C₁₄-C₁₉ fatty acids are present as particles (Mochida et al., 2002). They originate from marine biota via the sea-to-air emission of fatty acids by bubble bursting process at the ocean surface (Barger and Garrett, 1970, 1976; Mochida et al., 2002).

Atmospheric transport of dicarboxylic acids from the continent, their primary emissions from the ocean, and in-situ formation in the marine atmosphere may influence the biogeochemical cycle of heavy metals like Fe and Hg (Fu et al., 2013). Moreover, contributions of LMW dicarboxylic acids and related compounds to total aerosol carbon (TC) were estimated to be 1.3-4.6% for urban regions (Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994) and more than 10% for remote oceanic sites (Kawamura and Sakaguchi, 1999; Wang et al., 2006), signifying the atmospheric importance of these water-soluble organics in remote marine aerosols. The central Pacific is characterized by strong solar radiation, high ambient temperature and high relative humidity as well as high biological productivity associated with the upwelling in the eastern equatorial Pacific. These characteristics make this region as an interesting location for primary and secondary organic aerosols. However, information regarding sources, long-range transport, photochemical

processing of LMW dicarboxylic acids and related compounds is very limited in the central Pacific including the eastern tropical upwelling region.

The objectives of this study are to describe the longitudinal distributions of diacids and related compounds, and their photochemical processing in the central Pacific atmosphere, and to propose a possible mechanism of primary and secondary aerosol formation in the marine boundary layer of eastern tropical Pacific. In this study, we collected aerosol samples over the central Pacific between Japan and Mexico. The samples were analyzed for water-soluble dicarboxylic acids, ω -oxocarboxylic acids, pyruvic acid, α -dicarbonyls and fatty acids as well as organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), water-soluble organic nitrogen (WSTN) and total carbon (TC). Here, we report molecular distributions of diacids and related compounds and their longitudinal distributions in the central Pacific where continental influence is negligible. We also evaluate the contributions of diacids to WSOC and TC and discuss the sources and photochemical alteration of water-soluble organics in the remote marine atmosphere.

4.2. Aerosol sampling

Remote marine aerosol samples were collected in the central Pacific (1°59'N-35°N and 171°54'E-90°58'W) during the T/V *Shoyo Maru* cruise using pre-combusted (450°C) quartz fiber filters (Pallflex-2500QAT-UP, 20 × 25 cm) and high-volume air sampler during September-October, 1999. The sampler was placed on the upper deck and controlled with a wind sector ($\pm 60^\circ$) and wind speed ($\geq 5 \text{ m s}^{-1}$) system to avoid potential contamination from the ship exhausts (Kawamura and Sakaguchi, 1999). Sampling duration was from 6 to 28 hours. The cruise track is shown in Fig. 4.1. After sample collection, filters were stored in clean glass jars with a Teflon-lined screw cap at -20°C prior to analysis. Although the sample filters had been stored for ~14 years, degradation of organics on the filters should be

insignificant under such a low temperature (Wang et al., 2006; Kawamura et al., 2010). Blank filters were exposed to the marine air in the sample shelter for a few seconds and then recovered (Sempéré and Kawamura, 2003).

4.3. Backward air mass trajectory analysis

Backward air mass trajectories analyses were conducted by using Hybrid Single-Particle Lagrangian Trajectory (HYSPLIT) model to find the sources of air masses in the central Pacific (1°59'N-35°N and 171°54'E-90°58'W) during sampling period. Fig. 4.6 shows 7 day-backward trajectory analysis at 500 m above the ground for aerosol samples collected from the central Pacific.

4.4. Results and discussion

4.4.1. Carbonaceous components and water-soluble total nitrogen

As shown in Table 4.1, concentrations of total carbon (TC) in the Pacific aerosols ranged from 0.1 to 1.2 $\mu\text{g m}^{-3}$ (av. 0.50 $\mu\text{g m}^{-3}$, median 0.40 $\mu\text{g m}^{-3}$). These values are similar or little higher than those reported in aerosols from the Pacific including tropics (0.38 $\mu\text{g m}^{-3}$) (Kawamura and Sakaguchi, 1999) and the Arctic (av. 0.36 $\mu\text{g m}^{-3}$) (Kawamura et al., 2010a), but lower than those reported from the Western Pacific near the Asian Continent (av. 0.80 $\mu\text{g m}^{-3}$) (Sempéré and Kawamura, 2003). However, they are approximately 40 times lower than that reported from urban Tokyo (av. 19 $\mu\text{g m}^{-3}$) (Kawamura et al., 1995), and Christchurch (av. 20.5 $\mu\text{g m}^{-3}$) (Wang and Kawamura, 2005).

Aerosol WSTN contents in the present study ranged from 0.03 to 0.6 $\mu\text{g m}^{-3}$ (av. 0.2 $\mu\text{g m}^{-3}$, median 0.1 $\mu\text{g m}^{-3}$). Both of TC and WSTN show similar longitudinal distributions with higher levels in the eastern tropical Pacific (Fig. 4.2), which may be associated with the enhanced activity of marine biota and subsequent sea to air emission of carbonaceous and

nitrogenous components. Marine biota can emit amino acids, urea and proteins (Kunwar and Kawamura, 2014). A significant emission of organic nitrogen from ocean surface has been reported in the marine aerosols collected from the northern North Pacific where biological activity is high (Miyazaki et al., 2011).

WSOC concentrations in the central Pacific aerosols ranged from 0.04 to 0.8 $\mu\text{g m}^{-3}$ (av. 0.30 $\mu\text{g m}^{-3}$, median 0.20 $\mu\text{g m}^{-3}$). The WSOC concentrations are much lower than those reported in urban aerosols from Hachioji, Tokyo (av. 12.8 $\mu\text{g m}^{-3}$) (Sempéré and Kawamura, 1994) and in the tropical aerosols from Amazonia (18-51 $\mu\text{g m}^{-3}$) (Kundu et al., 2010a), but are comparable to those reported in the marine aerosols from the western Pacific (av. 0.33 $\mu\text{g m}^{-3}$) (Sempéré and Kawamura, 2003) and Hawaii (av. 0.39 $\mu\text{g m}^{-3}$) (Hoffman and Duce, 1977). Kawamura et al. (2010a) also reported lower concentration of WSOC (0.04-0.30 $\mu\text{g m}^{-3}$, av. 0.18 $\mu\text{g m}^{-3}$) in the Arctic aerosols. Concentrations of water-insoluble organic carbon (WIOC=OC-WSOC) in this study varied from 0.05 $\mu\text{g m}^{-3}$ to 0.50 $\mu\text{g m}^{-3}$ (av. 0.20 $\mu\text{g m}^{-3}$, median 0.20 $\mu\text{g m}^{-3}$). WIOC showed higher levels in the eastern tropical Pacific, suggesting that over the eastern Pacific Ocean WIOC is predominantly produced by the emissions of primary biological particles such as bacterial and viral debris as well as phytoplankton debris via wave breaking action (Fu et al., 2013). Moreover, near the sampling area of eastern tropical Pacific ((140°W-80°W, 20°S-0°N) dissolved and detritus organic matter absorption coefficient (m^{-1}) showed an increasing trends from summer to autumn (see Fig. 4.10).

4.4.2. Longitudinal variations of WSOC/OC ratios

Relative abundances of WSOC in OC varied from 28 to 75% (av. 50%, median 49%) in the central Pacific aerosols, these values are similar to those reported for ambient aerosols from Okinawa Island (av. 43%) in the western North Pacific rim (Kunwar and Kawamura, 2014), Mongolia (av. 53%) (Jung et al., 2010) and Christchurch (av. 48%) (Wang et al.,

2005). Hagler et al. (2007) reported higher WSOC/OC ratios (av. 81%) for Greenland summit aerosols. Elevated WSOC/OC ratios can be used as a marker of aged aerosols (Ho et al., 2006). As shown in Fig. 4.2, elevated WSOC/OC ratios (up to 75%) were observed in the upwelling eastern equatorial Pacific (140°W-80°W), which are significantly higher than those (av. 33%) obtained in the non-upwelling central Pacific (171°E-141°W), indicating an enhanced photochemical oxidation of VOCs emitted from the ocean surface near the equator (O'Dowd and De Leeuw, 2007) and the subsequent formation of organic aerosols during long-range atmospheric transport (Rudich et al., 2007) (see Fig. 4.6). It is of interest to note that we obtained the similar results for WSOC/TC ratios because EC was negligible and thus TC is very close to OC during the study period.

4.4.3. Molecular compositions and concentrations of diacids, ω -oxoacids, α -dicarbonyls, pyruvic acid and fatty acids

We detected straight chain (C_2 - C_{11}), branched chain, saturated and unsaturated diacids, diacids with additional functional groups, aromatic diacids, ω -oxoacids, α -dicarbonyls, pyruvic acid and fatty acids in the remote marine aerosols. Table 4.2 presents their concentration ranges, median and average concentrations as well as their relative abundances in each compound class. Concentrations of total diacids ranged from 14 to 59 $ng\ m^{-3}$ (av. 42 $ng\ m^{-3}$, median 45 $ng\ m^{-3}$). The total concentrations in the aerosols are much lower than those of urban aerosols from Tokyo (Kawamura and Yasui, 2005), Sapporo (Aggarwal et al., 2008), and the marine aerosols from the East China Sea and Japan Sea (Mochida et al., 2003b), but are comparable to those of marine aerosols from the North Pacific (Fu et al., 2013), the Pacific Ocean including tropics (Kawamura and Sakaguchi, 1999) and the western Pacific (Wang et al., 2006) (Table 4.3).

Oxalic acid (C₂) was found as the most abundant diacid species followed by malonic (C₃) and succinic (C₄) acid. Concentration of C₂ ranged from 8.6 to 45 ng m⁻³ (av. 31 ng m⁻³, median 34 ng m⁻³), comprising 73.6% of total diacids. The predominance of C₂ has been reported in the continental aerosols (Kawamura and Ikushima, 1993; Tran et al., 2000; Yao et al., 2002; Ho et al., 2007; Miyazaki et al., 2007; Kundu et al., 2010b), in the marine aerosols (Kawamura and Sakaguchi, 1999; Kerminen et al., 2000; Mochida et al., 2003a, 2003b) and in the Arctic aerosols (Kawamura et al., 2012). In general, longer chain diacids were less abundant, where azelaic acid (C₉) was the most abundant (1.4%) in the range of C₇-C₁₁ diacids, being consistent with previous study of atmospheric aerosols over the southern and western Pacific Ocean (Wang et al., 2006). This result may suggest that over the central Pacific biogenic emission from the ocean surface is also important contributor to the secondary formation marine organic aerosols.

Branched chain dicarboxylic acids such as methylmalonic (iC₄), methylsuccinic (iC₅) and methylglutaric acid (iC₆) were detected during the study period, which accounted for 0.8% of total diacids. However, they were significantly less abundant than the corresponding straight-chain dicarboxylic acids. Among branched chain diacids, methylsuccinic (iC₅) acid was the most abundant. Unsaturated dicarboxylic acids, i.e., maleic (M), fumaric (F), methylmaleic (mM), phthalic (Ph), isophthalic (iPh) and terephthalic (tPh) acids, were also detected in the aerosols, contributing 2.8% of total diacids. Dicarboxylic acids having an additional functional group including malic (hC₄), oxomalonic (kC₃), and oxopimelic (kC₇) acids were also detected as minor diacids species. These multifunctional organic compounds have been proposed as intermediates to produce oxalic acid in the remote marine atmosphere (Miyazaki et al., 2010; Wang et al., 2006; Kawamura and Sakaguchi, 1999).

Concentrations of total ω -oxoacids ranged from 0.3 to 1.2 ng m⁻³ (av. 0.7 ng m⁻³, median 0.7 ng m⁻³). Glyoxylic acid (ω C₂) was the most abundant ω -oxoacid species,

comprising 53.8% of total ω -oxoacids in this study. The second most abundant ω -oxoacids was 7-oxoheptanoic (ω C₇) or 8-oxooctanoic (ω C₈) acid, which are photooxidation products of unsaturated fatty acids (Kawamura and Gagosian, 1987). These results may signify that biogenic unsaturated fatty acids are the important sources of ω -oxoacids in the central Pacific atmosphere. Moreover, evolution of glyoxylic (ω C₂) acid is associated with photochemical oxidation of isoprene (Carlton et al., 2009). Concentration ranges of pyruvic acid and total α -dicarbonyls were 0.09 to 0.2 ng m⁻³ (av. 0.1 ng m⁻³, median 0.1 ng m⁻³) and 0.1 to 1.6 ng m⁻³ (av. 0.3 ng m⁻³, median 0.2 ng m⁻³), respectively. Bikkina et al. (2014) proposed that methylglyoxal is significantly produced in the atmosphere by the photochemical oxidation of isoprene and other VOCs emitted from biologically productive ocean. In this study, methylglyoxal (MeGly) is more abundant than glyoxal, suggesting that the formation of methylglyoxal in the central Pacific is associated with biogenic sources (e.g., isoprene).

Fatty acids (C₁₄, C₁₆-C_{18:0} and C_{18:1}) were also detected in the central Pacific aerosol samples. Higher abundance of low molecular weight fatty acids that are emitted from the ocean surface due to the algal activity were reported over the northern North Pacific during the same cruise (Mochida et al., 2002). Concentration of total low molecular weight fatty acids ranged from 0.4 to 5.4 ng m⁻³ (av. 2.4 ng m⁻³, median 2.4 ng m⁻³). During the present cruise, C₁₄ and C₁₆ were found as the most abundant fatty acids species (Table 4.2).

4.4.4. Spatial distributions of diacids, ω -oxoacids, pyruvic acid, α -dicarbonyls and fatty acids and their contributions to aerosol total carbon

Spatial distribution of total diacids over the central Pacific is presented in Fig. 4.3a. Their atmospheric concentrations are 2 times high in the upwelling zone (140°W-80°W) of the central Pacific than the non-upwelling zone (171°E-141°W), suggesting that they are photo-chemically formed by the oxidation of biogenic volatile organic species (BVOCs, e.g.,

isoprene) in the warmer regions of the central Pacific. As shown in Fig. 4.4a abundances of oxalic (C_2) acid showed 3 times higher values over the upwelling zone of the central Pacific. One of the possible explanations for the increased concentration of oxalic acid in the upwelling zone is due to aqueous phase formation of oxalic acid from the oxidation of unsaturated fatty acid. However, azelaic acid is an oxidation product of biogenic unsaturated fatty acid such as oleic acid ($C_{18:1}$). Abundances of azelaic acid also showed almost 2 times higher values in the upwelling zone than those of non-upwelling zone. Moreover, oleic acid ($C_{18:1}$) and stearic acid ($C_{18:0}$) ratios are used as an important indicators of aged aerosols. Lower their ratios indicate that more oxidation of oleic acid has been occurred to produce diacids and related compounds (Ho et al., 2011). Interestingly, their ratios showed ~30% lowered values in the upwelling zone (140°W - 80°W). These results indicate that in the upwelling zone of the central Pacific, where photochemical oxidation of oleic acid has been intensified to produce azelaic acid and other long chain diacids which are then finally oxidized to yield short chain diacid like oxalic acid.

In remote marine atmosphere, glyoxylic acid, pyrovic acid and glyoxal are produced from the photo-chemical oxidation of isoprene and others volatile organic compounds (VOCs), which are then finally oxidized to produce oxalic acid (Bikkina et al., 2014). During the study glyoxylic acid was found as a dominant ω -oxoacid, whose abundances showed 4 orders of magnitude higher values in the upwelling zone than those in the non-upwelling (Fig. 4.5a). Likewise, concentration of pyrovic acid and glyoxal showed 2 times higher values in upwelling zone (Fig. 4.5a, b). Their high abundances in the upwelling central Pacific is associated with aqueous phase oxidation of marine derived BVOCs. Moreover, a good correlation ($r^2 = 0.79$) between these VOCs oxidation products ($\omega C_2 + \text{Pyr} + \text{Gly}$) and oxalic acid were observed in this study, indicating aqueous phase formation of oxalic acid in the upwelling central Pacific through oxidation of marine derived biological precursors.

In the biologically-active oceanic atmosphere, malonic (C₃) and succinic (C₄) acids is photo-chemically derived from the oxidation of unsaturated fatty acids and their precursor compounds such as 3-Oxopropanoic (ω C₃) and 4-Oxobutanoic (ω C₄) acids. In the upwelling central Pacific abundances of malonic (C₃) and succinic (C₄) acids showed 2-3 times higher abundances than the non-upwelling zone (Fig. 4.6a, b). Over the remote oceanic regions, malonic (C₃) and succinic (C₄) acids are often degraded to produce oxalic acid through ketomalonic (kC₃) and malic (hC₄) acids and abundance of oxalic acid increases due to photo-chemical aging of aerosols (Miyazaki et al., 2010). Moreover, I found good correlation ($r^2=0.53-0.64$) between oxalic (C₂) acid with malonic (C₃) and succinic (C₄) acids, which provide evidence for aqueous phase secondary production of oxalic acid in the upwelling zone through degradation of longer chain (C₃-C₄) diacids.

Spatial distributions of low molecular weight fatty acids (LFAs) are shown in Fig. 4.3b. Their distributions also show spatial pattern similar to that of total diacids with 2 times higher values over the upwelling central tropical Pacific. A strong even carbon number predominance of LFAs was observed in this study (Table 4.2). This result may suggest that fatty acids of marine algal origin are the important precursors of diacids over the eastern tropical Pacific. Kawamura and Gagosian (1987, 1990) also proposed that diacids are mainly produced by the photochemical oxidation of biogenic organic compounds such as fatty acids. Both of ω -oxoacids and α -dicarbonyls also exhibit spatial distributions pattern similar to diacids (results are not shown as a figure). During the cruise, glyoxylic acid and methylglyoxal were the dominant ω -oxoacid (53.8%) and α -dicarbonyl (66.7%) species, respectively. In the remote marine atmosphere, glyoxylic acid is produced from methylglyoxal through photochemical processing, which is further oxidized to oxalic acid (Kawamura et al., 1996a). Oxalic acid comprised 73.6% of total diacids in the present aerosols.

Total diacids contribute from 1.1 to 9.7% of TC (av. 3.7%, median 2.6%), which are comparable to those reported for the marine aerosols from the western North Pacific (Sempéré and Kawamura, 2003) and Pacific Ocean including tropics (Kawamura and Sakaguchi, 1999). However, they are approximately 4 times higher than those reported for urban aerosols from Tokyo (Kawamura and Ikushima, 1993) (Table 4.3). ω -Oxoacids account for 0.05 to 0.6% of TC (av. 0.2%, median 0.1%), which are similar to those (0.2-0.6%) reported in the Arctic Alert aerosols (Kawamura et al., 2010) but are ~2 times higher than those (av. 0.1%) reported in the Arctic Ocean aerosols (Kawamura et al., 2012). Contributions of α -dicarbonyls to TC ranged from 0.01-0.6% (av. 0.1%, median 0.04%). Kawamura et al. (2012) also reported very low contributions of α -dicarbonyls to TC over the Arctic Ocean. Fatty acid-C/TC ratios in the present study ranged from 0.1% to 1.5% (av. 0.5%, median 0.5%). Higher contributions of fatty acids to TC than those of ω -oxoacids and α -dicarbonyls may signify the emission strength of those acids from marine biological sources.

The diacid-C/TC ratios showed 2 times higher values over the upwelling zone of the eastern tropical Pacific (Fig. 4.7a). The maximized diacid-C/TC ratio in the upwelling eastern tropical Pacific can be explained by intensive photochemical production of diacids in the warmer regions, where gas-to-particle conversion of biogenic volatile organic compounds (BVOCs) may be significant under strong sunlight (Bikkina et al., 2014), as well as heterogeneous reactions of organic compounds attached on aerosol surfaces (Kawamura and Sakaguchi, 1999). A positive correlation between air temperature and diacid-C/TC was observed in Tokyo urban aerosols (Kawamura and Ikushima, 1993). Kawamura and Gagosian (1990) reported that direct precursors of diacids such as unsaturated fatty acids are more enriched in warmer and productive water. These molecules are further emitted to the

atmosphere from surface water, stimulating the production of diacids through photochemical processing (Sempéré and Kawamura, 2003).

4.4.5. Longitudinal variations in the contributions of diacids to WSOC over the central Pacific

Total diacids accounted for 1.5 to 24.7% of WSOC (av. 8.0%, median 6.6%), which are comparative to those reported for marine aerosols collected in the western Pacific at 35°N-40°S (Sempéré and Kawamura, 2003) and western subarctic and subtropical North Pacific at 10°N-45°N (Bikkina et al., 2014), but are higher than those reported in urban regions (see Table 4.3). Diacids and related water-soluble organic compounds (ω -oxoacids, α -dicarbonyls and pyruvic acid) account for 1.8 to 29% of WSOC mass, suggesting that sea-to-air emissions of diacids and related compounds is not the main source of these organics in marine aerosols (Bikkina et al., 2014). The contributions of diacids to WSOC showed 2 times higher values in the upwelling eastern tropical Pacific (Fig. 4.7b). Higher diacid-C/WSOC ratios over the warmer regions of the central Pacific may suggest that considerable secondary formation of these compounds via photochemical processing from their biogenic precursors like isoprene and unsaturated fatty acids rather than direct sea-to-air emissions. Moreover, a positive correlation between diacid-C/WSOC ratios and air temperature was reported in marine aerosols from the western Pacific (Sempéré and Kawamura, 2003).

4.4.6. Primary and secondary aerosol formation over the eastern tropical Pacific

To better understand the enhanced emission of primary organic aerosols such as fatty acids and BVOCs from the biological active ocean surface in the eastern central Pacific near the equator, we obtained the satellite image of *Chlorophyll-a* concentrations in the Pacific Ocean as shown in Fig. 4.8, which showed a tongue of high *Chlorophyll-a* zone along the equator following the upwelling region off the Peru Coast. Interestingly, a high *Chlorophyll-*

a zone was detected in the south of the equator in the eastern central Pacific. It is of interest to note that, when we detected high concentrations of unsaturated fatty acid (C_{18:1}) and low molecular weight dicarboxylic acids and related compounds, the air mass trajectories originated from the south of the equator (Fig. 4.9), in which we detected high *Chlorophyll-a* zone (Fig. 4.8). This consistency supports that high abundances of dicarboxylic acids in the eastern central Pacific are involved with the emissions of BVOCs from the high biological ocean followed by atmospheric oxidation during the transport. It is interesting to note that, near the sampling area of eastern tropical Pacific (140°W-80°W, 20°S-0°N) (satellite image showed a tongue of high *Chlorophyll-a*), where area-averaged time series of *Chlorophyll-a* concentrations, dissolved and detritus organic matter absorption coefficient, and particulate organic carbon (POC) contents showed increasing trends from summer to autumn (Fig. 4.10). Although, the satellite derived POC and *chlorophyll-a* concentration showed significant difference, which is notable feature of the equatorial Pacific with high nutrients and low *chlorophyll-a* concentration [Peña et al., 1990].

Fig. 4.11 depicts the conceptual framework for the evolution of primary and secondary aerosols in the eastern upwelling tropical Pacific with high biological productivity. Marine-derived primary organic aerosols (POA) are produced by wave breaking and bubble-bursting process that are caused by the interaction between the wind and ocean surface (Rinaldi et al., 2010). The bubbles that are produced by breaking of waves scavenge surface-active organics such as humic substances, lipidic and proteinaceous materials and others (i.e. bacteria, viruses and detritus), which are enriched in oceanic surface layer. Bubbles are then injected into the atmosphere as POA through bursting (Blanchard, 1964; Barger and Garrett, 1970; O'Dowd et al., 2004; Gantt and Meskhidze, 2013). Marine POA plays an important role as precursor/source and sink for OH radical, leading to the degradation of organic matter and production of LMW organic compounds like dicarboxylic acids (Zhou et al., 2008), which

are the ubiquitous water-soluble components of secondary organic aerosols (SOA) (Bikkina et al., 2014).

The eastern upwelling tropical Pacific accounts for 23% of the primary productivity in the Pacific and 10% of global oceanic primary productivity (Pennington et al., 2006). Pennington et al. (2006) also proposed that, in the shadow zone between subtropical gyres where subsurface ventilation is limited, water mass with high primary productivity sinks and then phytoplankton decompose via bacterial assimilation, releasing abundant macronutrients such as nitrate, phosphorus and silicon to the nutricline zone in the water column. In the eastern tropical Pacific, dynamics of wind-driven surface flow can cause the thermocline to be shallow towards the euphotic zone (Barber and Chavez, 1983). The thermocline shoaling and upwelling are the main process to supply the nutrients to the euphotic zone of the eastern tropical Pacific (Pennington et al., 2006). Thus, the abundant nutrients supplied to phytoplankton community enhance the primary productivity in the open ocean, causing emissions of BVOCs such as aliphatic amines, isoprene and monoterpenes from the ocean surface to the atmosphere. Photooxidation of those BVOCs can form SOA in the marine boundary layer (Yassaa et al., 2008; Gantt et al., 2009; Myriokefalitakis et al., 2010).

4.5. Conclusions

Diacids, ω -oxoacids, pyruvic acid, α -dicarbonyls and fatty acids have been determined in the central Pacific aerosol samples together with organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), total carbon (TC) and water-soluble total nitrogen (WSTN). Abundances of oxalic acid showed 3 times higher values and azelaic acids showed 2 times higher levels over the upwelling central Pacific, indicating their origin associated with photooxidation of biogenic unsaturated fatty acids and isoprene. Spatial distributions of diacids and related compounds as well as fatty acids also showed 2

times higher levels in the upwelling zone of the central Pacific than the non-upwelling zone, again suggesting that diacids and related compounds are significantly produced in this region of the central Pacific through photochemical oxidation of unsaturated fatty acids, isoprene and other BVOCs produced by marine phytoplankton. Diacids accounted for 8% (average) of WSOC, indicating that they are the major components of water-soluble organic aerosols. The WSOC/OC ratios were enhanced in the upwelling eastern tropical Pacific. These results together with seven-day backward air masses trajectories and satellite image of *Chlorophyll-a* support that photochemical conversions of marine derived BVOCs emitted from the high biological ocean associated with upwelling are more significant in the warmer eastern equatorial Pacific than western North Pacific.

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Table 4.1. Mass concentrations of various organic components in the central Pacific aerosol samples and their concentration ratios.

Components	Minimum	Maximum	Average	Median
TC ($\mu\text{g m}^{-3}$)	0.1	1.2	0.5	0.4
WSOC ($\mu\text{g m}^{-3}$)	0.04	0.8	0.3	0.2
WIOC ($\mu\text{g m}^{-3}$)	0.05	0.5	0.2	0.2
WSTN ($\mu\text{g m}^{-3}$)	0.03	0.6	0.2	0.1
WSOC/OC (%)	28	75	50	49

Table 4.2. Concentrations (ng m^{-3}) of dicarboxylic acids, ω -oxoacids, pyruvic acid, α -dicarbonyls and fatty acids in the marine aerosol from the central Pacific (n=22).

Compounds	Minimum	Maximum	Average	Median	Average relative abundances (%)
Saturated straight chain diacids					
Oxalic, C ₂	8.6	45.0	31.0	34	73.8
Malonic, C ₃	2.0	9.7	6.3	6.8	15.0
Succinic, C ₄	0.7	3.1	1.7	1.6	4.0
Glutaric, C ₅	BDL ^a	0.4	0.07	0.02	0.2
Adipic, C ₆	BDL ^a	0.6	0.1	0.1	0.2
Pimelic, C ₇	BDL ^a	0.4	0.1	0.08	0.2
Suberic, C ₈	0.02	0.8	0.2	0.1	0.5
Azelaic, C ₉	0.1	1.2	0.6	0.5	1.4
Sebacic, C ₁₀	BDL ^a	1.1	0.1	0.04	0.2
Undecanoic, C ₁₁	BDL ^a	0.7	0.07	0.02	0.2
Unsaturated diacids					
Maleic, M	0.05	0.2	0.1	0.1	0.2
Fumaric, F	0.01	0.2	0.1	0.1	0.2
Methylmaleic, mM	0.04	0.8	0.2	0.1	0.5
Phthalic, Ph	0.02	1.4	0.5	0.4	1.2
Isophthalic, iPh	BDL ^a	0.2	0.1	0.1	0.2
Terephthalic, tPh	BDL ^a	0.4	0.2	0.2	0.5
Branched chain diacids					
Methylmalonic, iC ₄	BDL ^a	0.3	0.1	0.06	0.2
Methylsuccinic, iC ₅	BDL ^a	0.8	0.2	0.2	0.5
2-Methylglutaric, iC ₆	BDL ^a	0.1	0.03	0.02	0.1
Multifunctional diacids					
Hydroxysuccinic, hC ₄	0.01	0.3	0.1	0.1	0.2
Ketomalonic, kC ₃	BDL ^a	0.6	0.2	0.2	0.5
Ketopimelic, kC ₇	BDL ^a	0.2	0.04	0.02	0.1
Total diacids	14	59	42	45	-
ω -oxoacids					
Glyoxylic, ω C ₂	0.3	1.2	0.7	0.7	53.8
3-Oxopropanoic, ω C ₃	BDL ^a	0.9	0.1	0.05	7.9
4-Oxobutanoic, ω C ₄	BDL ^a	0.4	0.05	0.01	3.9
5-Oxopentanoic, ω C ₅	BDL ^a	0.4	0.06	0.06	4.7
7-Oxoheptanoic, ω C ₇	0.03	0.7	0.2	0.1	15.4
8-Oxooctanoic, ω C ₈	0.02	0.3	0.2	0.2	15.4
9-Oxononanoic, ω C ₉	BDL ^a	0.5	0.03	0.01	2.3
Total ω-oxoacids	0.4	2.6	1.3	1.2	-
Pyruvic acid, Pyr	0.09	0.2	0.1	0.1	-
α -Dicarbonyls					
Glyoxal, Gly	0.06	0.2	0.1	0.1	33.3
Methylglyoxal, MeGly	0.02	1.6	0.2	0.1	66.7
Total α-dicarbonyls	0.1	1.6	0.3	0.2	-
Fatty acids (FAs)					
C14 (Myristic acid)	0.02	1.2	0.6	0.5	25
C16 (Palmitic acid)	0.06	1.5	0.6	0.6	25
C17 (Margaric acid)	0.1	0.9	0.5	0.5	21
C18 (Stearic acid)	0.05	1.5	0.4	0.2	16.6
C18:1 (Oleic acid)	BDL ^a	1.5	0.3	0.3	12.5
Total FAs	0.4	5.4	2.4	2.4	-

^aBDL, below detection limit (0.005 ng m^{-3}).

Table 4.3. Comparisons of dicarboxylic acid concentrations and their contributions to WSOC and TC in atmospheric aerosols from different locations.

Sampling location	Sampling period	Size	Total diacids (av.) ng m ⁻³	Oxalic acid (ng m ⁻³)	Diacid-C/WSOC, % (Diacid-C/TC, %)	References
Urban regions						
Tokyo, Japan	Apr 1988-Feb 1989	TSP	90-1360 (480)	270	0.2-1.8	Kawamura and Ikushima (1993)
Sapporo, Japan	May-Jul, 2005	TSP	106-787 (406)	192	4.8	Aggarwal and Kawamura (2008)
Beijing, China	Aug-Sept 2006	PM _{2.5}	294-1440 (760)	449	6.5	Ho et al. (2010)
Hong-Kong, China	2003-2005	PM _{2.5}	404-4490	182-3073	2.6-15.5	Li and Yu (2010)
Polar regions						
Alert, Arctic	1987-1988	TSP	4.3-97 (25)	14	-	Kawamura et al. (1996a)
Alert, Arctic	Jan-Apr 1992	PM ₂	18-146 (64)	26	-	Kawamura et al. (2005)
Syowa, Antarctica	1991	PM _{0.7}	6-89 (30)	1.6-10	-	Kawamura et al. (1996b)
Marine regions						
Pacific Ocean	Oct-Dec 1990	TSP	10-248 (62)	40	(1.1-15.8)	Kawamura and Sakaguchi (1999)
Pacific Ocean	Aug-Oct 1992	TSP	7.1-605 (7.3)	2.8	2.1-14.7 (1.1-5)	Sempéré and Kawamura (2003)
East China Sea	Mar-Apr 2001	TSP	410-1500 (850)	-	-	Mochida et al. (2003b)
Japan Sea	Mar-Apr 2001	TSP	480-2100 (1200)	-	-	Mochida et al. (2003b)
Western Pacific	Nov 1994-Feb 1995	TSP	1.8-180 (63)	38	-	Wang et al. (2006)
North Pacific	Oct-Nov 1989	TSP	17-167 (61)	10-89	-	Fu et al. (2013)
Western-North Pacific	Feb-Mar 1990	TSP	225-285 (255)	139-173	-	Fu et al. (2013)
North Pacific (10°N-45°N)	Aug-Sep 2008	TSP	5-153	26	2.6-26.3	Bikkina et al. (2014)
Central Pacific (1°59'N-35°N)	Sept-Oct 1999	TSP	14-59 (42)	31	1.5-24.7 (1.1-9.7)	This study

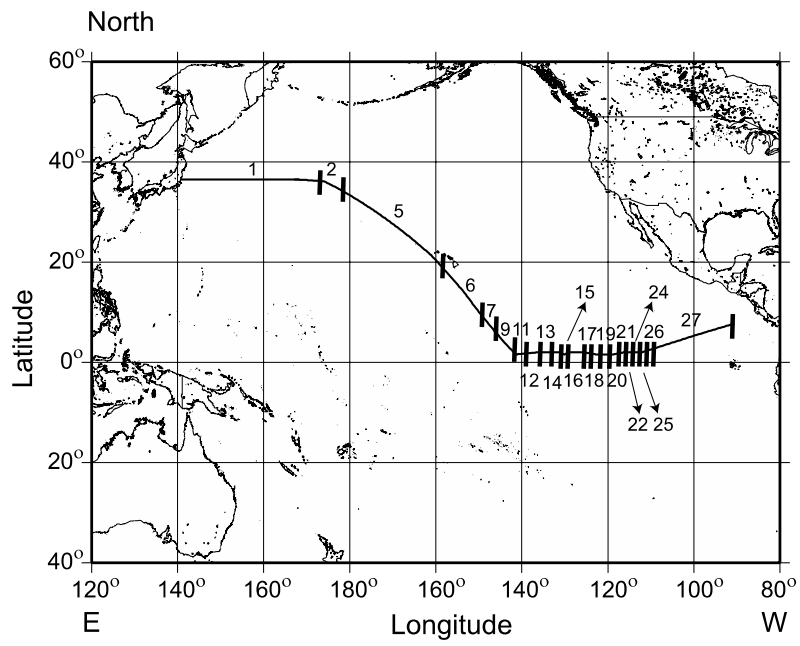


Fig. 4.1. Cruise track of T/V *Shoyo Maru* 1999. The numbers and thick black marks are shown in the map represent sample identification numbers and sampling locations, respectively.

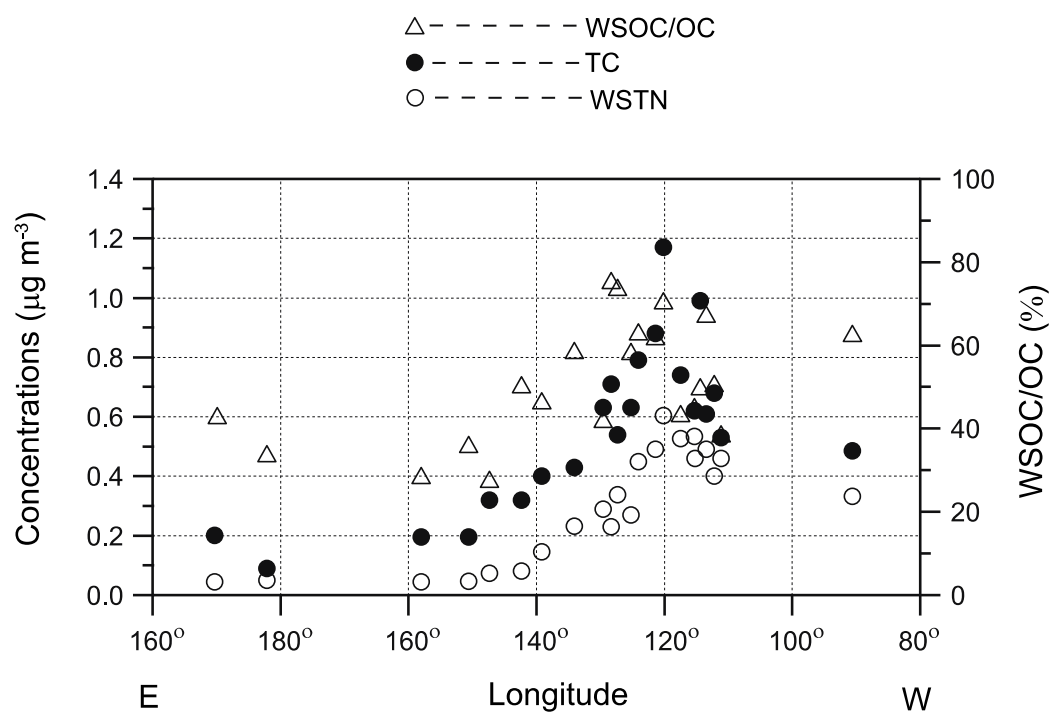


Fig. 4.2. Longitudinal distributions of WSOC/OC concentration ratios (open diamond), TC (solid circles) and WSTN (open circles) for the remote marine aerosols from the central Pacific.

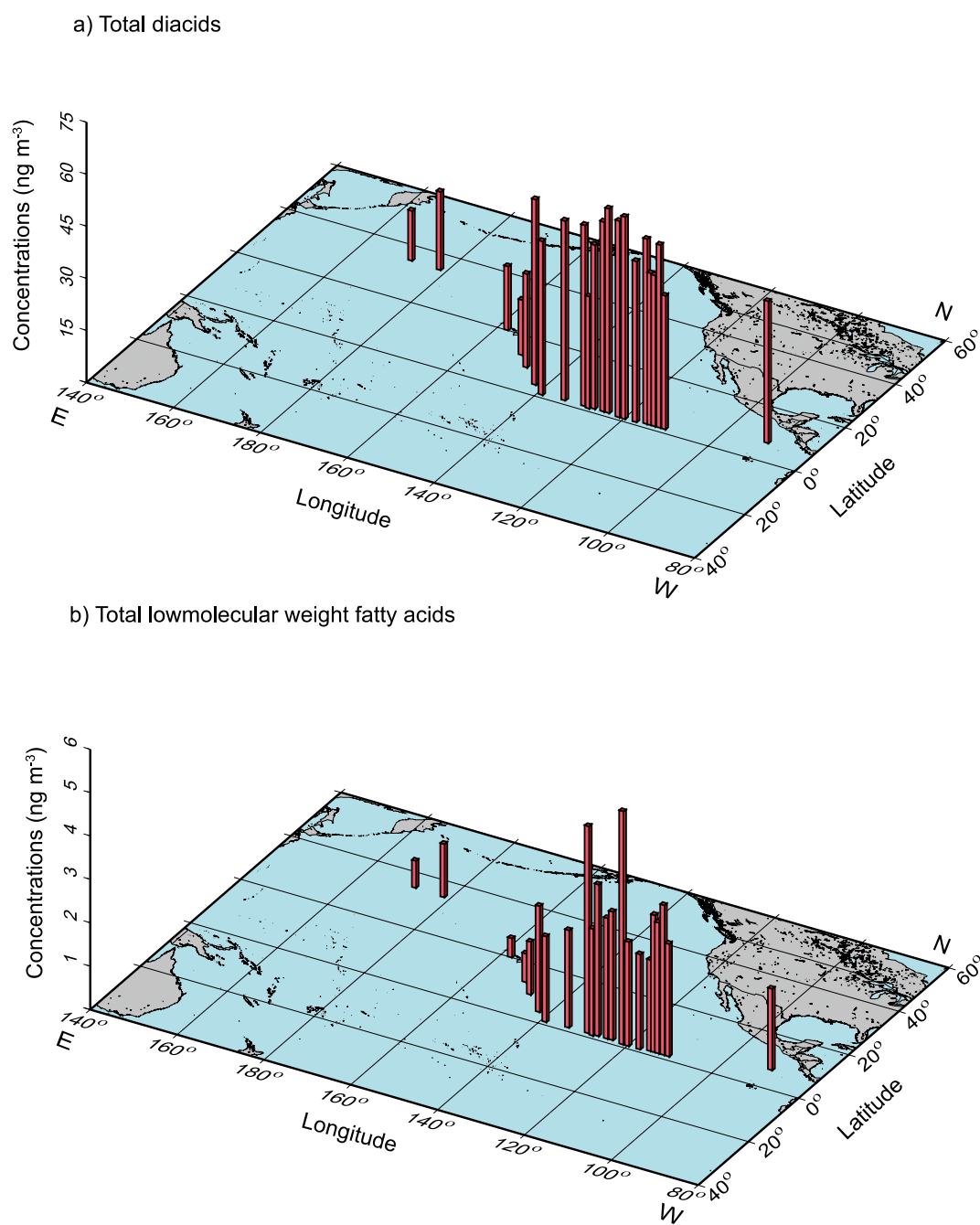


Fig. 4.3. Spatial distributions of (a) total dicarboxylic acids and (b) total low molecular weight fatty acids in the remote central Pacific aerosols.

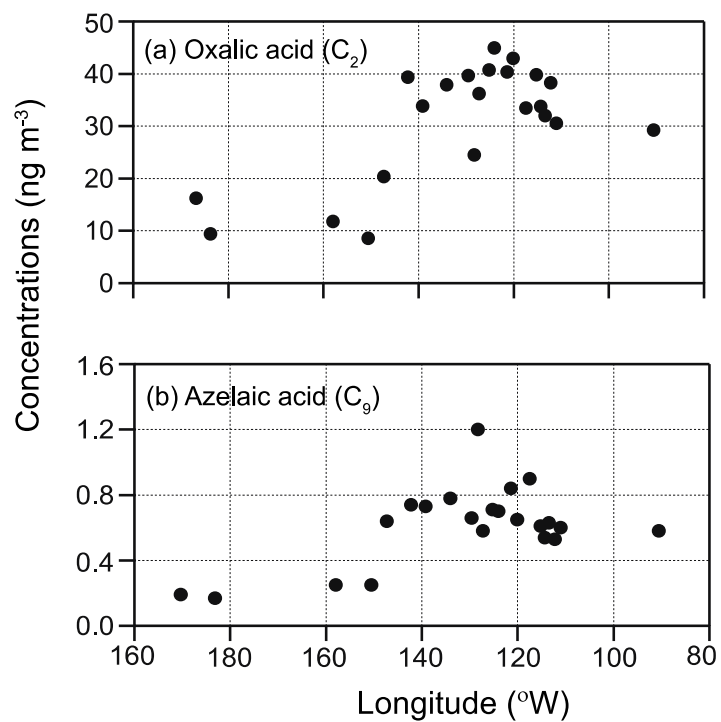


Fig. 4.4. Longitudinal distributions of (a) oxalic (C_2) acid and (b) azelaic (C_9) acid in the remote central Pacific aerosols.

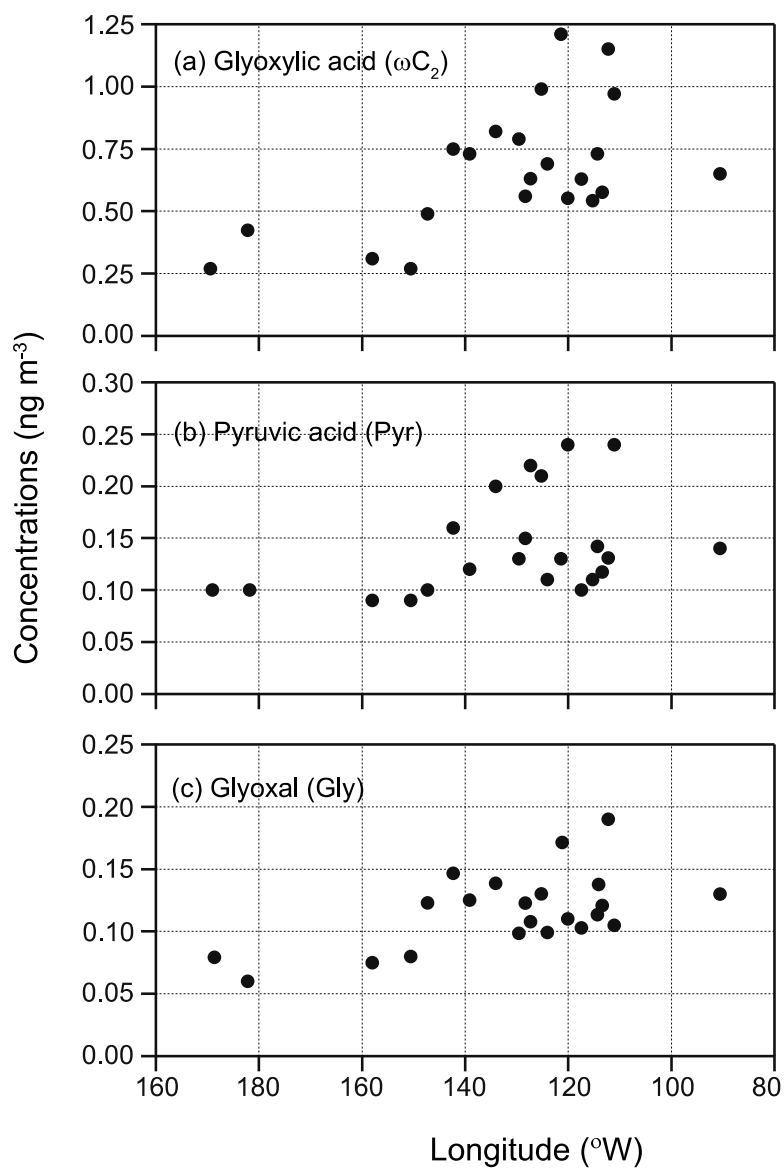


Fig. 4.5. Longitudinal distributions of (a) glyoxylic (ω C₂) acid, (b) pyruvic (Pyr) acid and (c) glyoxal (Gly) in the remote central Pacific aerosols.

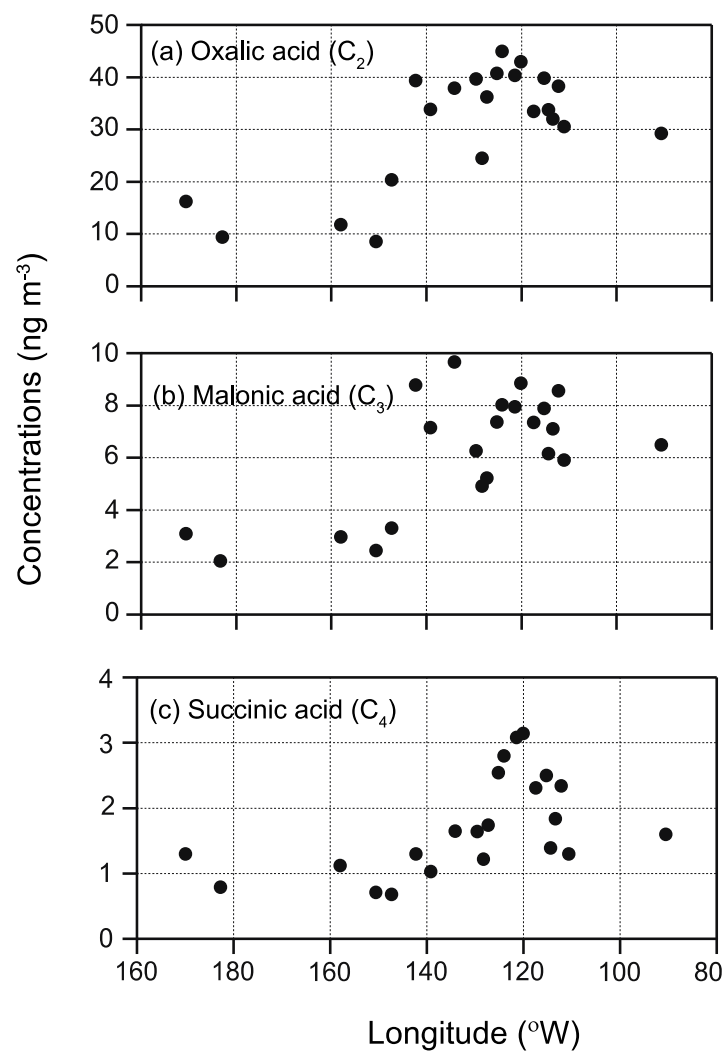
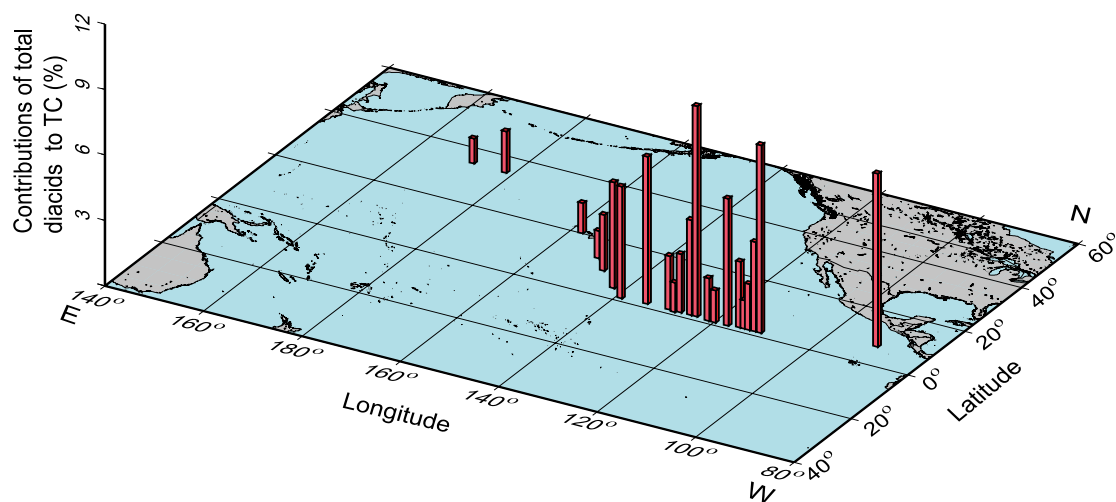


Fig. 4.6. Longitudinal distributions of (a) oxalic (C_2) acid, (b) malonic (C_3) acid and (c) succinic (C_4) acid in the remote central Pacific aerosols.

(a) Contribution of diacids to TC



(b) Contribution of diacids to WSOC

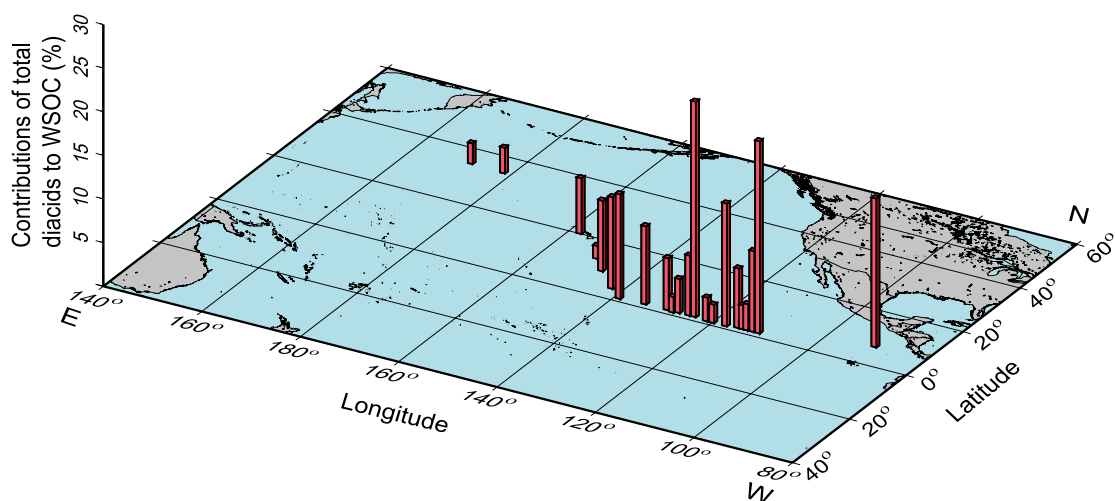


Fig. 4.7. Spatial distributions of (a) contributions of total diacids in aerosol total carbon and (b) contributions of total diacids in water-soluble organic carbon for the remote marine aerosols from the central Pacific.

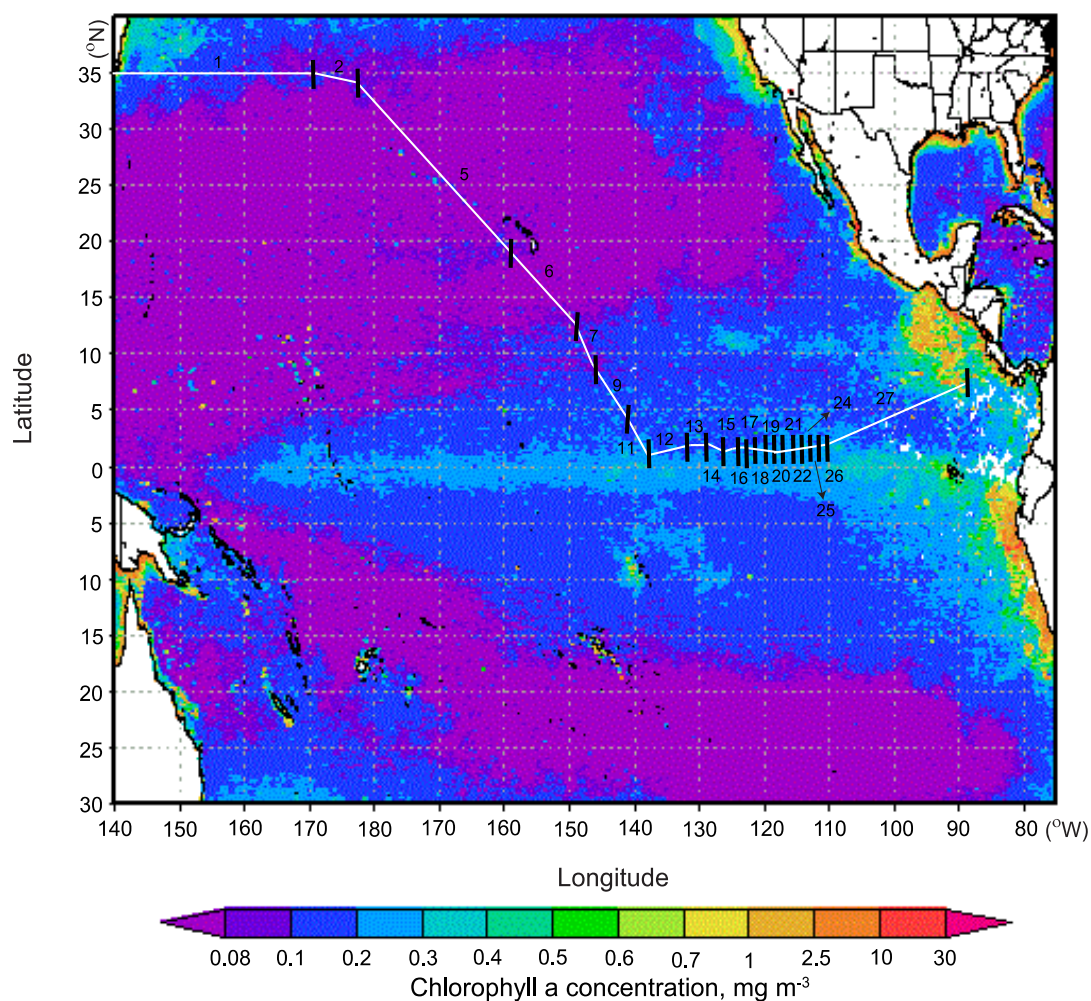


Fig. 4.8. Satellite image of *Chlorophyll-a* concentration (mg m^{-3}) in the surface ocean during September-October, 1999 when the aerosol samples were collected in the central Pacific ($1^{\circ}59'\text{N}$ - 35°N and $171^{\circ}54'\text{E}$ - $90^{\circ}58'\text{W}$). The white line, thick black marks and numbers are shown in the figure represent cruise track, sample locations and sample identification numbers, respectively. The figure was prepared with Giovanni online data system, NASA GES DISC.

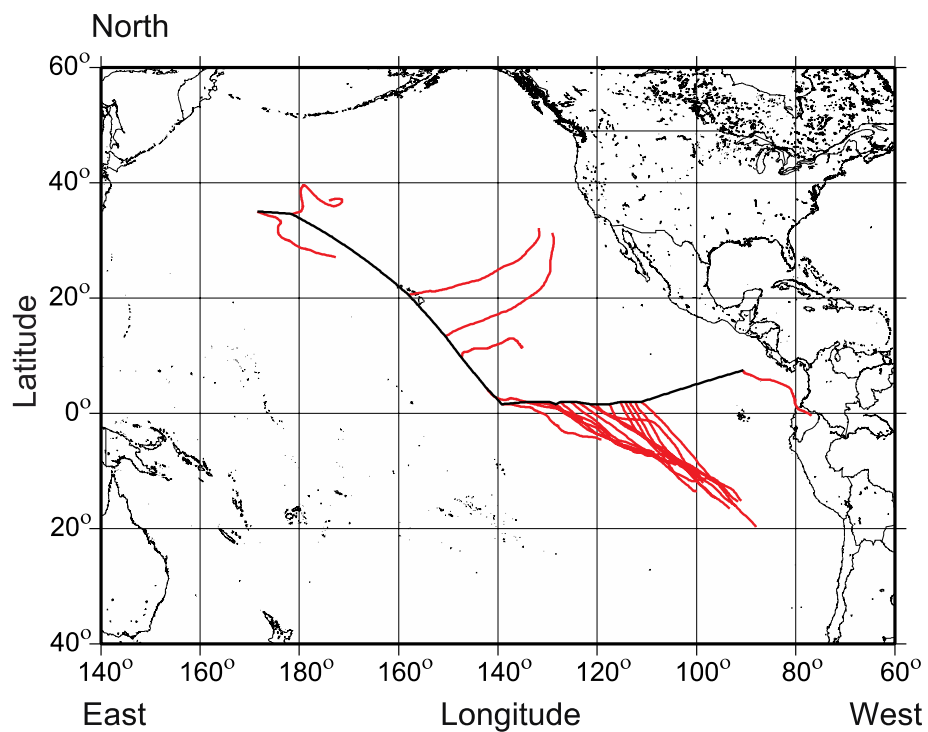


Fig. 4.9. Seven day backward air masses trajectories at 500 m above the ground were drawn with NOAA HYSPLIT model. Black line indicate cruise track. For details of the cruise track see Fig. 1.

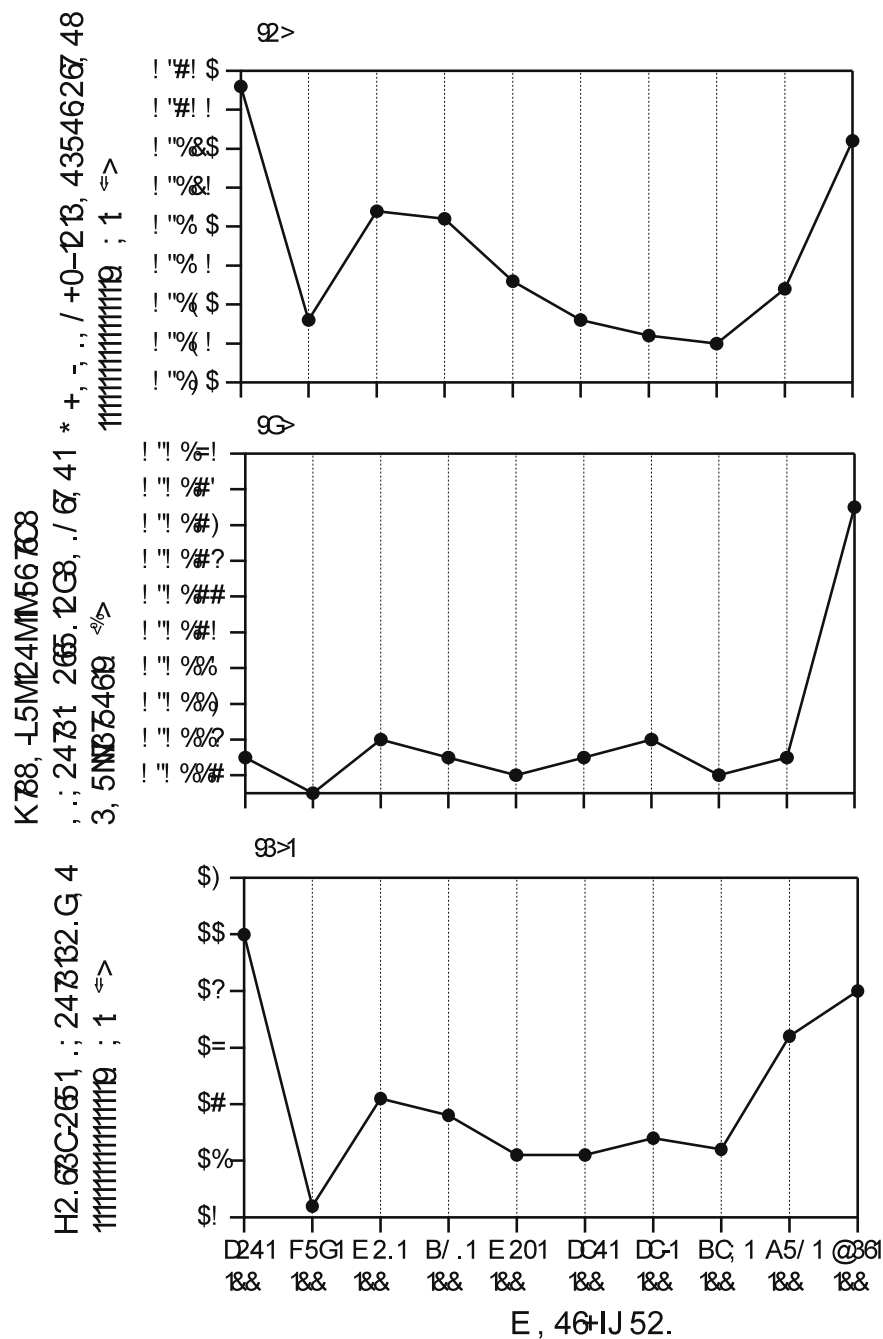


Fig. 4.10. Monthly variations of (a) *Chlorophyll-a* concentration, (b) dissolved and detritus organic matter absorption coefficient and (c) particulate organic carbon near the eastern tropical sampling site (140°W-80°W, 20°S-0°N) of the central Pacific. These figures are prepared with Sea WiFS.

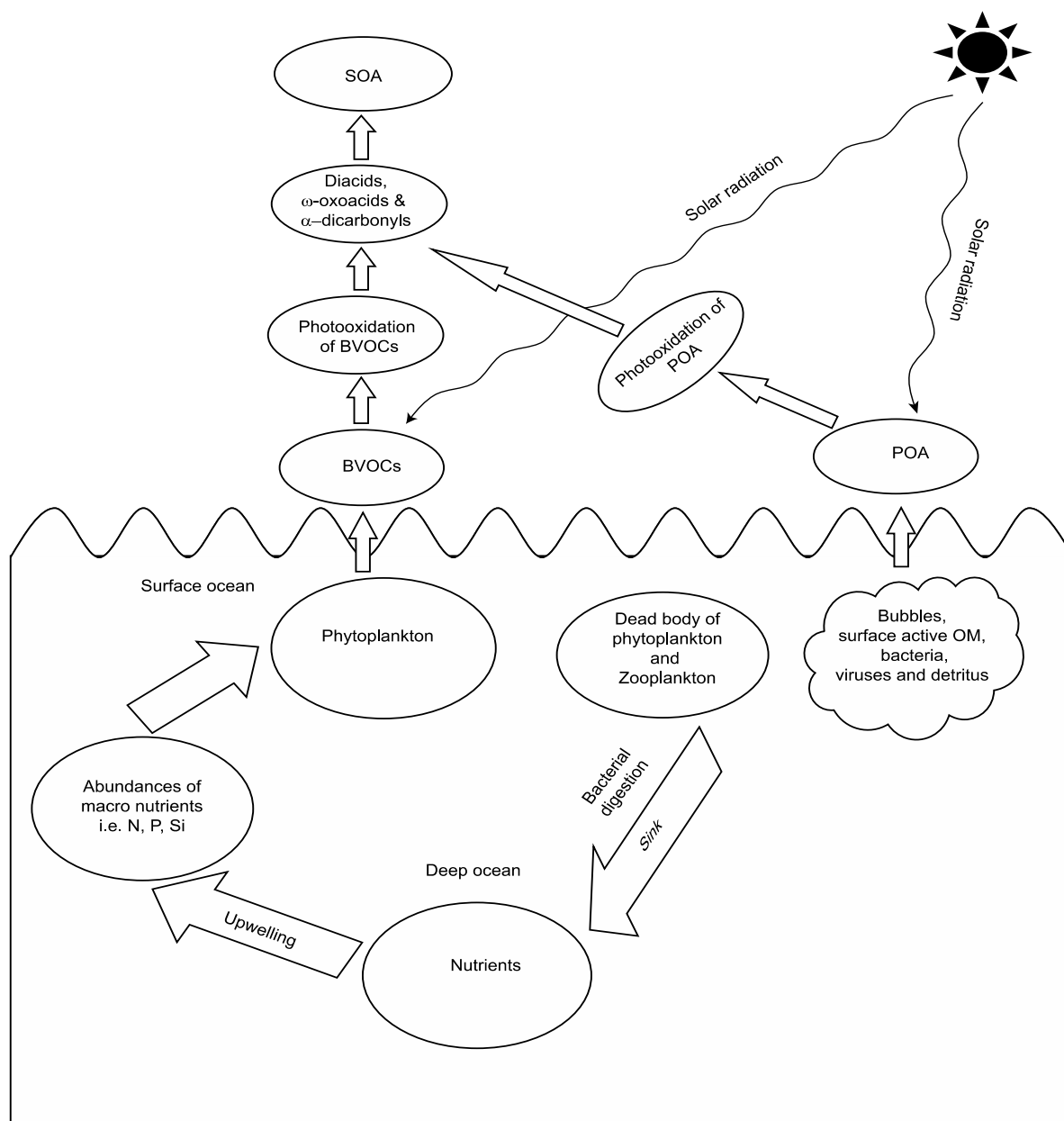


Fig. 4.11. Conceptual framework for primary and secondary aerosol formation pathways in the marine boundary layer of eastern tropical Pacific. POA, SOA and BVOCs stand for Primary Organic Aerosol, Secondary Organic Aerosol and Biogenic Volatile Organic Compounds, respectively.

Chapter 5: Geographical distributions of dicarboxylic acids, ω -oxoacids, pyruvic acid, α -dicarbonyls and fatty acids in the marine aerosols from the North and the South Pacific

5.1. Introduction

Atmospheric aerosols are composed of varieties of organic compounds which are significantly contribute to the aerosol load of the atmosphere and alter the physical and chemical properties (Mochida et al., 2003; Legrand et al., 2007). Marine-derived primary organic aerosol (POA) produced by wave breaking process through bubbles bursting that derives from the interaction of wind with the ocean surface (Rinaldi et al., 2010). On the other hand, marine secondary organic aerosols (SOAs) are essentially produced from atmospheric reactions of anthropogenic and biogenic volatile organic compounds (BVOCs) with oxidants including ozone (O_3), oxides of nitrogen (NO_x) and OH radicals (Claeys et al., 2004, 2007; Jaoui et al., 2005). However, the fate of organics in marine aerosols is highly indecisive (Miyazaki et al., 2014). Organic matter (OM) in marine primary organic aerosol may act as an important precursor/source and sink for OH radical therefore leads to the degradation of OM and the production of low molecular weight (LMW) organic compounds like dicarboxylic acids (Zhou et al., 2008). LMW dicarboxylic acids have potential influences on the properties of organic particles thus play an important role in the hygroscopic growth of particles (Prenni et al., 2003) and the activation of cloud condensation nuclei (Liss and Lovelock, 2007; Booth et al., 2009).

Both of the primary and secondary sources of LMW dicarboxylic acids and related compounds are well documented in literature. These compounds are primarily produced in the polluted areas through incomplete combustion of fossil fuels (Kawamura and Kaplan, 1987; Fraser et al., 1998; Kerminen et al., 2000), meat charbroiling emission (Rogge et al.,

1991), biomass burning plumes (Graham et al., 2002; Allen et al., 2004; Kundu et al., 2010) and directly by biogenic emissions (Kawamura and Gagosian, 1990). Matsumoto et al. (1998) proposed that primary sources of diacids in the remote marine atmosphere are associated with the sea salt particles. However, secondary formations of LMW diacids and related polar compounds from their anthropogenic and biogenic precursors are well characterized and supported by extensive interpretations (Agarwal et al., 2008; Bikkina et al., 2014; Carlton et al., 2006, 2009). The atmospheric distributions of LMW diacids in the remote marine environment is controlled by either long-range transport of pollutants from the continent (Kundu et al., 2010; Fu et al., 2013; Kawamura and Sakaguchi, 1999) or by photochemical processing of BOVCs in the source region which emitted from the ocean surface (Bikkina et al., 2014; Hoque et al., 2015). Although, several studies on atmospheric distributions of diacids and related compounds over the Pacific Ocean, most of them focuses on single hemispheric region. But it is interesting to understand the intra-hemispheric distributions of LMW diacids and studies on trans-hemispheric distributions are still very limited.

The study area including North and South Pacific is very interesting because of their dissimilarities in terms of meteorology, climatic conditions, as well as biological productivity and wind patterns. For example, the coastal western North Pacific is highly influenced by the different continental air masses transported from north China, Mongolia, Russia and Siberia. In contrast, the central North Pacific which is significantly influenced by the oceanic air masses as it far away from the continents. But the samples which are collected from the South Pacific, influenced by the inward continental air masses from Papua-New Guinea, Southern Australia and New Zealand. During the cruise, we collected aerosol samples covering North and South Pacific oceans during Feb. to April, 1994 for the determination of low molecular weight dicarboxylic acids, ω -oxoacids, pyruvic acids, α -dicarbonyls and fatty acids as well as organic and elemental carbon and water soluble total nitrogen. The aims of

the present study were (1) to find out the molecular compositions of diacids and related polar compounds over the North and South Pacific Ocean and (2) to map the distributions of aerosols mass together with dicarboxylic acids and contributions of water-soluble dicarboxylic acids to OC over the marine boundary layer of the North and South Pacific.

5.2. Aerosol sampling

During the cruise (from 16 February to 1 April, 1994) a total 17 marine aerosol (TSP) samples were collected in the North Pacific (3°05'N-34°02'N, 144°52'E-173°49'W) and in the South Pacific (6°59'S-25°46'S, 154°28'E-173°55'W) from the upper deck of the T/V *Bousei Maru* cruise using pre-combusted (450°C) quartz fiber filters (Pallflex-2500QAT-UP, 20 × 25 cm) and high volume air sampler. The sampler was controlled with a wind sector ($\pm 60^\circ$) and wind speed ($\geq 5 \text{ m s}^{-1}$) system to avoid potential contamination from the ship exhausts (Kawamura and Sakaguchi, 1999). Sampling time was about 48 to 72 hours. Fig. 5.1 shows the cruise track. Total aerosol mass was determined by weighing the filter before and after collection. After sample collection, each filter was stored individually in a pre-combusted clean glass jar with a Teflon-lined screw cap at -20°C prior to analysis. Although the sample filters had been stored for a long time, degradation of organics on the filters should be insignificant under such a low temperature (Wang et al., 2006; Kawamura et al., 2010). Blank filters were exposed to the marine air in the sample shelter for a few seconds and then recovered (Sempéré and Kawamura, 2003).

During the cruise, 7-day backward air mass trajectories were conducted in every 6 h interval using the Hybrid Single-Particle Lagrangian Trajectory (HYSPILT) model developed by the National Oceanic and Atmospheric Administration Air Resource Laboratory (<http://ready.arl.noaa.gov/HYSPILT.php>). Each back trajectory was determined at 500 m above the ground for aerosol samples collected during the cruise.

5.3. Results and discussion

5.3.1. General Characteristics of the marine Aerosols

As shown in Table 5.1 the aerosol mass concentrations over the North and South Pacific ranged from 36 to 95 $\mu\text{g m}^{-3}$ (av. 64 $\mu\text{g m}^{-3}$, median 63 $\mu\text{g m}^{-3}$) and 28 to 92 $\mu\text{g m}^{-3}$ (av. 54 $\mu\text{g m}^{-3}$, median 50 $\mu\text{g m}^{-3}$), respectively. Such values are parallel to those of previously reported for the western to central Pacific (19-404 $\mu\text{g m}^{-3}$, av. 48 $\mu\text{g m}^{-3}$) (Kawamura and Sakaguchi, 1999), the western Pacific (11-68 $\mu\text{g m}^{-3}$) (Sempéré and Kawamura, 2003), the North Pacific (11-232 $\mu\text{g m}^{-3}$, av. 44 $\mu\text{g m}^{-3}$) (Hoque et al., 2015) but higher than the aerosol mass concentrations which are reported for the tropical Indian Ocean (av. 15 $\mu\text{g m}^{-3}$) (Krishnamurti et al., 1998) and the Atlantic Barbados (11-31 $\mu\text{g m}^{-3}$) (Li et al., 1996). In the North Pacific Ocean, spatial distributions of aerosols mass showed almost 20% of higher values over western part of the North Pacific than those of the central Pacific, where the influences of continental air masses were observed as insignificant during the study (see Fig. 5.2a and 5.7). This result indicates that sea salt particles and sea-to-air emission of biogenic volatile organic compounds are the source of marine aerosol over the central Pacific, where as over the western North Pacific continental influence also an important contributor for marine aerosol. Interestingly, over the South Pacific, the higher aerosols mass concentrations also observed in the samples those were collected near the Islands, suggesting that continental aerosols has travelled long distances along the coastal areas of the North and South Pacific (Fig. 5.2a).

Concentration of total carbon (TC) for the remote aerosol samples ranged from 0.15 to 1.9 $\mu\text{g m}^{-3}$ (av. 0.62 $\mu\text{g m}^{-3}$, median 0.36 $\mu\text{g m}^{-3}$). The relative abundances of TC to aerosol mass, which ranged from 0.2% to 4.5% (av.1.1%, median 0.8%) (Table 5.1). Spatial distributions of TC and the TC% of the aerosols also showed similar pattern those of aerosols

mass, with 2 times higher values over the North Pacific supporting a significant atmospheric transport of continent-derived organics over the remote marine atmosphere (Hoque et al., 2015).

Aerosol water-soluble total nitrogen (WSTN) concentration ranged from 0.01 to 0.80 $\mu\text{g m}^{-3}$ (av. 0.16 $\mu\text{g m}^{-3}$, median 0.10 $\mu\text{g m}^{-3}$). These values are in the same order of magnitude of those previously reported for the North Pacific (0.02-0.90 $\mu\text{g m}^{-3}$, av. 0.20 $\mu\text{g m}^{-3}$) (Hoque et al., 2015) but are ca. 3 orders of magnitudes lower than those (0.07-3.02 $\mu\text{g m}^{-3}$, av. 0.58 $\mu\text{g m}^{-3}$) reported for the ambient aerosols collected from the Okinawa Island in the western North Pacific rim (Kunwar and Kawamura, 2014). Similar spatial distributions (TC) are obtained for WSTN; having 6 times higher values over the western North Pacific, which is highly influenced by the upcoming air masses from the Asian continents (see Fig. 5.7). This finding may imply that particulate nitrogen is of continental origin, which has transported long distances to the remote western North Pacific. In contrast, the samples collected in the central North Pacific showed lowest concentration of WSTN. Interestingly, these samples are free from continental influences (Fig. 5.7), suggesting sea-to-air emission of aerosols are not the main source of water soluble organic nitrogen over the remote areas. The nitrogenous fraction (WSTN%) of the aerosols mass ranged from 0.02 to 1.0% (av. 0.25%, median 0.10%) (Table 5.1). These values are similar to those are reported in our previous study for the North Pacific (Hoque et al., 2015) and the Pacific Ocean including tropics (Kawamura and Sakaguchi, 1999), but significantly lower than those reported for TN from urban Tokyo (Kawamura and Ikushima, 1993).

5.3.2. Molecular distributions of diacids, ω -oxoacids, pyruvic acid, fatty acids and α -dicarbonyls

During the expedition, low molecular weight dicarboxylic acids (C_2 - C_{11}), ω -oxoacids (C_2 - C_5 and C_7 - C_9), pyruvic acid, fatty acids and α -dicarbonyls (Gly and MeGly) were detected. The molecular distributions of diacids were characterized by the predominance of oxalic (C_2) acid followed by malonic (C_3) and succinic (C_4) acid (Fig. 5.3a), which is a common occurrence as reported in the previous studies of marine aerosols from the different locations from the Pacific Ocean (Bikkina et al., 2014; Hoque et al., 2015). In average, the atmospheric abundances of C_2 , C_3 and C_4 diacids showed 3 to 4 times higher values in the North Pacific than in the South Pacific aerosols samples (Table 5.2). Specifically, the samples, which are collected from the western North Pacific, showed 5 to 10 time higher values of C_2 than those of the central North Pacific and the South Pacific (Fig. 5.3a, b and c). It is of interest to note that glyoxylic (ωC_2) acid and methylglyoxal (MeGly) are relatively abundant in the same aerosols samples in which C_2 is dominant (Fig. 5.3c, d). Interestingly, these samples (QFF 605, 606) having higher concentration of ωC_2 and MeGly are influenced by the up-coming polluted continental air masses from the north China and Siberia where coal and bio-fuels burning are very intensive (see Fig.5.7). It is of note worthy to mention that in the same samples, where I found a strong correlation between C_2 and ωC_2 ($r=0.89$) and C_2 and MeGly ($r=0.96$) but their correlations are significantly weak for the rest of the samples. Hence, I conclude that both of the ωC_2 and MeGly are derived from the photochemical oxidation of aromatic hydrocarbons in polluted-continental air masses and then serve as a precursor of C_2 during long-range atmospheric transport.

However, the molecular distributions of diacids in one sample (QFF 606), which was collected in the coastal western North Pacific near the Japanese Islands, showed a predominance of C_2 followed by C_4 and C_3 (Fig. 5.3d). Such a typical molecular distribution

is different from those of other samples that exhibited $C_3 > C_4$ (Fig. 5.3a, b, c and d). This might be happened due to photochemical degradation of C_3 in aqueous phase of aerosols in the presence of Fe and the decomposition of C_3 may be speed up under foggy atmospheric condition together with strong solar irradiation (Kawamura et al., 2012; Pavulari and Kawamura, 2012). Similar molecular distribution pattern of $C_4 > C_3$ has been well reported in the continental aerosols collected during the 1997 Indonesian forest fires (Narukawa et al., 1999) and for marine aerosols collected during a round the world cruise (Fu et al., 2013) where influence of biomass burning was significant as reported.

Among ω -oxoacids, glyoxylic (ωC_2) acid was the dominant, which is almost 6 times more abundant in the North Pacific than in the aerosols samples, which were collected from the South Pacific (Table 5.2). This result indicates that in the North Pacific atmosphere anthropogenic emission is more significant as compare to that of the South, because glyoxylic acid is produced from the atmospheric oxidation of glyoxal during long-range transport and the sources of glyoxal are associated with the oxidation of aromatic hydrocarbons (Smith et al., 1999; Kleindienst et al., 2004). Methylglyoxal was the foremost α -dicarbonyls species, comprising 88% and 77% of the total α -dicarbonyls from the North and South Pacific, respectively. Such finding may indicate that hydrocarbon emissions from the anthropogenic activities are the precursor of methylglyoxal in the trans-hemispheric regions of the Pacific Ocean (Kleindienst et al., 2004). However, atmospheric abundance of total fatty acids was ~ 2 times higher in the South Pacific than in the North Pacific (Table 5.2). In fact, Azelaic acid (C_9) which is evolved through photochemical oxidation of biogenic unsaturated fatty acids emitted from the surface ocean (Kawamura et al., 1996; Kawamura and Sakaguchi, 1999), also showed increased level in the same aerosol sample collected from the South Pacific where unsaturated fatty acids were maximized (Fig. 5.3a).

5.3.3. Spatial distributions of diacids and related compounds and contributions (%) of diacids carbon to aerosol organic carbon (OC) over the North and South Pacific

During the observation, concentrations of the total diacids, ω -oxoacids, pyruvic acid, α -dicarbonyls and fatty acids were ranged from 17-207 ng m⁻³ (av. 54.4 ng m⁻³, median 25.2 ng m⁻³), 0.6-28 ng m⁻³ (av. 4.0 ng m⁻³, median 1.3 ng m⁻³), 0.04-10 ng m⁻³ (av. 1.0 ng m⁻³, median 0.2 ng m⁻³), 0.1-15 ng m⁻³ (av. 3.7, median 1.2 ng m⁻³), and 0.1-3 ng m⁻³ (av. 0.8 ng m⁻³, median 0.6 ng m⁻³), respectively. Atmospheric abundances of diacids showed 2 times higher in the North Pacific than those of the South Pacific (Table 5.2). In comparison, concentration of total low molecular fatty acids showed ~2 times higher values in the South Pacific than the North (see Table 5.2), suggesting more algal activities in the South Pacific during the cruise (Mochida et al., 2002). Fig. 5.2b shows the spatial variability of total diacids over the North and South Pacific during the study period. As expected, diacids concentrations observed over the pelagic oceans exhibited several times lower values than those measured in the adjacent coastal areas such as western North Pacific, where total diacids concentrations showed 10 times higher values than those are measured far from the continents/landmass for example the central North Pacific, supporting the idea of that the land have significant impacts on the atmospheric abundances of diacids over the remote oceanic regions.

During the cruise, the highest diacids concentrations were measured over the North Pacific (Table 5.2), especially in those samples, which were collected in the western North Pacific (Fig. 5.2b). It is of interest to note that, ω -oxoacids, pyruvic acids and α -dicarbonyls are relatively abundant in the marine aerosols in which diacids are dominant. Higher level of diacids and related compounds over the western North Pacific were observed because of East Asian polluted air masses containing precursors of diacids (i.e. VOCs, soot, mineral dusts, O₃) are transported long distances to the western North Pacific due to backward air

masses trajectory (see Fig. 5.7). When the ship moved downward from mid to low latitudinal regions, the concentrations of diacids decreased significantly (Fig. 5.2b). The seven-day calculated backward air mass trajectory analyses also indicate that there are no continental influences during sampling in the low latitudinal regions of the sub-tropical Pacific (Fig. 5.7). However, the spatial distributions of diacids over the South Pacific Ocean were noticeably uniform, except for one sample, which was collected near the Suva port, where oxalic acid showed almost 2 times higher values than rest of the samples collected from the south Pacific and is influenced by the continental air masses due to backward air mass trajectory. Spatial distributions of the total diacids over the North Pacific showed 2 times higher than those of the South Pacific (Fig. 5.2b). Lower diacids concentration in the South Pacific as compare to the North Pacific, might be observed due to significant anthropogenic activities in the Northern Hemisphere than in the Southern Hemisphere (Jaward et al., 2004).

In this study, the measured total low molecular weight diacids and related polar organic compounds are accounted for 1.6 to 14% (av. 5.2%, median 5.2%) of OC, where diacids were the major contributor, accounting 1.4 to 11% (av. 4.2%, median 4.0%) (Table 5.1) followed by α -dicarbonyls 0.03 to 2.1% (av. 0.4%, median 0.3%), ω -oxoacids 0.1 to 0.9 (av. 0.4%, median 0.3%) and pyruvic acids 0.01 to 0.3% (av.0.05%, median 0.03%) of OC. Diacid-C/OC ratios are consistent with previous studies those were conducted in the western North Pacific (5.7 to 11.2%), the North pacific (3.6-16.8%), and in the South China Sea (av.18.7%) (Fu et al., 2013), but are several times higher than those reported in urban/continental aerosols from China (av. 1.3%) (Ho et al., 2007) and Mongolia (av. 0.9%) (Jung et al., 2010). The calculated higher diacid-C/OC ratios in the marine atmosphere than those of the source regions (i.e. China and Mongolia) indicate that photochemical aging of continent-derived organic aerosols during long range atmospheric transport (Fu et al., 2013).

Fig. 5.4 shows the spatial distributions of relative abundances of diacid-C in aerosol organic carbon (OC). In general, diacid-C/OC ratios showed 15% higher values in the North Pacific than those of the South Pacific. Spatial distributions of diacid-C/OC ratios over the North Pacific show higher values in the western North Pacific, where the influence of polluted continental air masses are important than the central North Pacific (Fig. 5.4 and 5.7). Some studies have identified that atmospheric transport of O₃ and its precursors such as NO_x and VOCs from East Asia to the western North Pacific have been increased significantly (Hoell et al., 1996; Naja and Akimoto, 2004). Tropospheric O₃ plays a crucial role in controlling the oxidizing capacity of the atmosphere. Hence, I suspect that diacid-C/OC ratios may be intensified over the western North Pacific under highly oxidizing atmospheric condition. Amongst the North Pacific, the highest diacids-C/OC ratio (10.6%) was observed in the western North Pacific around 29°N (Fig. 5.4), where the concentration of oxalic (C₂) acid was measured as higher level and its contribution to aerosol organic carbon maximized (6.6%) during the expedition. In fact, 7-days backward air masses trajectory model also revealed that the same sample (29°N) is highly impacted by the continental air mass from Mongolia (Fig. 5.7). As shown in Fig. 5.4, highest diacid-C/OC ratio over the South Pacific was observed around 25° 46'S, which is influenced by the forwarded continental air masses from Tasmania (see Fig.5.7), again supporting the idea of photochemical aging of continental aerosols during long-range transport.

5.3.4. Photochemical production of short chain (C₂-C₃) diacids over remote Pacific Oceans

Oxalic (C₂) acid was the dominant diacid species in the marine aerosols studied. But the atmospheric abundances of C₂ were fluctuated in the marine atmosphere of the North and South Pacific (Fig. 5.3), which might be occurred due to the variability of ambient air temperature, photochemistry and the availability of precursor polar compounds. As for

example, the dominant presence of succinic (C_4) acid as reported in the Antartic aerosols (Kawamura et al., 1996), in the spring snowpack samples (Narukawa et al., 2002), in winter samples from Tokyo (Sempéré and Kawamura, 1994), and in Los Angeles aerosols samples (Kawamura et al., 2001). Thus, higher relative abundance of C_4 is a common trend in the cold environmental condition (Sempéré and Kawamura, 2003). But in the marine aerosols, the abundance of succinic acid is often depleted to oxalic and malonic acids due to photochemistry (Kawamura and Sakaguchi, 1999; Hoque et al., 2015). Fig. 5.5a shows the spatial distribution of C_2/C_4 ratios during the cruise. The C_2/C_4 ratios are high in the equatorial regions of the North and South Pacific than those of the higher latitudes. These results indicate that photochemical degradation of C_4 to C_2 has maximized in the warmer zones of the north and South Pacific. Moreover, a negative correlation between relative abundance of C_4 diacid and ambient air temperature has been reported in Sempéré and Kawamura (2003). In contrast, our data set showed a weak correlation between C_2 and C_4 diacid ($r^2=0.29$). This result indicates that photochemical degradation of C_4 is not the main source of C_2 in this study. Bikkina et al. [2014] proposed that glyoxylic (ωC_2) acid, glyoxal (Gly), methylglyoxal (MeGly) and pyruvic (Pyr) acid, which are the oxidation products from both of marine and continent, derived volatile organic compounds (VOCs). These VOCs further oxidized to produce oxalic acid. However, in this study, sum of VOCs oxidation products ($\omega C_2 + \text{Gly} + \text{MeGly} + \text{Pyr}$) showed strong correlation with C_2 ($r^2=0.84$). This finding suggests that photochemical oxidation of VOCs are the major source of oxalic acid in the present study rather than the degradation of succinic acid.

In the ambient atmosphere, succinic (C_4) acid can be degraded to malonic (C_3) acid due to abstraction of its hydrogen by hydroxyl radicals through subsequent decarboxylation and thus C_3/C_4 ratios can be used as an indicator of enhanced photochemical production of diacids (Kawamura and Ikushima, 1993). The C_3/C_4 ratios in the current study varied from

0.8 to 7.6 (av. 3.0, median 2.0). These values are comparable to those (av. 4.0) reported for the Pacific ocean aerosols (Kawamura and Sakaguchi, 1999), marine aerosols collected during a round the world cruise (0.9-5.8, av. 2.3) (Fu et al., 2013), and Chichijima Island in the western Pacific (av. 2.1) (Mochida et al., 2003) but are several times higher than urban aerosols from Tokyo (av. 1.6) (Kawamura and Ikushima, 1993), Chinese cities (0.74) (Ho et al., 2007), Chennai aerosols (av. 1.4) (Pavuluri et al., 2010) and New Delhi (av. 0.6) (Miyazaki et al., 2009). Higher C_3/C_4 ratios in the marine aerosols than in the urban aerosols suggest that malonic (C_3) acid is photochemically produced from succinic (C_4) acid during long-range atmospheric transport from the continents to the remote marine atmosphere or in their source region (Fu et al., 2013). As shown in Fig. 5.5b, spatial distributions of C_3/C_4 ratios show similar distributions pattern those of C_2/C_4 ratios with high values in the low latitudes of the North and South Pacific. This result suggest that an enhanced photochemical production of C_3 from its precursor (C_4) in the warmer regions. Similar occurrences have been reported in the marine aerosols collected from Gosan site of Jeju Island in the western North Pacific, where C_3/C_4 ratios enhanced in summer than those of other seasons (Kundu et al., 2010). During the present expedition, succinic (C_4) acid strongly correlated with malonic acid (C_3) ($r^2=0.89$), indicating photochemical degradation of C_4 might be the source of C_3 .

5.3.5. Anthropogenic vs biogenic emissions

Adipic (C_6) acid is a potential tracer of continental aerosol (Kawamura and Usukura, 1993), which has been identified in laboratory studies as secondary organic aerosol products of the reaction of O_3 with cyclohexene (Hatakeyama et al., 1985; Legrand et al., 2007). Phthalic (Ph) acid is also an important tracer of continental aerosol, which is potentially derived by the atmospheric oxidation of polynuclear aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993). High abundance of phthalic acid has been reported in continental aerosols samples from Los Angeles (Kawamura et al., 1985; Simoneit

and Mazurek et al., 1989) and Tokyo (Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994). During the study, phthalic acid well correlated with adipic acid ($r^2=0.67$), suggesting they are emitting from similar source of fossil fuel combustion. In contrast, azelaic (C₉) acid has been well documented as a secondary photooxidation product of biogenic unsaturated fatty acids with a double bond at the C₉ position like cis-9-octadecenoic (oleic) acid (Kawamura and Gagosian, 1987; Matsunaga et al., 1999). The Ph/C₉ and C₆/C₉ ratios are frequently used to find out their source strength from anthropogenic and biogenic emissions (Fu et al., 2013; Hoque et al., 2015). The higher ratios indicate more emissions from anthropogenic sources. Fig. 5.6a and 5.6b show the spatial distributions of C₆/C₉ and Ph/C₉ ratios, respectively. During the North Pacific cruise, higher C₆/C₉ and Ph/C₉ ratios were observed in the western North Pacific (24°N-34°N) than the central North Pacific, because of trans-Pacific transport of atmospheric pollutants from the East Asia due to backward air mass trajectory (Fig. 5.7). C₆/C₉ and Ph/C₉ ratios peaked around (24°N), which was expected due to fact that the polluted air masses came from North China (see Fig. 5.7), where coal and other fossil fuels combustion are significant (Liu et al., 2007). Over the South Pacific Ocean, C₆/C₉ and Ph/C₉ ratios also showed higher values in those samples, which are influenced by the forthcoming continental air masses from Papua new Guniea, Tasmania and New Zealand (see Fig. 5.6a, b and 5.7). These findings indicate that anthropogenic emissions are significant than the biogenic emissions over the western North Pacific and in the coastal countries of the Southern Hemisphere.

5.3.6. Comparison of distributions of diacids in the Pacific Ocean with previous studies

To better understand the sources, abundances, formation, and atmospheric processing of diacids in the Pacific Ocean, recent findings are compared with previous observations, which are reported for the different oceanic locations of the Pacific. Fig. 5.8 shows geographical distributions of diacids in the marine aerosols collected from the different

locations of the Pacific Ocean. During the present study, in the coastal western North Pacific, abundances of diacids showed 4 times higher values than the lower latitudes and 2 times higher values than those of higher latitudes of the western North Pacific as shown in yellow and white bar. Similar distributions pattern also have been proposed by previous studies for example Kawamura and Sakaguchi (1999) as shown in red bar and Sempéré and Kawamura (2003), which is represented by blue bar, where diacids concentrations were maximized near the coastal regions with more influences from the Asian continents (Fig. 5.8). These results further suggest that high abundances of diacids near the coasts are influenced by the continental anthropogenic input. However, over the high latitudinal regions of the western North Pacific (yellow bar) and upwelling zones of the central Pacific (green bar), diacids concentrations have been intensified by 5-10 times than the previous studies of pelagic ocean covering north and south central Pacific (red bar). These increments in diacids concentrations are due to high biological activity during the cruises as discussed earlier. Although, abundances of diacids have been increased in remote oceanic regions associated with oxidation of unsaturated fatty acids and photochemical processing of marine derived VOCs but they are still significantly lower than corresponding coastal areas where anthropogenic contributions are important. These findings further supporting the idea that diacids and its precursors are abundantly produced in the continent and are transported to the coastal areas.

5.4. Conclusions

Spatial distributions of water-soluble dicarboxylic acids and other related polar compounds (ω -oxoacids, pyruvic acid, α -dicarbonyls and fatty acids) in the atmospheric aerosols over the North and South Pacific were reported in this study. High abundances of diacids and related compounds were observed over the western North Pacific rim. The western North Pacific is most likely influenced by the out flow from East Asia, which leads

to high abundances of these water soluble-organics in this oceanic region. Molecular distributions of dicarboxylic acids in the marine aerosols collected during the cruise showed predominance of oxalic (C_2) followed by malonic (C_3) and succinic (C_4) acid. However, one sample (QFF 606) collected in the coastal western North Pacific showed the abundance of C_4 over C_3 diacid where continental influence was significant from the Mongolian region due to air mass backward trajectory. C_6/C_9 and Ph/ C_9 diagnostic ratios maximized in the aerosol samples collected over the coastal regions of the western North Pacific and in the South Pacific, which are influenced by the continental air masses from Papua new Guinea, Tasmania and New Zealand, suggesting considerable anthropogenic emissions than its biogenic counterpart over the coastal western North Pacific and in the coastal countries of the Southern Hemisphere. Diacids accounted for 1.6 to 14% of OC with higher values in the western North Pacific, where concentration of oxalic (C_2) was measured as higher level during the study. This result together with 7-day calculated backward air mass trajectory indicates that photochemical aging of continental aerosols have been exploited during long-range atmospheric transport to the out flow regions of the Asian dusts.

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Table 5.1. Aerosol mass, concentrations of various carbonaceous and nitrogenous components, their concentration ratios and contribution of diacid-C to OC in the North and South Pacific aerosol samples.

Components	Minimum	Maximum	Average	Median
Aerosol mass ($\mu\text{g m}^{-3}$)	36	95	64	63
TC ($\mu\text{g m}^{-3}$)	0.2	1.9	0.6	0.4
OC ($\mu\text{g m}^{-3}$)	0.1	1.4	0.5	0.3
WSTN ($\mu\text{g m}^{-3}$)	0.01	0.8	0.2	0.1
TC/Aerosol mass (%)	0.2	4.5	1.1	0.8
TN/Aerosol mass (%)	0.02	1.0	0.3	0.1
Diacids-C/OC (%)	1.4	11	4.2	4.0

Table 5.2. Concentrations (ng m⁻³) of dicarboxylic acids, ω-oxoacids, pyruvic acid, α-dicarbonyls and fatty acids in the marine aerosol from the North (n=11) and South (n=6) Pacific.

North Pacific (n=11)					South Pacific (n=6)			
Compounds	Range	Average	Median	RA ^b (%)	Range	Average	Median	RA ^b (%)
Oxalic acid, C ₂	12-163	44.4	32.8	65.5	11-41	19.3	15.6	64.5
Malonic acid, C ₃	2.3-34.4	9.1	4.5	13.4	3.2-7.3	4.6	4.1	15.4
Succinic acid, C ₄	0.4-26.2	6.2	3.7	9.1	0.7-3.8	1.9	1.5	6.4
Glutaric acid, C ₅	BDL ^a -7.1	1.5	0.6	2.2	0.1-0.6	0.2	0.1	0.7
Adipic acid, C ₆	0.1-4.3	0.8	0.4	1.2	0.2-0.5	0.3	0.3	1
Pimelic acid, C ₇	BDL ^a -1.2	0.3	0.2	0.4	0.1-0.3	0.1	0.1	0.3
Suberic acid, C ₈	BDL ^a -0.7	0.2	0.2	0.3	0.1-0.6	0.2	0.1	0.7
Azelaic acid, C ₉	BDL ^a -1.6	0.4	0.3	0.6	0.2-2.6	0.7	0.4	2.3
Sebacic acid, C ₁₀	BDL ^a -0.2	0.1	0	0.01	BDL ^a -0.1	0.1	0.1	0.3
Undecanoic acid, C ₁₁	BDL ^a -0.2	0.1	0.1	0.01	BDL ^a -0.3	0.2	0.2	0.7
Phthalic acid, Ph	0.2-10	2	1.1	3	0.3-1.0	0.8	0.9	2.7
Glyoxylic acid, ωC ₂	0.3-20.3	3.5	0.9	66	0.4-1.0	0.6	0.5	40
Glyoxal, Gly	BDL ^a -3.4	0.7	0.3	13.8	0.1-0.5	0.2	0.1	22.2
Methylglyoxal, MeGly	0.1-13.7	4.5	1.1	88.2	0.1-2.0	0.7	0.3	77.8
Total diacids	17-207	68	50	-	18-62	30	25	-
Total ω-oxoacids	0.6-28	5.3	2.2	-	1.2-2.2	1.5	1.3	-
Total α-dicarbonyls	0.1-15	5	1.4	-	0.2-2.1	0.9	0.5	-
Total fatty acids	0.1-2.1	0.7	0.6	-	0.3-3.0	1	0.7	-

^aBDL, below detection limit (0.005 ng m⁻³)

^bRA, average relative abundance

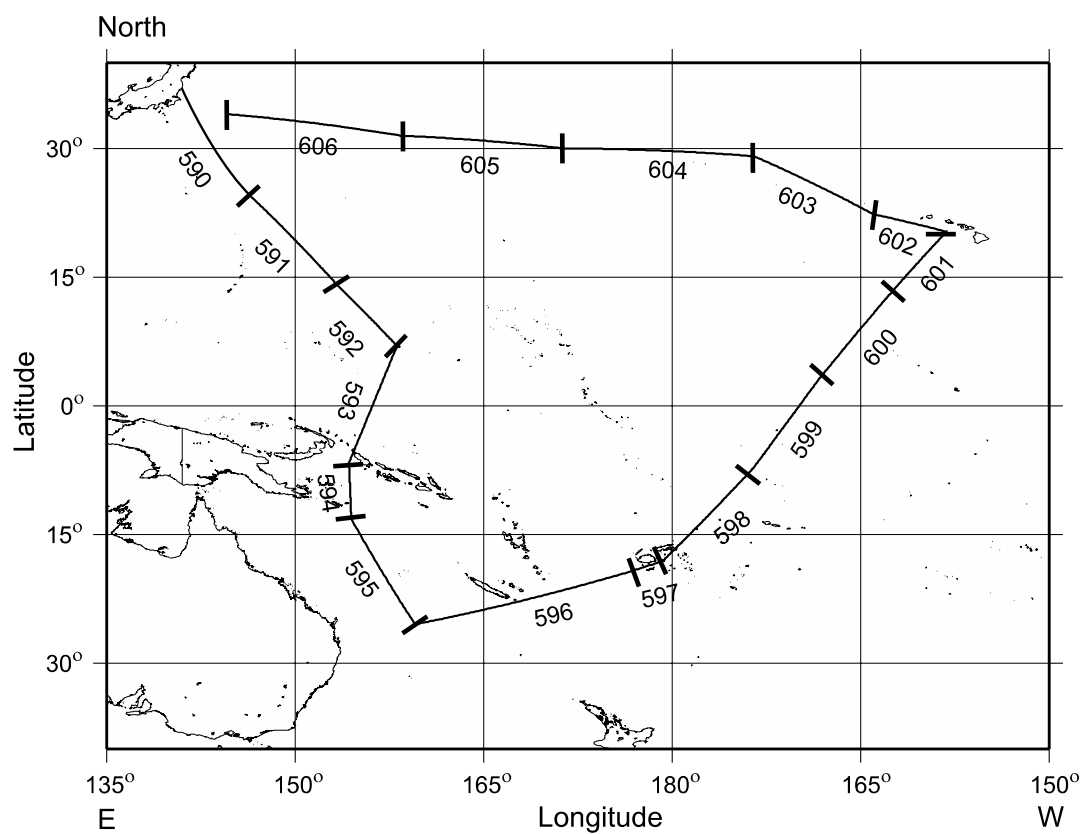


Fig. 5.1. Cruise track of T/V *Bousei Maru* 1994. The numbers and the thick black marks are shown in the map represent sample identification numbers and sample location, respectively.

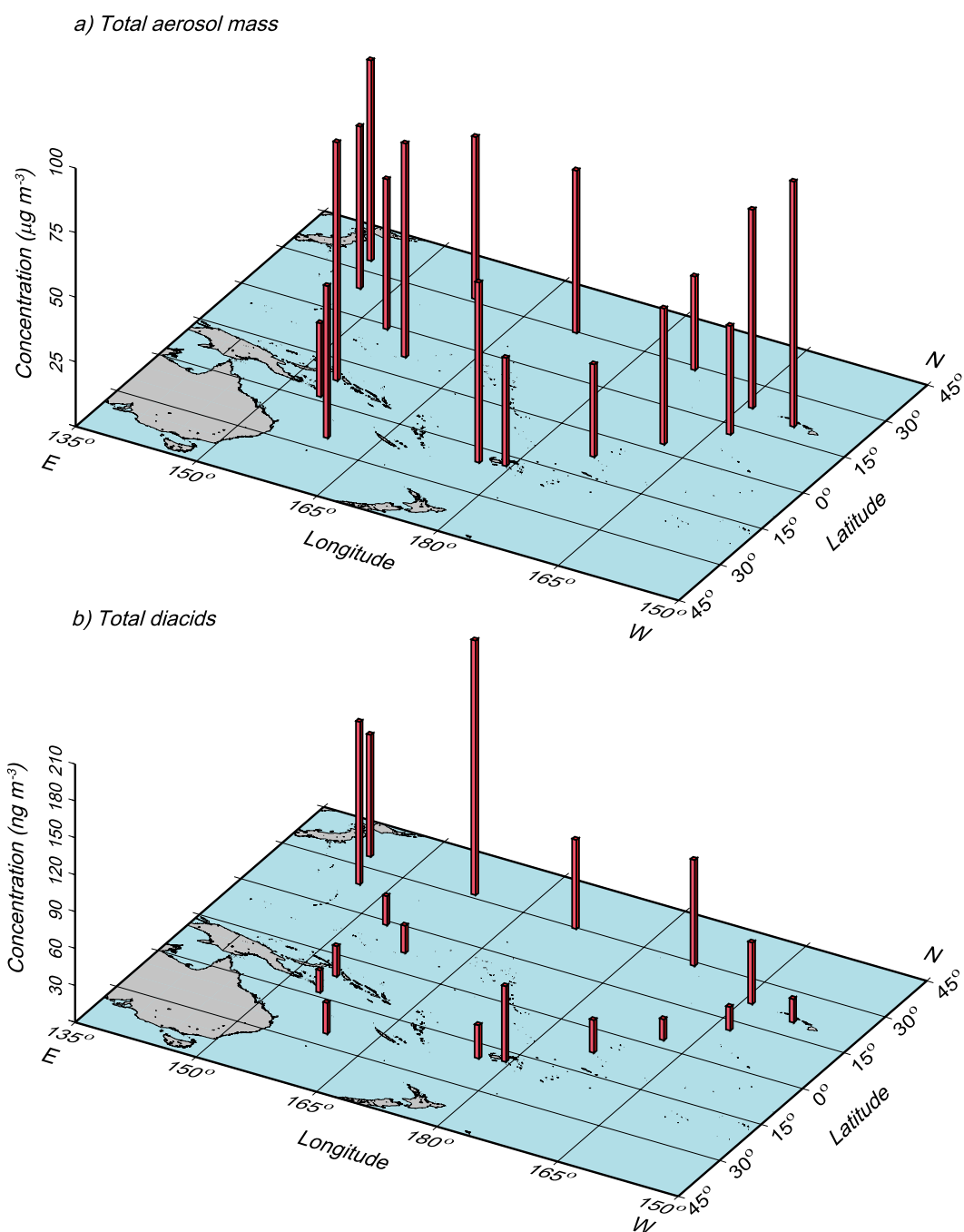


Fig. 5.2. Spatial distributions of (a) total aerosol mass and (b) total diacids in the marine aerosols collected during the North and the South Pacific cruise.

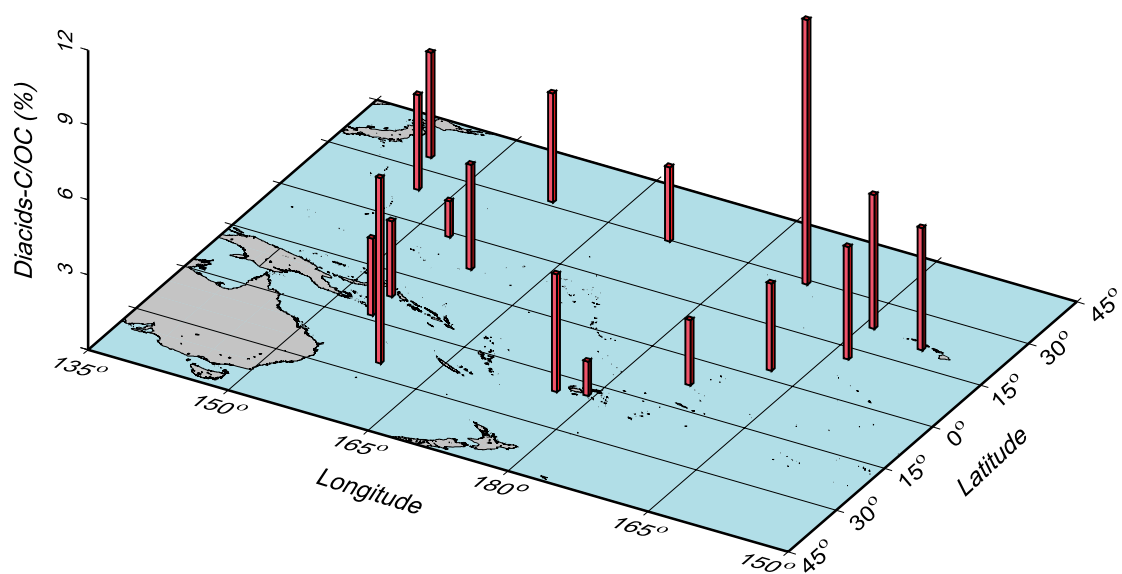


Fig. 5.4. Spatial distributions of contributions of total diacids in organic carbon for the marine aerosols collected during the North and the South Pacific cruise.

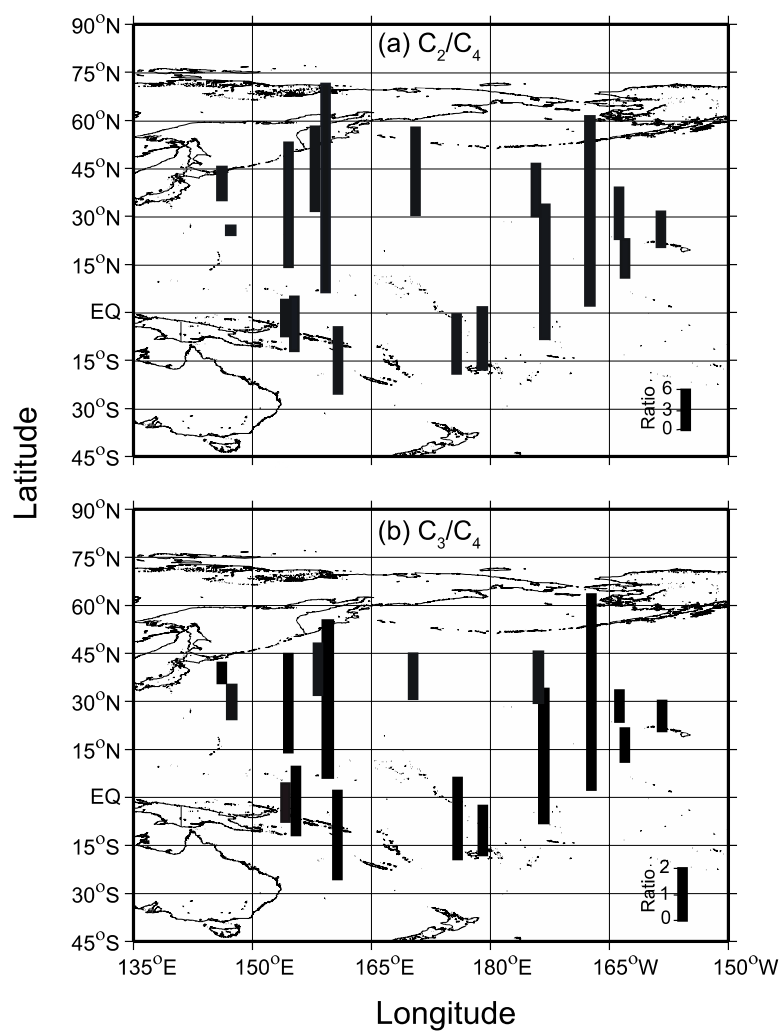


Fig. 5.5. Geographical distributions of the concentration ratios of (a) oxalic/succinic (C_2/C_4), (b) malonic/succinic (C_3/C_4) measured in the North and South Pacific aerosols collected during *Bousei Maru* cruise.

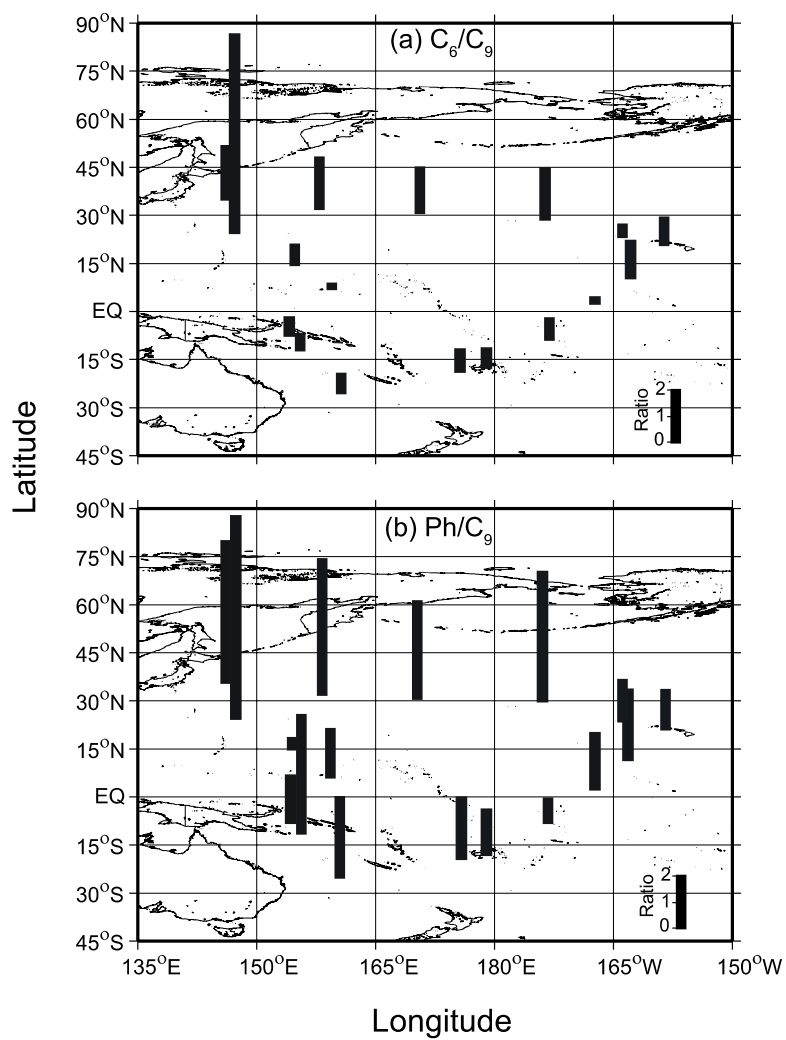


Fig. 5.6. Geographical distributions of the concentration ratios of (a) adipic/azelaic (C_6/C_9), (b) phthalic/azelaic (Ph/C_9) measured in the North and South Pacific aerosols collected during *Bousei Maru* cruise.

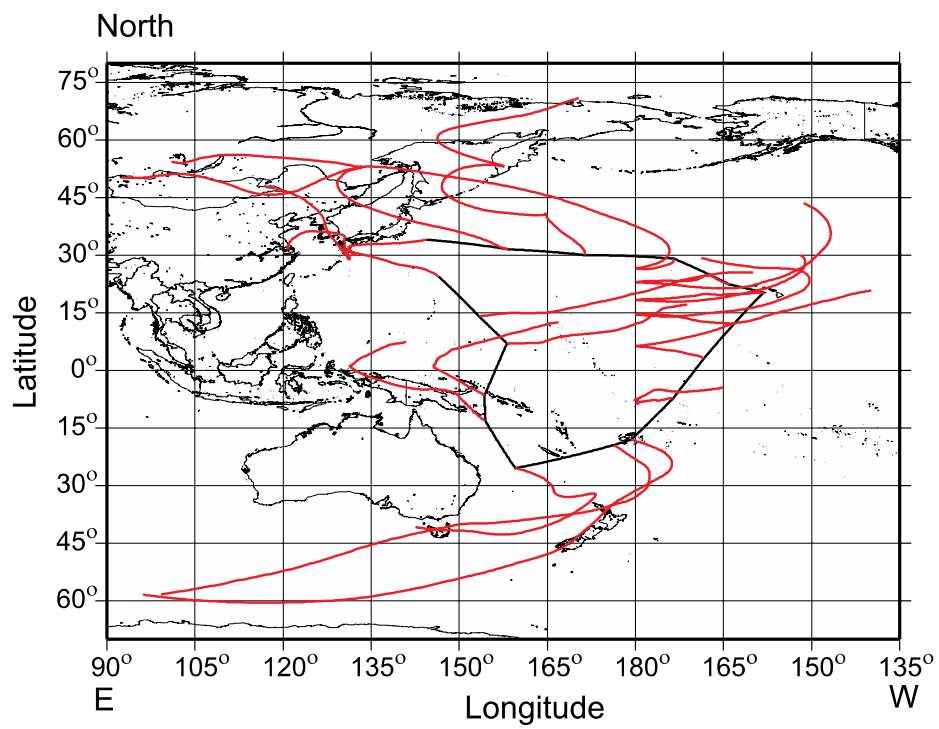


Fig. 5.7. Seven day backward air masses trajectories at 500m above the ground were drawn with NOAA HYSPLIT model. The black line indicate cruise track. For details of the cruise track see Fig. 5.1.

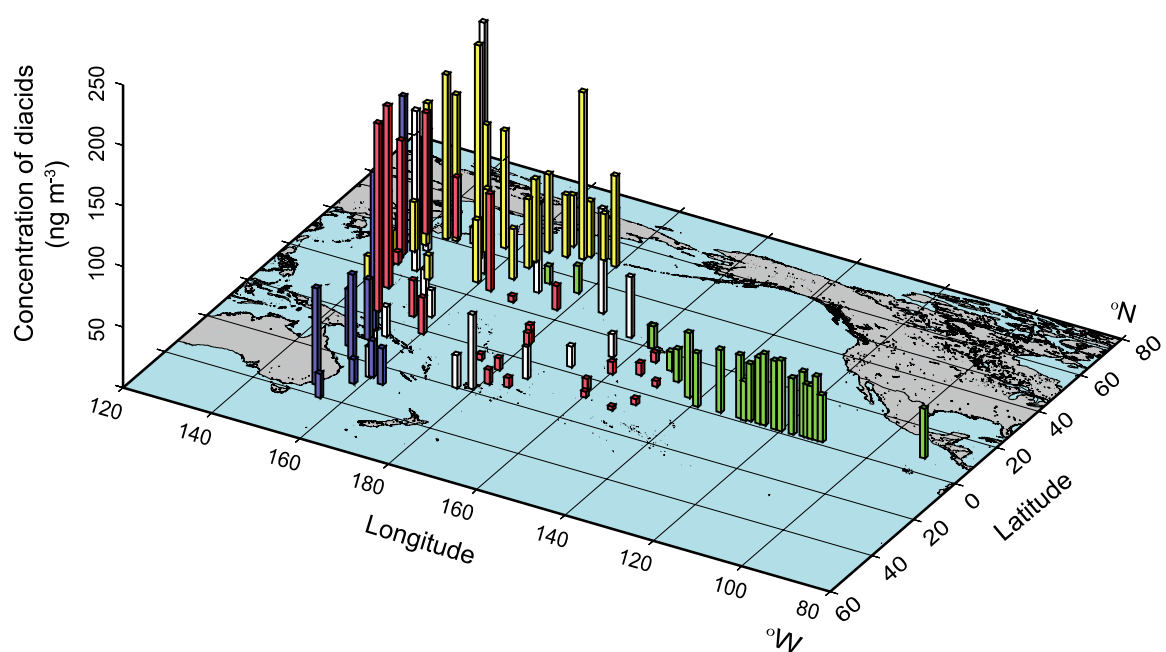


Fig. 5.8. Average concentrations of diacids in the marine aerosols collected from different locations of the Pacific Ocean. Diacids data compiled from Kawamura and Sakaguchi, 1999 (red bar), Sempéré and Kawamura, 2003 (blue bar), yellow, white and green bars represent present study.

Chapter 6: Summary and conclusions

Diacids, ω -oxoacids, pyruvic acid, α -dicarbonyls and fatty acids together with organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), total carbon (TC), water-soluble total nitrogen (WSTN) have been studied in remote marine aerosol samples collected from the western North Pacific (13°14'N-53°37'N and 140°46'E-179°54'W), the central Pacific (1°59'N-35°N and 171°54'E-90°58'W) and the North-South Pacific (3°05'N-34°02'N and 6°59'S-25°46'S). Molecular distributions of water-soluble dicarboxylic acids generally showed a predominance of oxalic (C_2) acid, followed by malonic (C_3) and succinic (C_4) acids. In contrast, one third of the high latitudinal western North Pacific samples showed a predominance of C_3 and C_4 diacids, where phytoplankton activities were higher during the cruise. These results indicated that molecular distributions of diacids over remote and biologically more productive oceanic regions are controlled by oceanic primary production and availability of unsaturated fatty acids followed by atmospheric oxidation.

During the western North Pacific cruise, spatial distributions of diacids and related compounds showed 4 times higher levels in mid latitudes followed by high and low latitudes of the western North Pacific, suggesting that diacids and their precursors are of continental origin and transported long distances over the remote western North Pacific. Short chain (C_2 - C_4) diacids account for 0.7-17% of total aerosol carbon (0.1 - $2.7 \mu\text{g m}^{-3}$) with higher values in high latitudinal western North Pacific, where *Chlorophyll-a* showed higher concentrations (0.2 - 10 mg m^{-3}) during the sampling period. These results demonstrate that short chain diacids are largely produced in higher latitudes of the western North Pacific by the photochemical oxidation of unsaturated fatty acids and isoprene produced by marine phytoplankton.

However, during central Pacific cruise, abundances of oxalic and azelaic acid showed 2 to 3 times higher values over the upwelling central Pacific than those of the non-upwelling regions, indicating that their origin associated with photooxidation of biogenic unsaturated fatty acids and isoprene. Spatial distributions of diacids and related compounds as well as fatty acids also showed 2 times higher levels in the upwelling zone of the central Pacific than the non-upwelling zone, suggesting that diacids and related compounds are significantly produced in this region of the central Pacific through photochemical oxidation of unsaturated fatty acids, isoprene and other BVOCs produced by marine phytoplankton. Diacids accounted for 8% (average) of WSOC, indicating that they are the major components of water-soluble organic aerosols. The WSOC/OC ratios were enhanced in the upwelling eastern tropical Pacific. These results together with seven-day backward air masses trajectories and satellite image of *Chlorophyll-a* support that photochemical conversions of marine derived BVOCs emitted from the high biological ocean associated with upwelling are more significant in the warmer eastern equatorial Pacific than western North Pacific.

Moreover, during the North-South Pacific cruise, abundances of diacids and related compounds were observed at higher level over the western North Pacific rim. The western North Pacific is most likely influenced by the out flow from east Asia, which leads to high abundances of these water soluble-organics in this oceanic region. During this cruise, diacids accounted for 1.6 to 14% of OC with higher values in the western North Pacific, where concentration of oxalic (C_2) was measured as higher level during the study. This result together with 7-day calculated backward air mass trajectory indicates that photochemical aging of continental aerosols have been exploited during long-range atmospheric transport to the out flow regions of the Asian dusts.

During the present study, abundances of diacids showed 2-4 times higher values in the coastal zones of the Pacific ocean than those of the pelagic ocean, which confirmed that

their abundances over the coastal areas are influenced by continental outflow but in remote oceanic regions diacids formations are associated with sea-to-air emission of unsaturated fatty acids and biogenic volatile organic compounds (BVOCs) followed by photochemical processing. I found that abundances of diacids in the pelagic ocean have been intensified by 5-10 times higher values than those of the previous studies of the Pacific Ocean but these increments in diacids concentration are very specific to oceanic locations and seasons of the year. However, this study suggests that for obtaining real scenario of oceanic primary production based diacids formation over the Pacific Ocean, long-term observations as well as global model based studies are recommended.