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Title	Trans-hemispheric contribution of C2-C10 α , ω -dicarboxylic acids, and related polar compounds to water-soluble organic carbon in the western Pacific aerosols in relation to photochemical oxidation reactions
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Description	'An edited version of this paper was published by AGU.' Copyright 2003, American Geophysical Union, Global Biogeochemical Cycles,17
Citation	Global Biogeochemical Cycles, 17(2), 1069 https://doi.org/10.1029/2002GB001980
Issue Date	2003-06
Doc URL	https://hdl.handle.net/2115/1465
Type	journal article
File Information	GBC17-2L.pdf



Trans-hemispheric contribution of C₂-C₁₀ α , ω -dicarboxylic acids and related polar compounds to water soluble organic carbon in the Western Pacific aerosols in relation to photochemical oxidation reactions

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AGU Index terms : 0305; 0312; 0317; 0320; 0330.

Key words : Aerosols; Atmospheric Chemistry; Water soluble organic compounds; Diacids; Western Pacific

Submitted to Global Biogeochemical Cycles

2002/08/23

Abstract. Marine aerosol samples were collected during a western Pacific cruise covering the latitude range between 35° N and 40° S (140-180° E). They were analyzed for total carbon (TC), total nitrogen (TN), water soluble organic carbon (WSOC) as well as the molecular distributions of C₂-C₁₀ α , ω -dicarboxylic acids and related polar compounds, mainly, ω -oxocarboxylic acids (C₂-C₉) and α -dicarbonyls (C₂-C₃). Oxalic acid (C₂) was the most abundant followed by malonic (C₃) and succinic (C₄) acids. Total diacid concentration range was 7-605 ng m⁻³ (av. 85 ng m⁻³) and the diacid-carbon accounted for 2-15 % (av. 8 %) of WSOC which comprized 29-55 % (av. 40 %) of TC. Dry depositions of total diacids over the Northern and Southern Pacific Ocean were estimated to be 256-1907 $\mu\text{g m}^{-2} \text{yr}^{-1}$ (av. 735; n = 4) and 22-396 $\mu\text{g m}^{-2} \text{yr}^{-1}$ (av. 134; n = 14), respectively whereas the air-to-sea flux of TC in the Northern and Southern Hemispheres were calculated to be 1.88-16.3 $\text{mg m}^{-2} \text{yr}^{-1}$ (av. 6.06) and 0.60-2.84 $\text{mg m}^{-2} \text{yr}^{-1}$ (av. 1.53). We observed that the concentration ratios of diacid-C/WSOC, azelaic acid (C₉) / ω -oxononanoic acid, maleic acid (iC₄ cis)/fumaric (iC₄ trans) acid and succinic acid (C₄) / total diacids are correlated with the air temperature. These findings showed that the intensity of photochemical oxidation reactions and thus the variations of the sunlight intensity characterized here by the air temperature, significantly control the molecular distribution of water soluble organic compounds during long range transport of anthropogenic and/or biogenic higher molecular weight organic compounds.

1. INTRODUCTION

Remote area aerosol studies have been focused on the non-seasalt sulphates [Charlson et al., 1987; 1992; Ayers and Gras, 1991; Hegg et al., 1991a, b] and mineral dust distribution [Uematsu et al., 1985; Prospero and Savoie, 1989; Li et al., 1996] as well as on their contribution to the earth's radiative balance [Houghton et al., 1995; Tegen et al., 1996; Andreae and Crutzen, 1997]. On the other hand, although biomass burning and their impact on the climate have been partly studied [Andreae, 1996] most of the organic aerosol studies in remote area were related to a long range transport of lipids [Gagosian et al., 1987; Pelzer and Gagosian, 1989; Sicre et al., 1990] as well as to the associated photochemical oxidation reactions [Kawamura and Gagosian, 1987; Stephanou, 1992; Kawamura and Usukura, 1993; Kawamura et al., 1996]. Water soluble organics such as diacids in the aerosols probably play a non negligible role on the light scattering balance as well, since they participate the formation of clouds and fogs [Saxena et al., 1995; Saxena and Hildemann, 1996] and may act as cloud condensation nuclei [Novakov and Penner, 1993; Saxena and Hildemann, 1996; Novakov and Corrigan, 1996, Kerminen et al., 1999]. However, very little is known about the distribution of water soluble organic compounds in remote marine atmosphere covering the Northern and Southern Hemispheres.

Among water soluble organic compounds, low molecular weight (LMW) α , ω -dicarboxylic acids and related compounds i.e. ω -oxocarboxylic acids (C₂-C₉) and α -dicarbonyls (C₂-C₃) are likely the most abundant. These compounds are abundantly produced in polluted area from incomplete combustion of fossil fuels [Kawamura and Kaplan, 1987; Kerminen et al., 2000], meat cooking [Rogge et al., 1991; Schauer et al., 1999], biomass burning [Andreae, et al., 1991; Talbot et al., 1992; Narukawa et al., 1999] or directly from biogenic emission [Kawamura and Gagosian, 1990], whereas the ozonolysis and photooxidation of numerous organic compounds significantly produce α , ω -dicarboxylic acids and their ketoacid and dicarbonyl homologues [Shuetzle et al., 1975; Grosjean et al., 1978; Norton et al., 1983; Bandow et al., 1985; Hatakayama et al., 1987; Kawamura and Gagosian, 1987; Kawamura and Ikushima, 1993]. Consequently, these compounds have been reported at significant concentration levels even in remote marine atmosphere [Stephanou,

1992; Kawamura and Usukura, 1993; Sempéré and Kawamura, 1996; Kawamura and Sakaguchi, 1999], in semi-urban atmosphere [Khwaja, 1995], in rural atmosphere [Limbeck et al., 2001] as well as in polar atmospheric [Kawamura et al., 1992; Li and Winchester, 1993; Kawamura et al., 1995; 1996] and ice core samples [Kawamura and Yasui, 1991; Legrand and De Angelis, 1996; Kawamura et al., 2001a].

Dicarboxylic acids are polar and have low vapor pressure, and some of them should be associated with atmospheric aerosols and other condensed phases [Kawamura and Kaplan, 1987; Grosjean, 1989; Baudet et al., 1990; Clegg et al., 1996; Saxena and Hildemann, 1996; Hara et al., *in Press*]. Thus, we could expect that if they are significantly abundant due to their continuous photochemical source in the atmosphere, aerosols enriched with diacids would act as cloud condensation nuclei. In addition, oxalate and other organic anions are important in the photo-redox chemistry of iron in aerosols in cloud droplet [Zuo and Hoigné; 1992] whereas previous aerosol studies conducted in the Arctic and Antarctic atmospheres indicated that photochemical oxidation reactions significantly alter the molecular distribution of diacids in atmospheric particles [Kawamura et al., 1995; 1996; Narukawa et al., 2002]. These results suggested that far from their main anthropogenic sources the photochemical oxidation reactions control the molecular distribution of diacids, ketoacids and dicarbonyls.

To our knowledge, there are no available data on the concentration of water soluble organics over the Pacific Ocean covering the latitude range between 35° N and 40° S (140-180° E). In this paper, we report the total concentration of water soluble organic carbon (WSOC) as well as C₂-C₁₀ α, ω-dicarboxylic acids and related polar compounds, i.e., ω-oxocarboxylic acids (C₂-C₉), α-dicarbonyls (C₂-C₃), pyruvic acid and aromatic (phthalic) diacid. We also present an estimate of their standing mass over the Pacific Ocean together with their annual dry deposition rate. Molecular distribution of these organic compounds will be discussed in relation to the sources and production mechanisms of these compounds as well as their role in the remote marine atmosphere.

2. EXPERIMENTAL

Aerosol samples were collected at the upper deck of the R/V Hakuho Maru (*ca.* 14 m above the sea surface) with a pre-combusted (500 °C) Pallflex quartz fiber filter (20 x 25 cm) using a high volume air sampler (Shibata HVC 1000) during the cruise KH92-4: August - October 1992. The cruise track is shown in Figure 1. Total aerosol mass was determined by weighing the filter before and after sample collection. Filters were stored in a clean glass jar with a Teflon-lined screw cap and stored at -20°C prior to analysis. Blank filters were exposed to the air in the sample shelters for a few seconds and were recovered.

A part of the filter sample was cut off and subjected to a CHN corder (Yanagimoto, MT 3) for the determination of total carbon (TC) and total nitrogen (TN). The analytical error based on duplicate analyses was *ca.* 10 %. WSOC determination was described elsewhere [Sempéré and Kawamura, 1994]. Briefly, a part of the filter was cut in pieces and extracted with pure water. The water extracts were analyzed for dissolved organic carbon determination using a Shimadzu TOC 500. Analytical precision of the WSOC measurement was 6 % based on duplicate analysis.

Dicarboxylic acids and related compounds were analyzed by the method of Kawamura and Ikushima [1993]. Briefly, an aliquot of the filters were extracted for low molecular weight dicarboxylic acids and other water-soluble organics with pure water. The water extracts were concentrated by a rotary evaporator under a vacuum and dried in a nitrogen air stream. The dried samples were then reacted with 14 % borontrifluoride in n-butanol (0.3 ml) to derive carboxyl and aldehyde groups to the butyl esters and dibutoxyacetals, respectively. The derivatives were determined by a Hewlett Packard (HP 5890) gas chromatograph (GC) equipped with a split/splitless injector, a fused silica capillary column (HP-5 0.32 mm id. x 25 m x 0.52 µm), and an FID detector. Identification of the derivatives was performed by a comparison of GC retention times and mass spectra with those of authentic standards. Identification of the compounds was confirmed by a GC-spectrometer system (Finnigan-MAT ITS-40 and ThermoQuest Trace MS). Recovery was 70 % for oxalic acid and better than 90 % for malonic, succinic and adipic acids. Procedural blanks only showed small peaks

of oxalic, pyruvic and phthalic acid derivatives in the GC chromatograms; however they presented less than 4 % of the actual samples. Analytical errors in the determination of diacids were within 5.5 % for dicarboxylic acids, 15 % for ketoacids, 8 % for glyoxal and 26 % for methylglyoxal based on duplicate analysis. The concentrations of the acids presented here are corrected for the procedural blanks. All the analyses have been finished in 1993.

3. RESULTS AND DISCUSSION

3.1 General characteristics of the aerosols

The aerosol mass concentrations (Table 1, Fig. 2a) ranged from 11 (5 °N) to 68 $\mu\text{g m}^{-3}$ (40° S near Australia). Such values are in the same order of magnitude of that already reported for the Pacific atmosphere [Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999] or other remote sites such as tropical Indian Ocean [av. 15 $\mu\text{g m}^{-3}$; Krishnamurti et al., 1998], and Atlantic Barbados [11 to 31 $\mu\text{g m}^{-3}$; Li et al., 1996]. However, the values we report here are one order of magnitude lower than the aerosol concentrations reported for the urban area of Tokyo [Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994].

Concentrations of TC and TN (Table 1) for remote aerosol samples ranged from 190 to 5174 ng m^{-3} and from 16 to 1461 ng m^{-3} making up 0.7-18 % and 0.09-5.2 % of the aerosol mass, respectively (Fig. 2b and 2c). C/N ratios showed diversity, ranging from 3.3 (28 °S) to 28 around equator: (5° N-5° S). WSOC showed a concentration range of 88-2324 ng m^{-3} and comprized 29-55 % of TC (Table 1). Such high WSOC/TC ratios are close to the values reported for urban aerosols for which yet 1-2 orders of magnitude higher TC are usually observed [Cadle and Groblicki, 1982; Mueller et al., 1982; Sempéré and Kawamura, 1994]. Similar WSOC/TOC ratios have also been reported in relation to biomass burning [Novakov and Corrigan, 1991; Narukawa et al., 2002]. Interestingly, our previous results indicated higher WSOC/TC ratios during day time compared to the night and during summer compared to winter, suggesting photochemical production of these compounds [Sempéré and Kawamura, 1994]. Although dicarboxylic acids, ketoacids and dicarbonyls have been

identified in the water soluble fraction of the aerosols [Sempéré and Kawamura, 1994; Narukawa et al., 1999], low molecular weight polyols and amino acids and other multi functional groups may contribute to the water soluble fraction [Saxena and Hildemann, 1996]. This fraction of the aerosols most likely contributes to the CCN ability of particles [Saxena and Hildemann, 1996]. Because of their water solubility properties as well as their photochemical reactivity, these compounds are likely to have short life time in the atmosphere, suggesting that water soluble organic compounds are produced during long range transport and/or in a local source region through photochemical oxidation reactions of higher molecular weight organic compounds.

The carbonaceous fraction of the aerosols (TC %) near the Japanese Islands (TC = 18 %) was more than five times higher compared to the rest of samples, suggesting a significant atmospheric transport of continent-derived organic materials over the Pacific Ocean (Fig. 2b). Such high TC %, as well as C/N ratio (3.5; Fig. 2c) and WSOC/TC % ratios (45; Table 1) were found to be similar to the values reported already for Tokyo area [Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994] or other Asian urban areas [Hashimoto et al., 1991; Sekine et al., 1992; TC % only reported]. TC concentrations in the remote Pacific aerosols were similar to those obtained from remote Pacific Ocean (69-5270 ng m⁻³) [Kawamura and Sakaguchi, 1999], Chichi-Jima Island in the western North Pacific (400-1450 ng m⁻³) [Moshida et al., submitted] and Antarctic aerosols (440-1020 ng m⁻³) [Kawamura et al., 1996]. TN concentrations were close to the values already reported for Pacific Ocean (26-1440 ng m⁻³) [Kawamura and Sakaguchi, 1999] and one order of magnitude lower than those of urban area at least from the Tokyo atmosphere [Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994]. We also found that TC % were slightly lower in South Pacific (0.7-3.1 %) than in its northern part (3.1-18 %), probably in relation with the large quantities of land-derived dusts and anthropogenic particles which are transported from source regions in Asia to the North Pacific Ocean [Duce et al. 1980; Uematsu et al., 1985].

Interestingly, our aerosol samples collected near equator (0°-5° S) showed low concentrations (11-18 µg m⁻³) of aerosols, high C/N ratios (24-29) and moderately high TC % values (*ca.* 5%), being in contrast with the values observed for the North and South sub-

tropical area (20 °S and 20°N) (Fig. 2a) This suggests that at low latitudes, tropospheric aerosols are not only influenced by diffusive and wind transport from the two hemispheres but also very likely by vertical mixing between lower and upper troposphere, being in agreement with the work of Plumb and McConaloug [1988]. High C/N ratios (6-89), and then relatively nitrogen depleted aerosols have been reported in Antarctic and Arctic aerosols [Kawamura et al., 1995; 1996] whereas lower C/N ratios were found in Tokyo area [Sempéré and Kawamura, 1994] where anthropogenically derived-NO_x likely lead to particulate nitrates. Since organic content of the aerosol (TC %) was high near the Equator, the low C/N ratios might be due to preferential destruction of nitrogenous compounds or to a mixing with a nitrogen-poor air mass. Except for nitrates, other nitrogenous compounds might be present in aerosols such as peroxyntiric acid (PNA or HO₂NO₂) and dinitrogen pentoxide (N₂O₅). These compounds are thermally labile and have poor stability in the warmer lower troposphere where thermal decomposition can occur in less than a day [Bradshaw et al., 2000 and references therein]. However, high temperatures measured in the North Pacific did not give rise to such a high C/N ratio, then, it is likely that the change in the C/N ratio was also due to air mass exchange between the boundary layer and the upper troposphere, which is a common feature at low latitudes [Bradshaw et al., 2000 and references therein]. Such assumption would suggest that upper tropospheric aerosols might be characterized by high C/N ratios. Another explanation would be that aerosols at low latitudes originated from South East Asia are associated with biomass burning during the dry season [Narukawa et al., 1999].

3.2 Concentration levels and relative abundance of water-soluble compounds

α , ω -Dicarboxylic acids (C₂-C₉) and aromatic acid (phthalic) as well as ω -oxocarboxylic (C₂-C₆; C₂-C₉) acids, α -ketoacid (pyruvic acid) and α -dicarbonyls were detected in the North and South Pacific aerosols. Their chemical structures are given in Figure 3. Dicarboxylic acids are the most abundant compound class (7.07-605 ng m⁻³) followed by ketoacids (0.58-42 ng m⁻³) and α -dicarbonyls (0.28-8.81 ng m⁻³) (Table 2; Figure 4a-c).

α , ω -Dicarboxylic acids

Diacids accounted for 1.07-4.94 % (av. 3.17 %) of TC and for 2.09-14.65 % (av. 8.15 %) of WSOC (Fig 5). This indicates that diacids are a major component of the water-soluble organic fraction of marine aerosols. Interestingly, lower ratios of diacids-C/TC and diacids-C/WSOC were observed in the Southern Hemisphere. Diacids with more carbon number are generally less abundant whereas oxalic acid (C_2) was the most abundant (30-71 %) followed by malonic acid (C_3 : 12-27 %) and succinic acid (C_4 : 3-18 %) (Figure 6a-c). Interestingly, a similar molecular distribution was observed in some aerosol samples collected from North Pacific [Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999], from Tokyo [Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994] as well as in other urban areas [Tran et al., 2000; Neussus et al., 2000; Yao et al., 2002]. Azelaic acid is the most abundant in the range of C_5 - C_{10} diacid being even the third abundant diacid (QFF 545).

Although they are less abundant than corresponding straight-chain dicarboxylic acids, branched chain saturated diacids including methylmalonic (iC_4) and methyl succinic (iC_5) were also detected in the Pacific aerosols. Two aliphatic unsaturated diacids were also detected in the marine aerosol samples: maleic (*cis* configuration) and fumaric (*trans* configuration). Note that the *cis/trans* ratio largely fluctuated, being usually higher than 1 near the Australian Continent and the Japanese Islands and lower in between (Fig. 7). The latter case indicates that the *trans* configuration (fumaric acid (F)) was equal or more abundant than the *cis* configuration (maleic acid (M)) at low latitudes. Generally, *trans* configuration is more abundant in the marine atmosphere whereas the opposite was reported for the continental aerosols [Kawamura and Sakaguchi, 1999 and references therein] a point to be discussed later. In addition, we detected α,ω -dicarboxylic acids with an additional functional group i.e. ketomalonic (kC_3), 4-oxopimelic [kC_7] and hydroxysuccinic acid (malic: hC_4). However, all of these compounds are relatively minor species as they comprized less than 6 % of total diacids.

Ketoacids and dicarbonyls

Total concentrations of ketoacids ranged from 0.58 to 42 $ng\ m^{-3}$ (av. 5.4 $ng\ m^{-3}$) and the

general distribution parallels those of α,ω -dicarboxylic acids although the concentrations are about an order of magnitude lower (Fig 4 a-c). The highest value was observed near Japan (QFF 538: 41.61 ng m⁻³) followed by South Pacific sample near Australia (QFF 553: 8.28 ng m⁻³). Total ketoacids accounted for 0.09-0.37 % (av. 0.23 %) of TC and for 0.16-1.10% (av. 0.58 %) of WSOC. Glyoxylic acid (ω C₂) was always the dominant or second (QFF 541) ketoacid followed by 9-oxononanoic, pyruvic or 4-oxobutanoic acids (Fig. 8a-b). Predominance of ω C₂ and ω C₄ were frequently reported for Antarctic aerosol samples [Kawamura et al., 1996] and Greenland ice core samples [Kawamura et al., 2001]. Surprisingly, high relative abundance of 9-oxononanoic was observed in the northern tropical area where we found also high relative abundance of C₉ diacid (QFF539-541). Except for this compound, ω -oxoacids with the longer chain length was less abundant.

Concentrations of α -dicarbonyls ranged from 0.15 to 8.8 (av. 1.1 ng m⁻³). Their latitudinal distribution is similar to those of diacids and ketoacids, although concentrations were much lower (Fig. 4). Total dicarbonyls accounted for 0.02-0.11 % (av. 0.50 %) of TC and 0.07-0.22 % (av. 0.14 %) of WSOC (Table 2). Methylglyoxal was more abundant than glyoxal near the Japanese Islands (QFF 538) and in the southern tropical area, whereas opposite trend was observed for other samples, particularly for the southernmost samples (Fig. 9). Dicarbonyls are moderately soluble and largely present in the gas phase [Betterton, 1992]. Methylglyoxal and glyoxal are tracers of the photochemical oxidation of a number of aromatic or straight chain unsaturated hydrocarbons such as benzene, toluene and isoprene [Bandow et al., 1985; Munger et al., 1995]. These compounds may be intermediates in the photochemical oxidation reactions of aromatic hydrocarbons to oxalic acid [Norton et al., 1983], and are removed by photolysis and reaction with OH [Atkinson et al., 1993]. Munger et al. [1995] reported that 50 % glyoxal is partitioned to the aqueous phase during cloudy period and glyoxal and methylglyoxal have been reported in the marine air [Zhou and Mopper, 1990], rain and fog samples [Grosjean et al., 1990] and snow and ice samples from Greenland [Kawamura et al., 2001]. Glyoxal was more abundant than methylglyoxal in southernmost South Pacific and *vice versa* in the tropical and sub-tropical South Pacific (Fig. 9) which was also observed for the rainwaters collected during the same cruise [Sempéré and

Kawamura, 1996]. Methylglyoxal is also an important precursor of peroxyacetylnitrate (PAN) [Munger et al., 1995].

3.3 Depositions of total and water soluble organic carbon over the Western Pacific

Diacids comprized a significant fraction of aerosol TC (1-5 %) and WSOC (2-15 %). Clearly our results indicated that the concentrations of the diacids and related polar compounds, as well as the WSOC and the diacid-C/WSOC ratio largely varied with the latitude. The highest concentrations of diacids were found near the Japanese Islands and Australia. This can be explained by that the main sources of these compounds, includes direct emission from incomplete combustion of fossil fuels and photochemical oxidation of organic pollutants of continental origin as well as biomass burning [Kawamura and Ikushima, 1993; Stephanou et al., 1993; Narukawa et al., 1999]. Although the concentrations are much lower in remote area than in urban atmosphere, water soluble organic compounds are still enriched in the remote Pacific atmosphere probably due to enhanced photochemical production of polar compounds such as dicarboxylic acids. As WSOC did not show any spectacular concentration decrease and since short life time has been reported for diacids [Grosjean, 1989], it is likely that these compounds are continuously produced in the remote atmosphere.

Wet deposition of oxalate

Furthermore, these results are in good agreement with rainwater studies conducted in the same areas indicating that they comprized up to 5% (av. 3%) of rainwater DOC [Sempéré and Kawamura, 1996]. Among the total diacids, oxalate has been proposed to play an important role of condensation nuclei growth [Baudet et al., 1990; Kerminen et al., 1999; Hara et al., *In Press* and references therein]. Oxalic acid was found to be predominantly distributed in the atmospheric aerosols through the uptake of gaseous oxalic acid into fine or coarse particles or sea-salts [Kerminen et al., 1999]. A strong Aitken mode has been reported for oxalic acid, indicating that the growth of secondary particles to cloud condensation nuclei may be affected by oxalic acid, especially of marine origin [Kerminen et al., 1999]. To study the

relationship between the oxalic acid concentration in aerosols and rainwater, we can consider a simple case of in-cloud scavenging of a pre-existing oxalic acid in aerosol. The oxalic acid concentration in rainwater is described by the following equation [Charlson and Rhode, 1982 and references therein]:

$$[C_2O_4^{2-}]_{rain} = [C_2O_4^{2-}]_{aerosol} \times \varepsilon DE/90L \quad (1)$$

, where ε is the scavenging efficiency for $C_2O_4^{2-}$ aerosol particles in the cloud, 90 is the oxalic acid molecular weight ($g\ mol^{-1}$) and L is the liquid water content ($l\ m^{-3}$) of the cloud. For soluble particles of 0.1-1 μm radius, ε is expected to be 0.5-1.0 [Junge, 1963]. D and E are the dilution and the evaporation of the cloud and rainwater. For a long range transport of air pollutants, $\varepsilon DE/L$ is in the range ($0.6-1.6 \times 10^3\ m^3\ kg^{-1}$; av. $1.1 \times 10^3\ m^3\ kg^{-1}$) [Charlson and Rhode, 1982]. Based on the aerosol oxalic acid concentrations we measured, and by using a cloud liquid water content of $1\ g\ m^{-3}$ [Charlson and Rhode, 1982], a rough calculation predicts a concentration of oxalic acid in the marine rainwater of 44.6-471 $\mu g\ l^{-1}$ (av. 163; n = 4) and 2.62-96 $\mu g\ l^{-1}$ (av. 26.3; n = 14) for the North and South Pacific, respectively. These values are in the same order of magnitude than that found (18.7-461 $\mu g\ l^{-1}$; (av. 134; n = 4) and 82-106 $\mu g\ l^{-1}$; (av. 103; n = 10)) for North and South Pacific rainwaters collected during the same cruise [Sempéré and Kawamura, 1996]. We may expect some limitations to the partition of oxalic acid into the aqueous phase under the conditions such as highly acidic aerosol, low relative humidity and ambient temperature greater than $15^\circ\ C$; except for the temperature the others factors are not likely to occur in remote marine area. On the other hand, photochemical production of oxalic acid is very likely in cloud. This could enhance the theoretical concentrations of oxalic acid. These results suggest a contribution of oxalate to CCN may be significant in the Western Pacific atmosphere.

Dry deposition of diacids

Assuming that diacid are equally distributed in the lower troposphere, diacid standing masses in the first 3000 m were estimated to 243-1814 $\mu g\ m^{-2}$ (av. 699 ; n = 4) and 21-376 μg

m^{-2} (av. 127; $n = 14$) $\mu\text{g m}^{-2}$ in the Northern and Southern Pacific, respectively (Table 3). Similarly, ketoacid standing masses would be 13.6-125 $\mu\text{g m}^{-2}$ (av. 42; $n = 4$) and 1.7-24.8 $\mu\text{g m}^{-2}$ (av. 9; $n = 14$) in the Northern and Southern Pacific, respectively.

In order to compare the importance of dry deposition to the surface ocean, we estimated a dry deposition flux for TC, TN as well as for the two main classes of organic compounds studied *i.e.* diacids and ketoacids. Assuming a dry deposition velocity of 0.01 cm s^{-1} for aerosol particles [Slinn and Slinn, 1980], we estimated the TC deposition to be 1.88-16.3 $\text{mg m}^{-2} \text{ yr}^{-1}$ (av. 6.1; $n = 4$) and 0.60-2.84 $\text{mg m}^{-2} \text{ yr}^{-1}$ (av. 1.5; $n = 14$) for the Northern and the Southern Pacific, respectively (Table 3). This estimate indicates that dry deposition is about three orders of magnitude lower than organic-C produced through primary production (less than 50 to 100 $\text{g m}^{-2} \text{ yr}^{-1}$) in Western Pacific waters [Kennish, 2000]. TN dry depositions would be 0.24-4.61 $\text{mg m}^{-2} \text{ yr}^{-1}$ (av. 1.44; $n = 4$) and 0.05-0.78 $\text{mg m}^{-2} \text{ yr}^{-1}$ (av. 0.23; $n = 14$) for the Northern and the Southern Pacific, respectively (Table 3). Similarly, by using diacid and ketoacid concentrations found for each aerosol samples, we evaluated the air-to-sea fluxes of the diacids by dry deposition to be 256-1907 $\mu\text{g m}^{-2}$ (av. 735; $n = 4$) and 22-396 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ (av. 134; $n = 14$) for the Northern and Southern Pacific, respectively. Similar calculations indicated that dry deposition of ketoacids would be 14.3-131 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ (av. 44; $n = 4$) and 1.81-26.9 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ (av. 9.2; $n = 14$) for Northern and Southern Pacific (Table 3). Diacid dry depositions are two orders of magnitude higher than the estimated dry depositions of alkanes, n-alcohols and fatty acids measured in the North Pacific [Kawamura et al., *in Press*]

Similar calculations give rise to a dry deposition for oxalic acid of 128-1351 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ (av. 466; $n = 4$) and 7.52-275 $\mu\text{g m}^{-2} \text{ yr}^{-1}$ (av. 75; $n = 14$) for the Northern and Southern Pacific, respectively. Taking into consideration concentrations of oxalic acid found in rainwaters during the cruise at similar locations [Sempéré and Kawamura, 1996], and assuming a precipitation volume in the range of 70-800 mm yr^{-1} [<http://www.ingrid.ldeo.columbia.edu/>], we can estimate the annual wet deposition of oxalate to be 27 to 107 $\text{mg m}^{-2} \text{ yr}^{-1}$ ($n = 4$) and 21 to 82 $\text{mg m}^{-2} \text{ yr}^{-1}$ ($n = 14$) for the Northern and Southern Pacific, respectively. These values are about two orders of magnitude higher than

those estimated for dry deposition, indicating that diacid deposition is mainly driven by rainfall in Western Pacific. However, large variations of rainwater volume can be observed in the Western Pacific, and large uncertainties are probably associated to our estimates. Figures given for the remote Western Pacific and obtained from satellite observations indicate that 3 month-precipitation rates were in a range of 10-400 mm, whereas higher annual precipitation volumes were recorded in North Australia (1500 mm), Southeast China (~ 2000 mm), or in Micronesia (2250-5000 mm) (<http://ingrid.ldeo.columbia.edu/>).

For a 3 km-air column scale height (H), the standing mass of oxalic acid in the Northern and Southern Pacific is something around 122-1286 $\mu\text{g m}^{-2}$ (av. 443; n = 4) and 7.2-262 $\mu\text{g m}^{-2}$ (av. 72; n = 14), respectively. Then, the residence time of oxalate ($\tau = \text{HC} / \text{F}$) in the lower troposphere calculated from the oxalic acid standing mass (HC) and the sum of the wet and dry depositions (F), would be about 4.3-17 days for North Western Pacific and 0.28-1.3 days for the South Western Pacific. Interestingly, these values are near the turnover time of CCN (~1 day) calculated from purely physical data in the atmosphere [Charlson and Rhode, 1982 and references therein], on mass-concentration and rainfall amount. Thus, our simple calculation seems to be in reasonable agreement with the rain and aerosol concentrations reported. Although these numbers give reasonable estimate in remote and coastal area, large uncertainties may probably be associated with dust injections during biomass burning events during the dry season in Southeast Asia.

3.4 Photochemical production of water soluble organic compounds

Total diacids

The spatial distribution of diacid-C/TC and diacid-C/WSOC ratios shows higher values at low latitudes (Fig. 5) and in the Northern Pacific atmosphere where highest temperatures were recorded. The Northern Pacific maxima in the diacid-C/WSOC ratios suggested that in the Western Pacific, the diacids are produced in the atmosphere by photochemically induced secondary reactions or that they are preferentially injected to the atmosphere at these latitudes. Interestingly, a positive correlation was found between the diacid-C/WSOC ratios ($r = 0.7788$; $p = 0.0001$) and the air temperature (Fig. 10) suggesting that secondary

photochemical reactions (gas-to particle conversion), oxidations of hydrocarbons and other organic precursors are the main sources of diacids in this area. Many oxidation reactions, several sources and sinks have been proposed. Dicarboxylic acids have been considered to be mainly produced by secondary photochemical oxidation of anthropogenic and natural organic compounds such as biogenic fatty acids [Kawamura and Gagosian, 1987; 1990]. The present results seem to be consistent with previous studies which reported a diurnal distribution for C₃-C₆ diacid [Satsumabayashi et al., 1990] with a maximum in daytime and summer maximum concentrations of C₂-C₆ diacids in atmosphere [Kawamura and Ikushima, 1993]. Moreover, the diacid-C/WSOC relationship with temperature obtained in this study is consistent with the positive correlation obtained for diacid-C/TC vs temperature in Tokyo [Kawamura and Ikushima, 1993].

It is important to note that primary sources are also important in the marine atmosphere near industrialized areas such as the Japanese Islands and Australia. It is now well established that LMW-diacids are produced by ozone and cycloalkene reaction [Hatakeyama et al., 1987; Kawamura and Ikushima, 1993] as well as by the emissions from automobile exhausts [Kawamura and Kaplan, 1987] or from biomass burning [Legrand and De Angelis, 1996; Narukawa et al., 1999]. The concentrations of diacids obtained here for the North Pacific are in good agreement with the previous work of Kawamura and Usukura [1993]. Those obtained at the site near the Japanese coasts (QFF 538) are much lower than those from the urban aerosols [90-3000 ng m⁻³; Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994]. This study suggests (Figure 4 and 7) that the main source of diacids be of anthropogenic origin in the North Pacific. Diacid concentrations decreased towards the Southern Hemisphere during the sampling although the QFF 553 sample indicated high concentrations (85 ng m⁻³). Then, concentration of diacids is driven by fossil fuel combustion and biomass burning and subsequent photochemical oxidation near the continent, whereas in remote areas, secondary photochemical reactions are probably the main sources.

Preferential production of oxalic acid and possible mechanisms

Although the relative abundance of total dicarboxylic acid-C in water soluble fraction

increased with the ambient temperature, a degree of the increase was found to depend on the carbon chain length and structure of the diacid species. Figure 11 (a-b) plots the individual relative abundance of succinic acid (C_4) and the ratio oxalic/succinic acid (C_2/C_4) ratio as a function of the air temperature. Interestingly, the relative abundance of succinic acid clearly showed a significant negative linear relationship with the air temperature ($r = 0.8427$; $p < 0.0001$) whereas the oxalic/succinic ratio stay relatively constant between 14° and 20° C and increase towards 28° C. The results again indicate that molecular distribution of LMW-diacids is modified by the air temperature or very likely by the enhanced photochemical reactions.

Interestingly, succinic acid was found to be more abundant than malonic acid in winter Tokyo [Sempéré and Kawamura, 1994], in Southeast Asia [Narukawa et al., 1999] and most of Arctic aerosol samples [Kawamura et al., 1995; Kerminen et al., 1999] as well as in Tokyo rain/snow/sleets [Sempéré and Kawamura, 1994], Los Angeles [Kawamura et al., 2001] and eastern Pacific rainwaters [Sempéré and Kawamura, 1996]. It is of importance to note that succinic acid was found to be the most abundant diacids in some Antarctic aerosol samples [Kawamura et al., 1996], in spring snowpack [Narukawa et al., 2002] and Greenland ice core samples [Kawamura et al., 2001b]. These results suggest that high relative abundance of C_4 succinic acid is a common trend in cold environment. On the other hand, lower relative abundance of succinic diacid was generally found for samples collected under sunny and hot conditions in urban area [Kawamura and Ikushima, 1993; Sempéré and Kawamura, 1994]. Although higher relative abundance of oxalic acid was observed for higher temperature, its linear relationship with the temperature is not significant. Thus, the increases in the C_2/C_4 ratios and the decrease in C_4 relative abundance with the temperature were mainly due to the low abundance of succinic acid at high temperature. This may suggest that succinic acid is a precursor of oxalic acid, which is further oxidized to CO and CO_2 .

The C_4 - C_{10} α , ω -dicarboxylic acids are likely produced by photo-oxidation of unsaturated fatty acids and their oxidation products [Kawamura and Gagosian, 1990; Kawamura and Sakaguchi, 1999]. Previous studies showed that atmospheric oxidation of longer chain diacids (e.g. C_8 - C_{10}) are more stable in the atmosphere than shorter ones (e.g.

C₅-C₆) which are likely precursors of lower diacids. It was also proposed that photo-induced hydroxylation of succinic acid produce malic acid which may be further oxidized in the atmosphere to result in oxalic acid or malonic acid, the latter being further oxidized in oxalic acid through intermediate compound such as hydroxymalonic acid or ketomalonic [Kawamura and Ikushima, 1993]. As a source of semi-volatile organics, monocarboxylic acids are probably important in addition to oxidation of cycloalkenes. It is important to note that mid-chain ketocarboxylic acids and hydroxy fatty acids have been reported in the marine atmosphere [Kawamura and Gagosian, 1990]. Interestingly, such relationships were not clearly found for relative abundances of other species including malonic acid (C₃), and C₅-C₁₀ diacids.

Cis/trans configuration of unsaturated dicarboxylic acids in Western Pacific atmosphere

Examination of the two configurations of C₄ unsaturated diacid in relation with the temperature may also provide useful information. Maleic acid (*cis* configuration) showed the highest concentrations for low air temperature (QFF 550-552-554) and also for samples collected near Australia (QFF 546, QFF 556) and Japanese Islands (QFF 538) (Fig. 12 and Fig. 1 for localization of the samples). By contrast, lower M/F ratios were observed for the most remote samples (QFF 539-543) and for the highest temperatures (QFF 547-549; 551). This is consistent with very low M/F ratios (0.06-1.3; av. 0.26) already reported for remote Pacific Ocean [Kawamura and Sakaguchi, 1999].

The predominance of precursor *cis* configuration should be associated with the photochemical oxidation of benzene or toluene, whose *cis* configuration is preserved in the structure of the oxidation product. The maleic acid may further be isomerized photochemically to *trans* configuration (fumaric acid) in the atmosphere under solar radiation [Kawamura and Ikushima, 1993 and references therein]. These results seem in contrast with those obtained by Kawamura and Ikushima [1993] who reported higher M/F ratios for Tokyo samples collected in summer-autumn. However, Tokyo samples showed M/F ratio usually higher than 1 and were probably strongly dependant on the oxidation of benzene-type structure, whereas Western Pacific samples were not only dependant on the source of maleic

acid but also for a large part on the subsequent isomerization of maleic to fumaric acid. It is interesting to note that we observed a moderately significant negative relationship between M/F ratios and air temperature for the most remote samples which showed a M/F ratio close to or lower than 1 (Fig. 12), indicating that isomerization and then the photochemical processes control the M/F ratio. Fumaric acid is an intermediate product of photochemical isomerization of maleic acid (Fig. 13). Because of the double bond fumaric acid would be further oxidized by ozone and other oxidizing agents like OH radical to produce smaller diacids such as oxalic acid (Fig. 13).

Azelaic acid distribution in relation to the air temperature

The relative abundance of other diacids did not show a clear relationship with the air temperature. However, the concentrations of C₉ azelaic acid clearly show a positive exponential relationship with the air temperature (Fig. 14a). The azelaic concentrations remained rather constant around 1 or 2 ng m⁻³ between 13° and ~ 21° C. In contrast, we observed large variations and the highest concentrations of this acid for temperature above 24°C. Interestingly, logarithmic relationship was found between C₉-azelaic acid and 9-oxononanoic acid which has been proposed as a precursor of azelaic acid [Kawamura and Gagosian, 1987]. As it was indicated above, longer chain-diacids are very likely produced by photo-oxidation of unsaturated fatty acids and their oxidation products such as semi-volatile and midchain ketocarboxylic acids [Kawamura and Gagosian, 1990]. The unsaturated fatty acids are abundant in terrestrial higher plant leaves and marine phytoplankton and are enriched in seawater microlayer. After their emission into the atmosphere, they are photochemically oxidized to result in diacids dominated by azelaic acid, and to a less extent, to 9-oxononanoic acid because of the double bond predominantly at C-9 position [Kawamura and Gagosian, 1987]. Higher concentration of the C₉-diacid compared to the ωC₉-ketoacid for warmer temperature and thus higher solar radiation, strongly suggest that the lower stability of the ketoacid which may act as a precursor of azelaic acid.

4. Summary and Conclusion

Molecular distribution of water soluble dicarboxylic acids in the marine aerosols samples collected from Western Pacific showed a predominance of oxalic acid (C_2) followed by malonic (C_3) and succinic acid (C_4). Diacids accounted for 3.17 % (av.) of TC and 8.15% (av.) of WSOC, indicating that they are a major component of the water soluble organic fraction of marine aerosols in Western Pacific. Our results indicated that although the level of aerosol mass was similar in the Northern and Southern Pacific, highest concentrations of organic components including diacids were observed in the North Pacific. Although the highest concentrations of oxalic diacid and its homologues were found near Asian or Australian continents (up to 604 ng m^{-3}), these results showed that diacids are still significantly abundant in remote marine atmosphere ($7\text{-}81 \text{ ng m}^{-3}$), suggesting that diacids are continuously produced from organic precursors.

We also found that the fraction of diacid in the water soluble organic carbon increased linearly with the air temperature. Diacids should act as cloud condensation nuclei, and play a role on the radiative balance by increasing the light backscattering and cooling the atmosphere. Because of their continuous production in remote area under high solar radiation, their role is probably not limited near the continent and their urban sources. This report confirmed that concentration levels and relative abundance of diacids are controlled by the continental and anthropogenic sources as well as by photochemistry in remote area. However, this study highlights that the signature of the photochemical oxidation could be well followed by the maleic/fumaric acid and on the oxalic/succinic acid ratios suggesting that these compounds might be useful tool for a better understanding present or past atmospheric photochemical reactions in the lower troposphere. Further studies are necessary to evaluate the significance of these compounds as tracers of atmospheric temperature or sun light intensity, however, this study also suggests that a water soluble fraction of the aerosol could be parameterized for global model calculation or for long term projection in relation with the global change.

Acknowledgements : The authors are very grateful to K. Tanaka for the help of sample collection, Y. Suzuki, J. P. Torretton and U. Lohmann for help with primary production and rainfall data research. We acknowledge the Japan Society for the Promotion of Science (JSPS) for financial support to R. S. Experimental work has been done at Department of Chemistry, Tokyo Metropolitan University, in which the authors stayed as a post-doctoral researcher (RS) and a faculty member (KK).

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Figure caption

Fig. 1

Cruise track of R/V Hakuho Maru: KH-92 started 16 September 1992 at Tokyo Japan, and ended 26 October 1992 at Cairns, Australia. The aerosol samples were continuously collected during the cruise. The consecutive sampling area are delimited by the sticks drawn on the cruise track, and the numbers in between correspond to the filter identification numbers.

Fig. 2

Latitudinal distribution of the (a) total aerosol concentration, (b) total carbon (TC) content and (c) C/N ratio of the western Pacific aerosol samples .

Fig. 3

Chemical structures of dicarboxylic acids, ketoacids (only the most abundant) and dicarbonyls detected in the marine aerosols. For abbreviation see Table 2. C_n means dicarboxylic acid . iC_n indicates branched chain (iso) diacid. M and F are abbreviations of unsaturated diacids: maleic and fumaric acids, respectively. $C_{n\omega}$ indicates ω -oxocarboxylic acid with n carbon numbers. Me-Gly, Pyr, Malic, Gly, Ph mean methylglyoxal, pyruvic, malic, glyoxylic and phthalic acids, respectively.

Fig. 4

Latitudinal distribution of the (a) total diacid, (b) ketoacid, and (c) dicarbonyl concentrations in the western Pacific aerosol samples.

Fig. 5

Latitudinal distribution of the diacid-C/TC (close circles) and diacid-C/WSOC (open circles) ratios in the western Pacific aerosol samples.

Fig. 6

Latitudinal changes in the relative abundance of the most abundant individual α , ω -dicarboxylic acids in the western Pacific aerosol samples.

(a): oxalic (C₂di), malonic (C₃di) and succinic (C₄di) acids.

(b): adipic (C₆di), pimelic (C₇di) and azelaic (C₉di) acids

(c): suberic (C₈di) and phthalic (C₈di) acids.

Fig. 7

Latitudinal changes in C₄-unsaturated α , ω -dicarboxylic acids (maleic (*cis* configuration) and fumaric acid (*trans* configuration)) in the western Pacific aerosol samples.

Fig. 8

Latitudinal changes in the relative abundance of the ω -oxoacids, dicarbonyls and pyruvic acid in the western Pacific aerosol samples.

(a): glyoxylic (ω C₂), 3-oxopropanoic (ω C₃), 4-butananoic (ω C₄) and pyruvic acids.

(b): 5-oxopentanoic (ω C₅), 6-oxohexanoic (ω C₆) and 9-oxononanoic (ω C₉) acids.

Fig. 9

Latitudinal changes in the relative abundance of the dicarbonyls (methylglyoxal: C₃ and glyoxal: C₂). in the western Pacific aerosol samples.

Fig. 10

Diacid-C/WSOC ratio (in %) in the western Pacific aerosol samples as a function of the ambient air temperature measured on the upper deck of the R/V Hakuho Maru (~14 m above the Sea level) during the cruise.

Fig. 11

(a) Relative abundance of succinic diacid (C₄ di) and (b) the oxalic / succinic diacids (C₂ / C₄) ratios in the western Pacific aerosol samples as the function of the ambient air temperature

measured during the R/V Hakuho Maru cruise.

Fig. 12

Distribution of C₄-unsaturated α , ω -dicarboxylic acids (maleic (*cis* configuration) and fumaric acid (*trans* configuration)) in the western Pacific aerosol samples as a function of the ambient temperature measured during the R/V Hakuho Maru cruise. Open circles are related to samples with M/F ratio of ~ 2 . Note that these samples correspond essentially to aerosol samples collected near Australia and Japanese Islands. Closed circles are related to samples with M/F ratios < 2 and correspond to samples collected in remote area. Numbers in the figure correspond to QFF sample ID numbers (see also Fig. 1). Possible anthropogenic and remote influences are also given in the figure.

Fig. 13

Reaction mechanisms (modified from Kawamura and Kaplan, 1987), proposed for the photochemical control of maleic and fumaric acid from the photo-oxidation production from benzene-type organic compound near continental area and from *cis/trans* isomerization in remote area.

Fig. 14

Azelaic acid (C₉ α , ω -dicarboxylic acid) *versus* ambient temperature measured during the R/V Hakuho Maru cruise. Azelaic acid (C₉ α , ω -dicarboxylic acid) *versus* 9-oxononanoic acid (ω C₉) in the western Pacific aerosol samples.

Table 1. Total Carbon (TC), Total Nitrogen (TN) contents and water soluble organic carbon (WSOC) in the Western Pacific aerosols with sampling dates and ambient temperatures

Sample I.D.	QFF 538	QFF539	QFF540	QFF541	QFF543	QFF544	QFF545	QFF 546	QFF 547	QFF 548	QFF 549	QFF 550	QFF 551	QFF 552	QFF 553	QFF 554	QFF 555	QFF 556
Sampling date (1992)	Sep.16-17	Sep.17	Sep.17-18	Sep.18-21	Sep.21-23	Sep.25-26	Sep.27-28	Sep.29-Oct.1	Oct.1-2	Oct.3-4	Oct.4-8	Oct.13-14	Oct.14-15	Oct.15-17	Oct.17-18	Oct.19-21	Oct.21-22	Oct.22-24
	Northern Hemisphere									Southern Hemisphere								
Latitude (°)	35°-30N	30°-20°N	20°-10°N	10°-5°N	5°N-5°S	5°-10°S	10°-15°S	15°-18°S	18°-25°S	25°-30°S	30°-33°S	33°-32°S	32°-38°S	38°-40°S	40°-35°S	35°-28°S	28°-24°S	24°S
Ambient air T (° C)	26	25.8	25	27.5	27.5	27.5	28	26.2	25.5	21.8	19	16	16.5	14	13.8	14.5	19.5	24.5
Aerosol mass ($\mu\text{g m}^{-3}$)	28	26	27	14	11	18	22	21	20	27	28	29	23	16	68	38	29	31
TC (ng m^{-3})	5174	1095	825	595	571	899	438	490	618	190	273	251	367	325	880	624	595	284
TN (ng m^{-3})	1461	176	76	109	24	32	133	80	224	23	36	31	64	16	246	35	46	40
C/N Ratio	3.5	6.2	10.9	5.5	23.9	28.5	3.3	6.1	2.8	8.1	7.7	8.1	5.7	19.8	3.6	17.6	12.8	7.2
WSOC (ng m^{-3})	2321	369	412	201	199	301	153	184	282	88	90	136	164	162	484	182	181	108
WSOC/TC (%)	45	34	50	34	35	33	35	37	46	46	33	54	45	50	55	29	30	38

Table 2. Concentration ranges and average concentrations of dicarboxylic acids, ketoacids and dicarbonyls collected from the Northern to the Southern part of the Western Pacific atmosphere (n = 18)

	Concentrations (ng m ⁻³)		Relative abundance (%)	
	range	av. ± sd	range	av. ± sd
Dicarboxylic acids				
Oxalic, C ₂	2.4-428.5	2.8 ± 13.7	34-71	51 ± 11
Malonic, C ₃	1.0-78.6	1.0 ± 4.5	12-27	17 ± 4
Methylmalonic, iC ₄	0.0-1.7	0.08 ± 0.15	0.2-20	0.8 ± 0.6
Oxomalonic, C ₃	0.0-4.3	0.11 ± 0.24	0.0-2.3	1.0 ± 0.8
Maleic, uC ₄	0.06-1.8	0.08 ± 0.17	0.2-1.7	0.8 ± 0.5
Succinic, C ₄	1.0-33.4	0.78 ± 2.3	2.9-17.5	8.9 ± 4.0
Methylsuccinic, iC ₅	0.0-2.5	0.09 ± 0.34	0.0-2.5	1.1 ± 0.6
Fumaric, uC ₄	0.02-0.67	0.04 ± 0.12	0.1-1.3	0.5 ± 0.3
Malic, hC ₄	0.0-0.18	0.0 ± 0.02	0.0-0.21	0.1 ± 0.2
Glutaric, C ₅	0.49-7.6	0.28 ± 0.72	0.7-6.4	3.0 ± 1.9
Adipic, C ₆	0.18-7.2	0.27 ± 0.55	0.3-4.9	2.0 ± 1.1
Pimelic, C ₇	0.12-0.79	0.09 ± 0.13	0.0-1.3	0.5 ± 0.3
Suberic, C ₈	0.20-3.7	0.29 ± 0.57	0.6-3.7	1.8 ± 0.9
Phthalic, C ₈	0.40-20.3	0.34 ± 2.2	1.1-9.4	4.9 ± 2.6
4-Oxopimelic, C ₇	0.0-6.1	0.09 ± 0.41	0.0-2.2	0.7 ± 0.6
Azelaic, C ₉	0.42-8.7	0.87 ± 1.8	1.1-14	5.3 ± 3.1
Sebacic, C ₁₀	0.0-0.57	0.08 ± 0.13	0.0-0.72	0.7 ± 0.9
Sub total	7.1-604.6	7.3 ± 28.1	100	
% of TC	1.1-5.0	2.6 ± 3.2		
% of WSOC	2.1-14.7	6.8 ± 8.1		
Ketoacids				
Pyruvic, C ₃	0.13-8.2	0.09 ± 0.33	4.9-31	13 ± 7.5
Glyoxylic, C ₂	0.34-24.6	0.39 ± 1.0	37-75	61 ± 12
3-Oxopropanoic, C ₃	0.0-3.6	0.02 ± 0.14	1.1-14	5.1 ± 3.4
4-Oxobutanoic, C ₄	0.0-3.7	0.05 ± 0.22	0.0-18	8.5 ± 4.8
5-Oxopentanoic, C ₅	0.0-0.40	0.04 ± 0.07	0.0-7.6	2.8 ± 1.7
6-Oxohexanoic, C ₆	0.0-0.42	0.0 ± 0.03	0.0-7.6	0.8 ± 2.0
9-Oxononanoic, C ₉	0.02-1.8	0.06 ± 0.23	1.0-47	8.8 ± 13
Sub total	0.58-41.6	0.65 ± 2.1	100	
% of TC	0.09-0.34	0.23 ± 0.23		
% of WSOC	0.16-1.1	0.60 ± 0.58		
α-Dicarbonyls				
Methylglyoxal, C ₃	0.0-5.0	0.07 ± 0.27	0.0-57	42 ± 14
Glyoxal, C ₂	0.14-3.8	0.07 ± 0.23	43-100	58 ± 14
Sub total	0.15-8.8	0.14 ± 0.50	100	
% of TC	0.03-0.12	0.05 ± 0.05		
% of WSOC	0.06-0.29	0.13 ± 0.14		

Table 3. Standing masses and dry depositions of total carbon (TC), total diacids, oxalic acid and ketoacids in Northern (0-35°) and Southern (0-40°) Western Pacific

	North Western Pacific	South Western Pacific
<i>Standing masses</i>		
TC; (av.) (mg m ⁻²)	1.79-15.5; (5.77)	0.06-2.7; (1.46)
TN; (av.) (mg m ⁻²)	0.23-4.38; (1.37)	0.05-0.74; (0.22)
Diacids (μg m ⁻²)	243-1814; (699)	21-376; (127)
Oxalic acid (μg m ⁻²)	122-1286; (443)	7.2-262; (72)
Ketoacids (μg m ⁻²)	13.6-124.8; (42)	1.7-24.8; (8.8)
<i>Dry depositions</i>		
TC; (av.) (mg m ⁻² yr ⁻¹)	1.88-16.3; (6.06)	0.60-2.84; (1.53)
TN; (av.) (mg m ⁻² yr ⁻¹)	0.24-4.61; (1.44)	0.05-0.78; (0.23)
Diacids; (av.) (μg m ⁻² yr ⁻¹)	256-1907; (735)	22-396; (134)
Oxalic acid; (av.) (μg m ⁻² yr ⁻¹)	18-1351; (466)	7.52-275; (75)
Ketoacids; (av.) (μg m ⁻² yr ⁻¹)	14.3-131; (44)	1.81-26.9; (9.2)

Dry depositions were calculated by using a dry deposition velocity of 0.01 cm s⁻¹ (Slinn and Slinn, 1980)

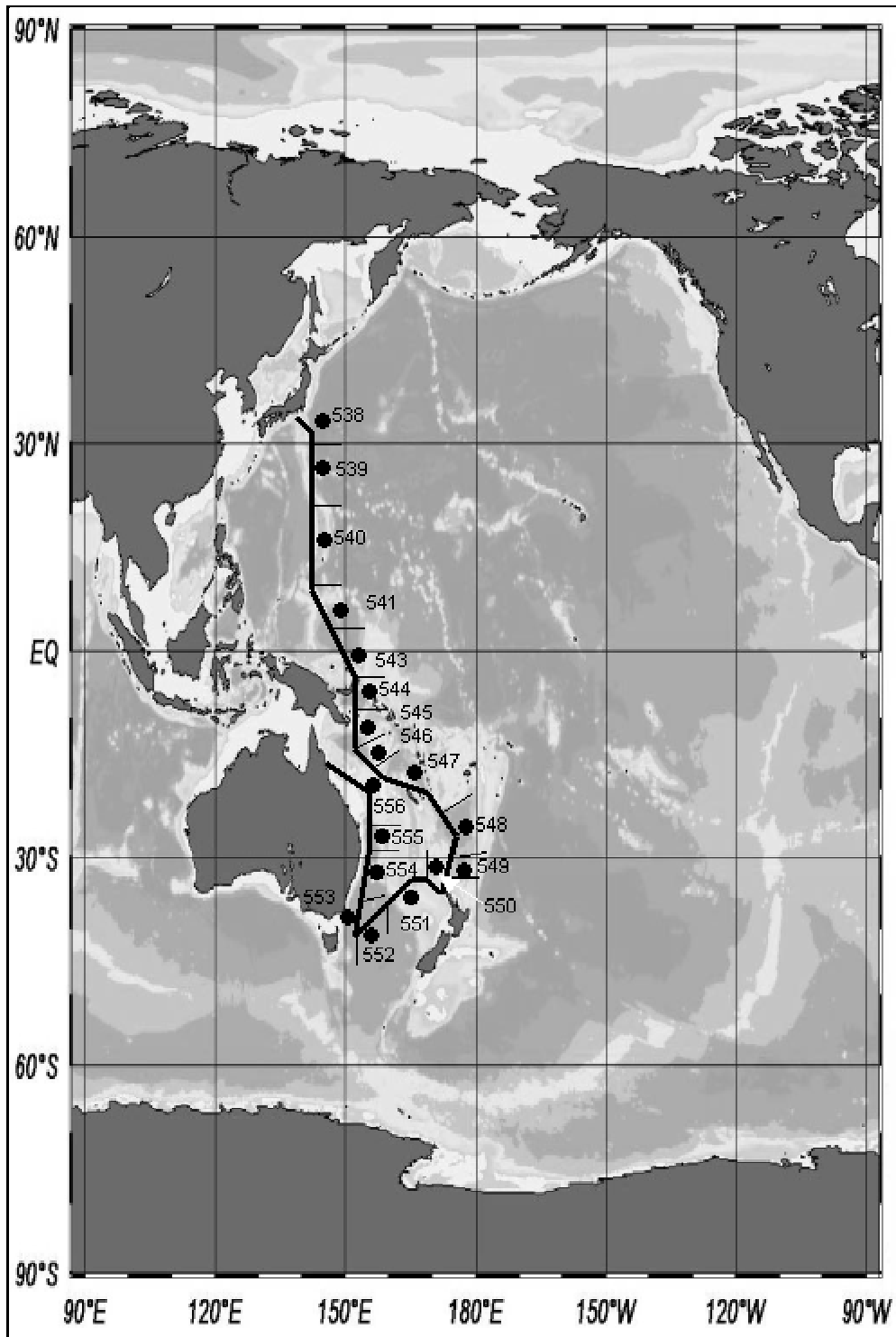


Fig. 1

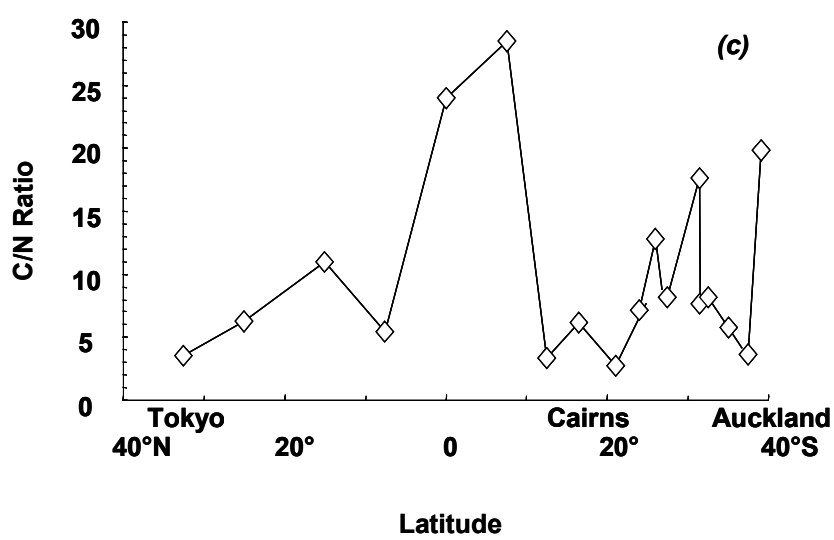
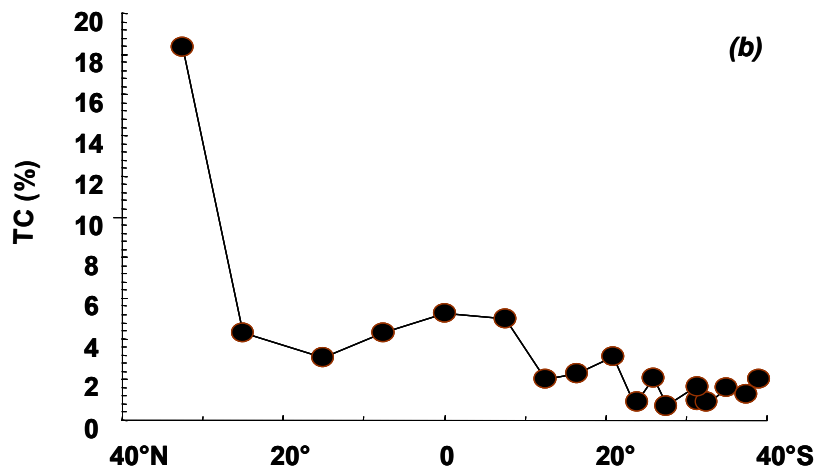
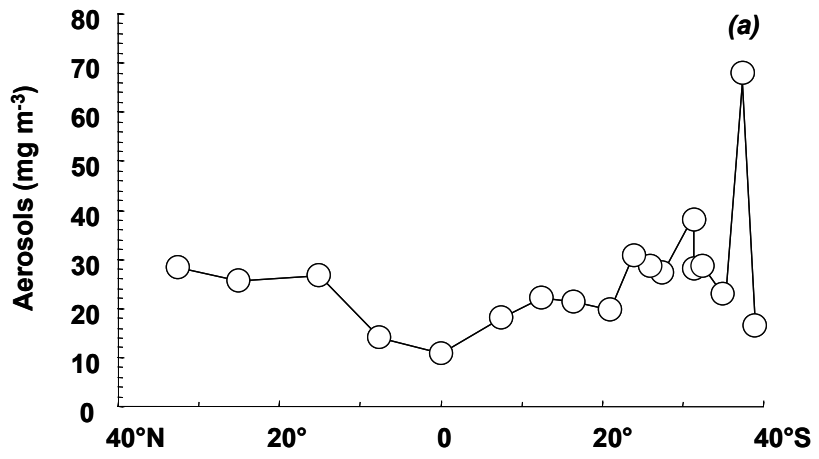


Fig. 2

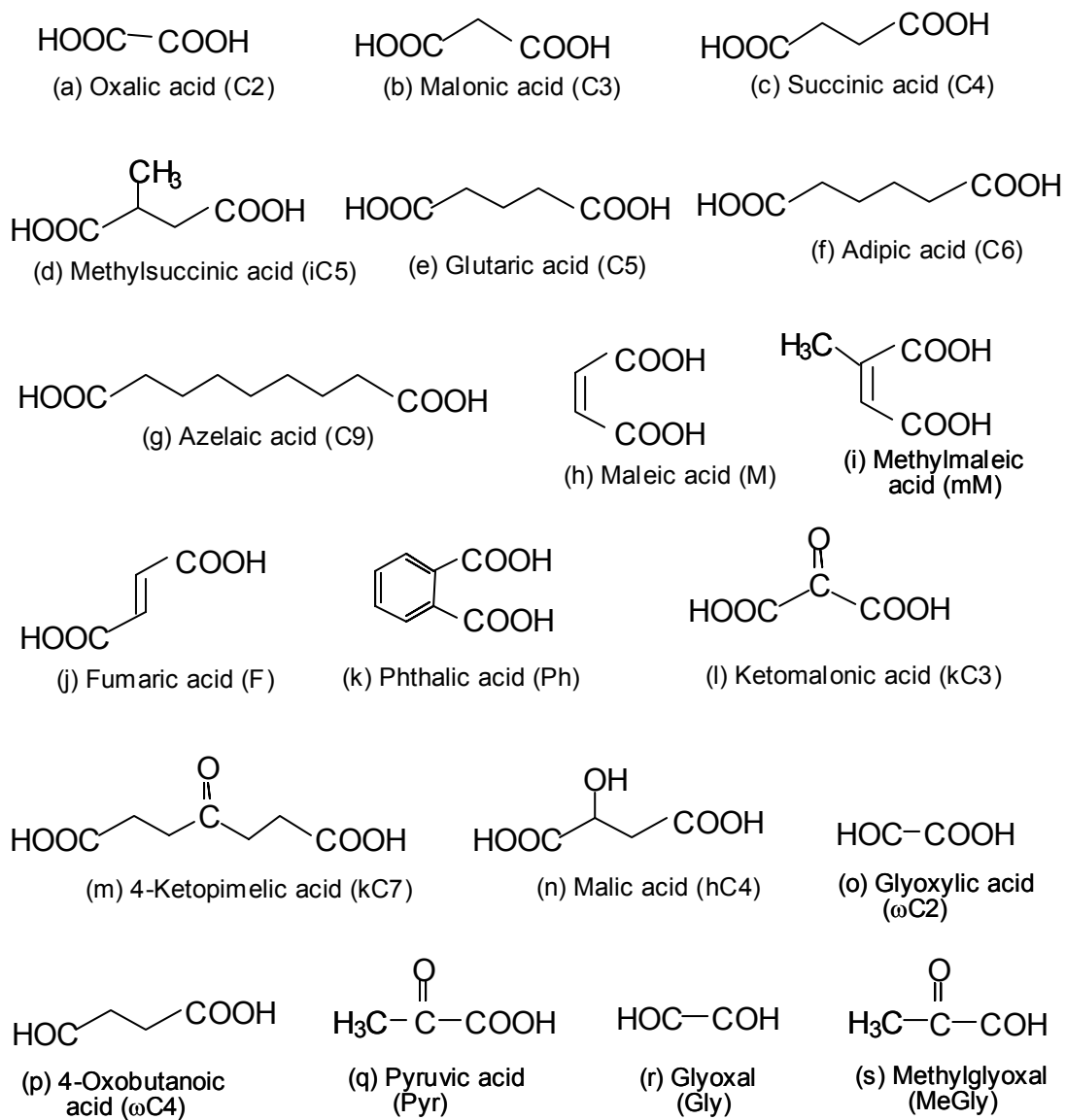


Fig. 3

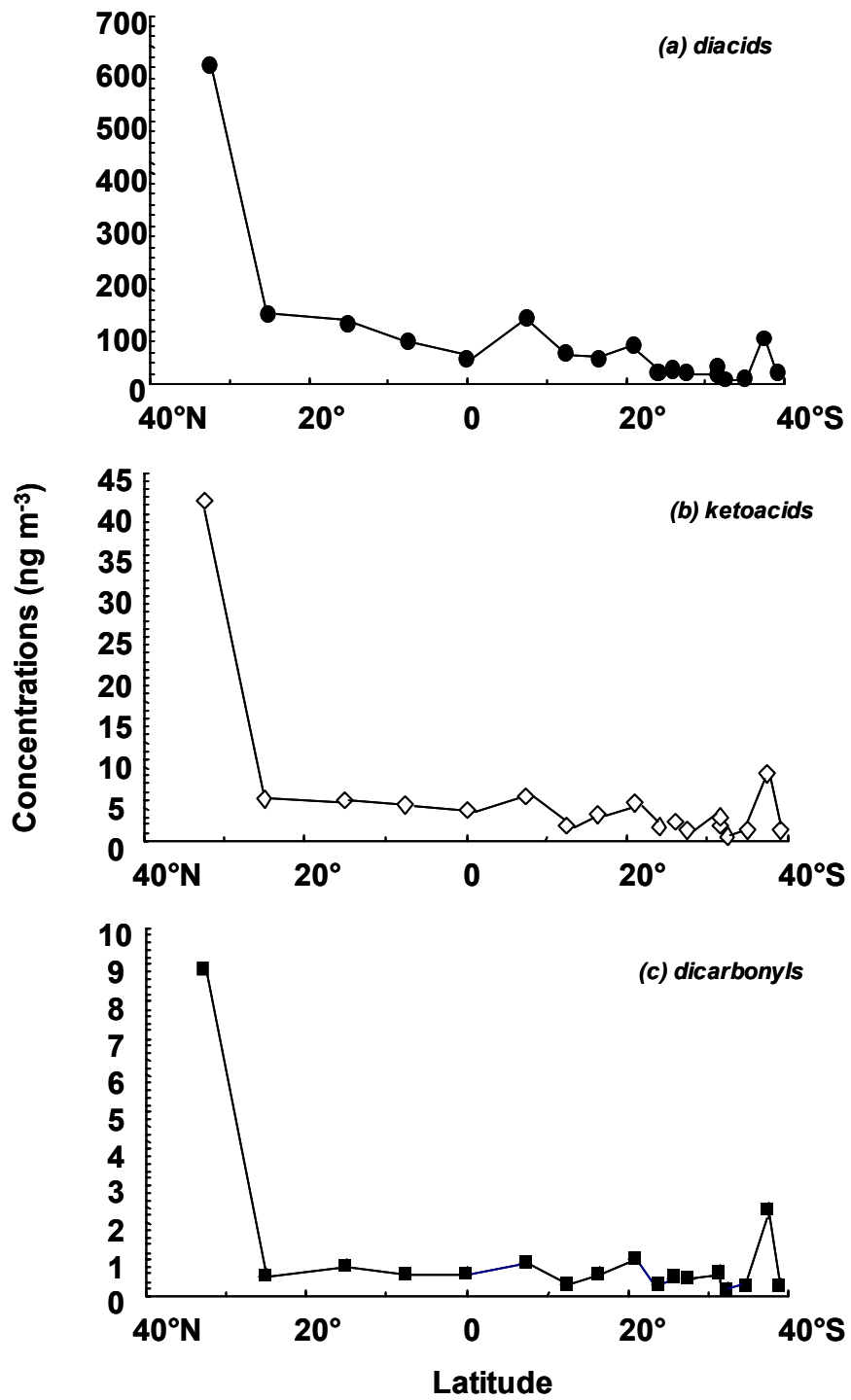


Fig. 4

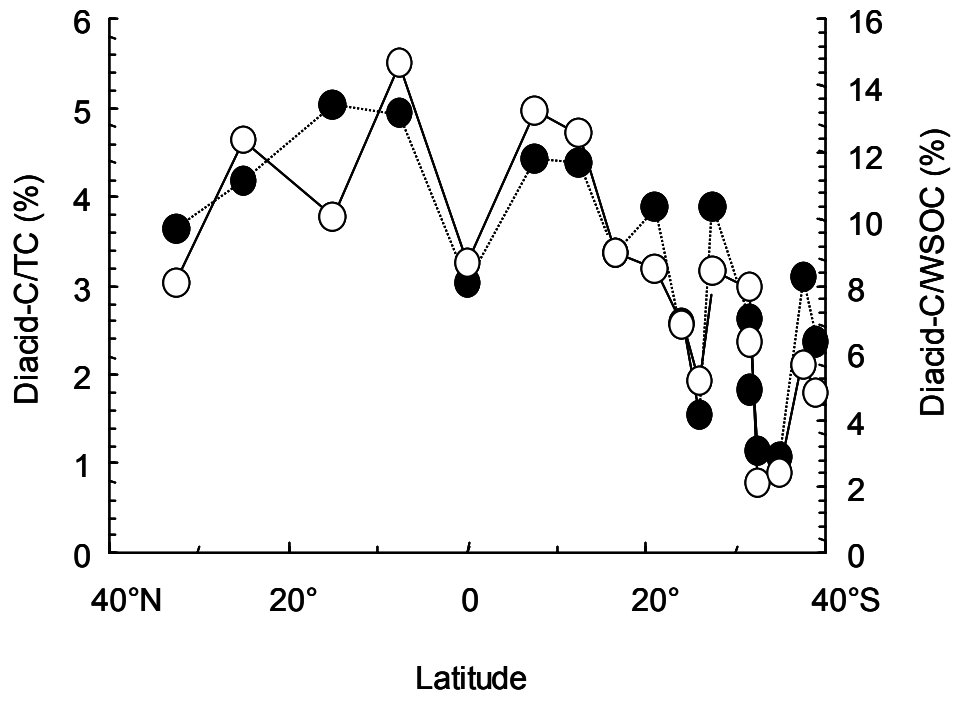


Fig. 5

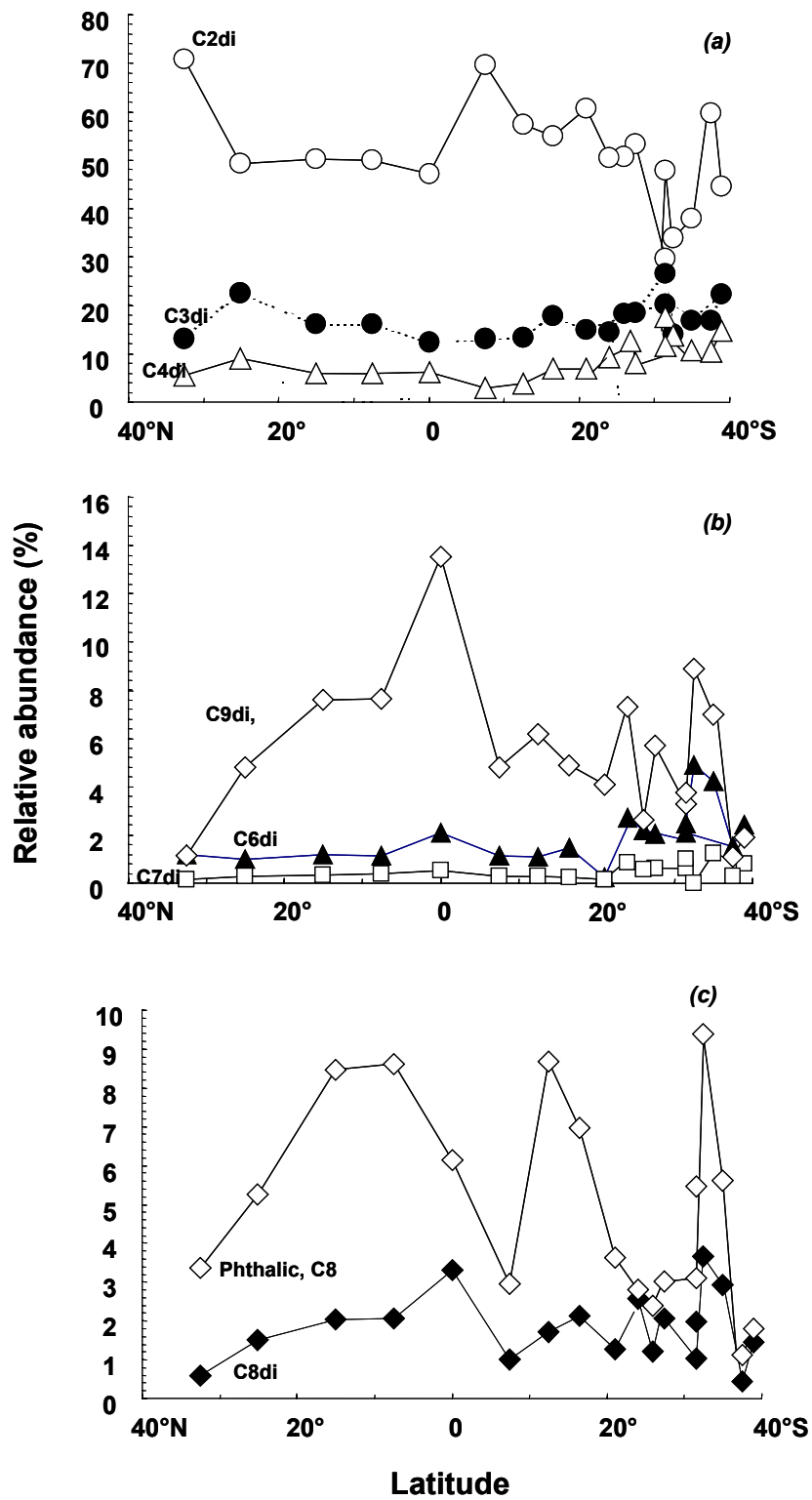


Fig. 6

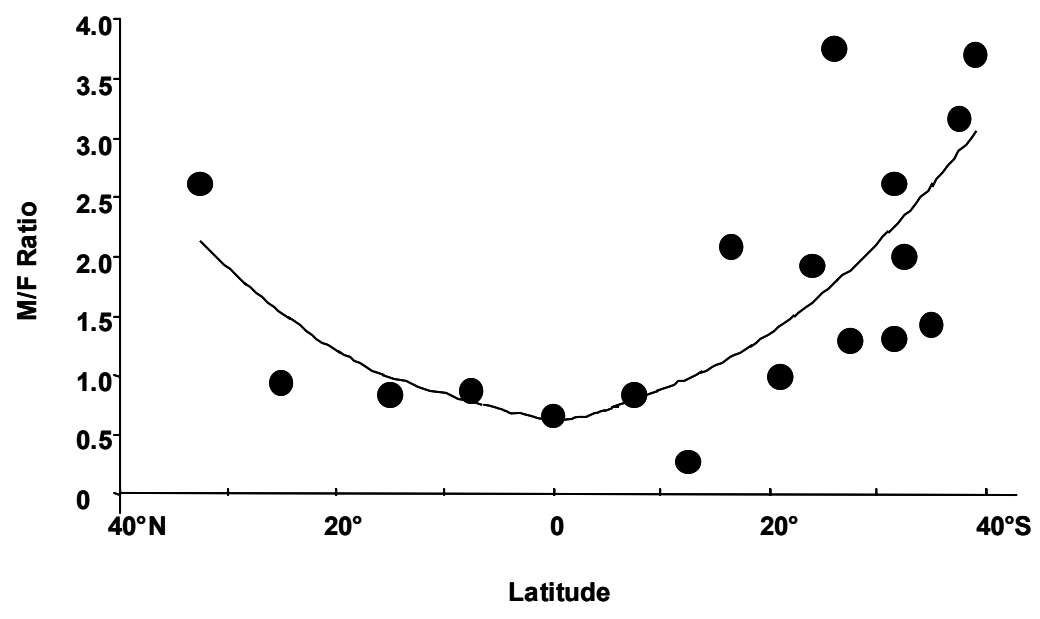
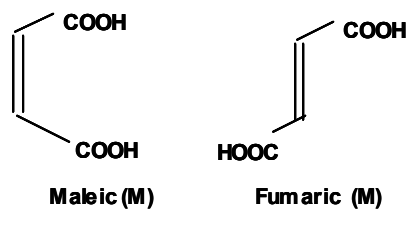


Fig. 7

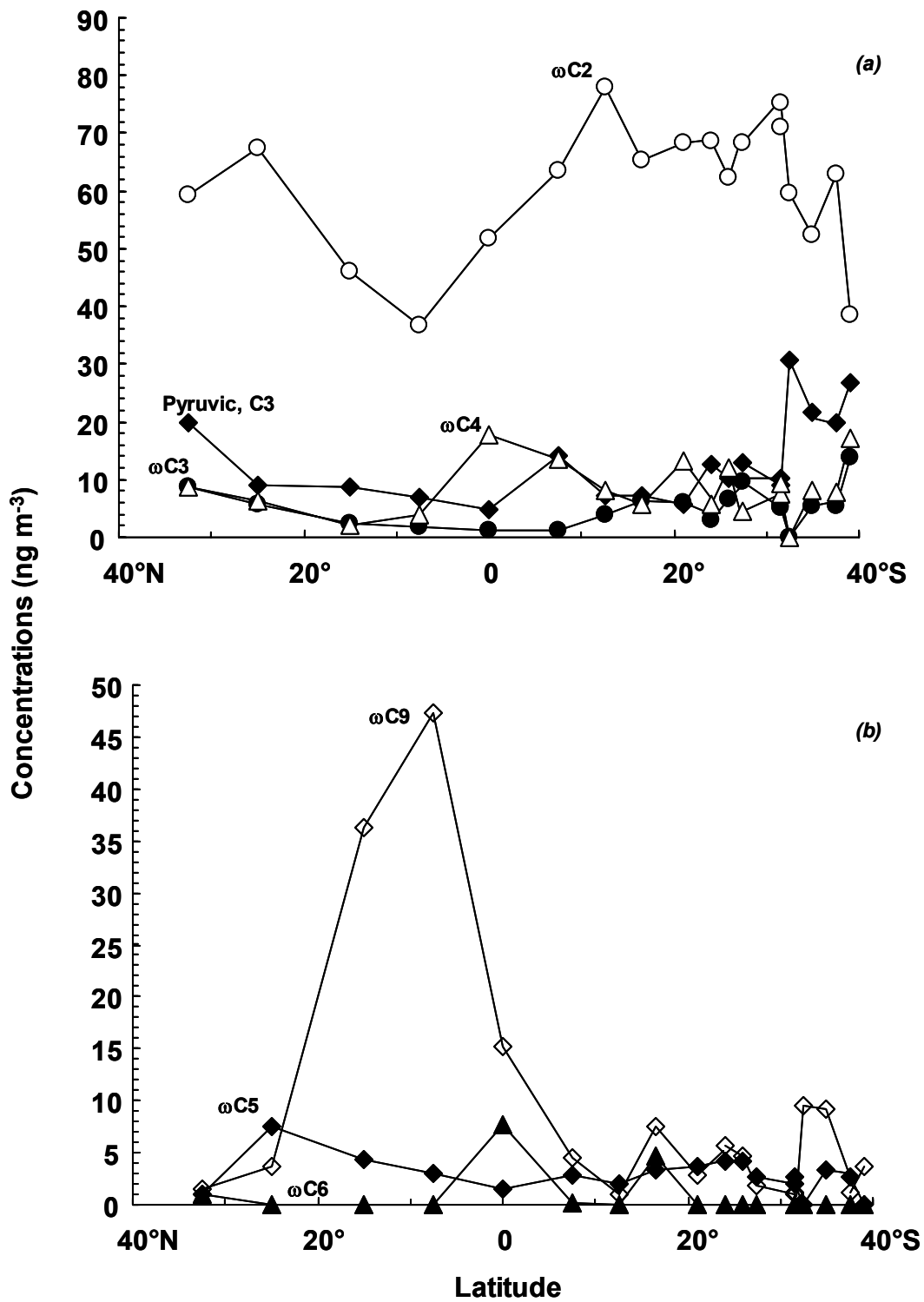


Fig. 8

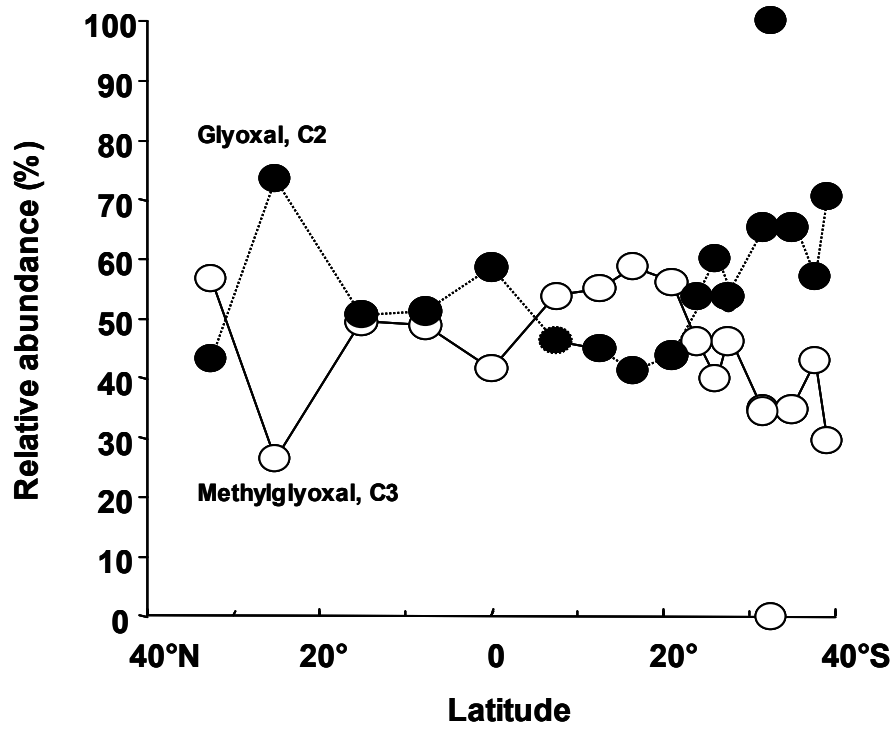


Fig. 9

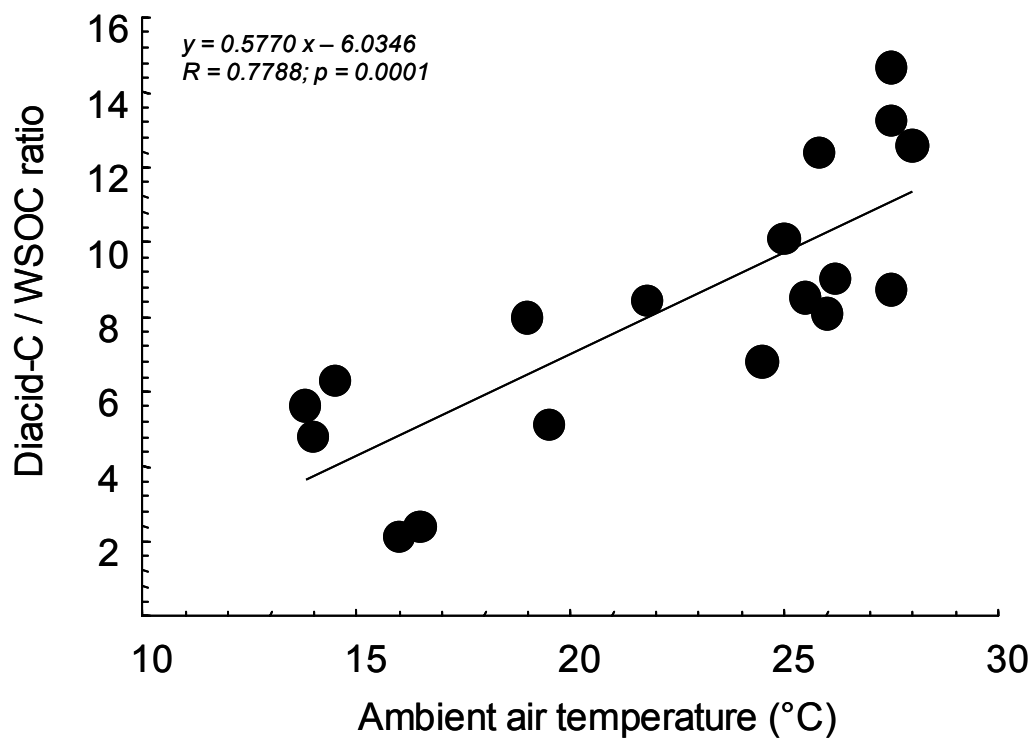


Fig. 10

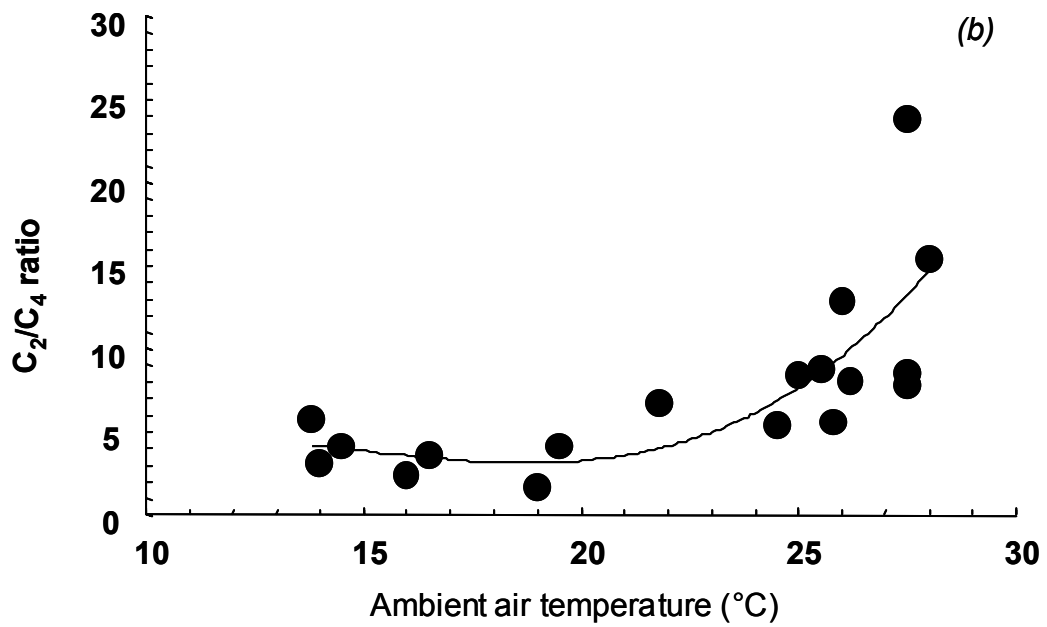
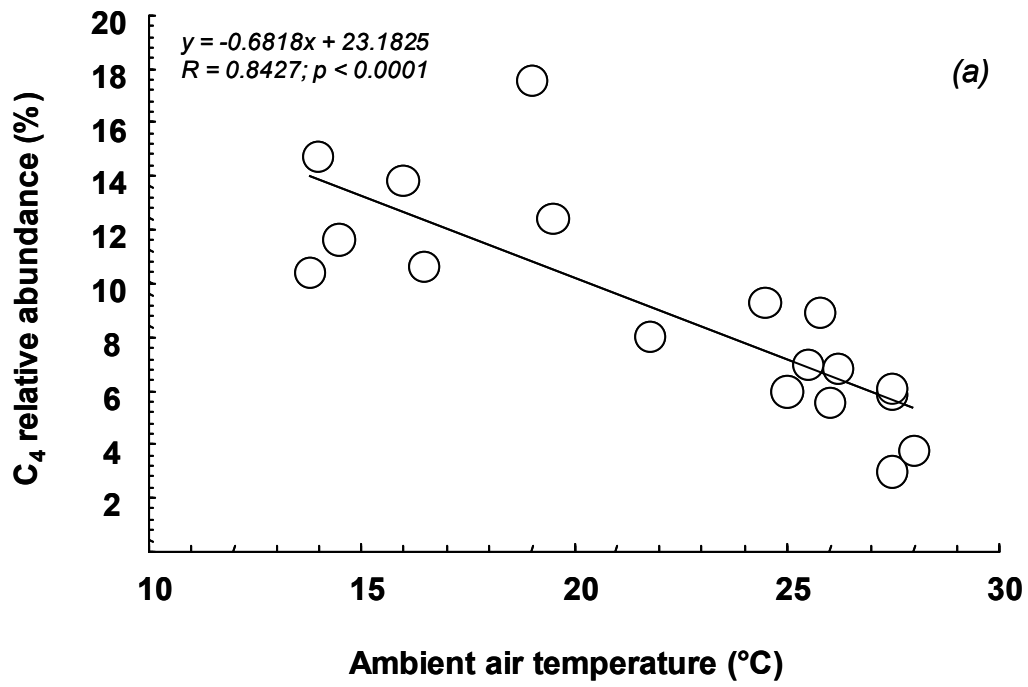


Fig. 11

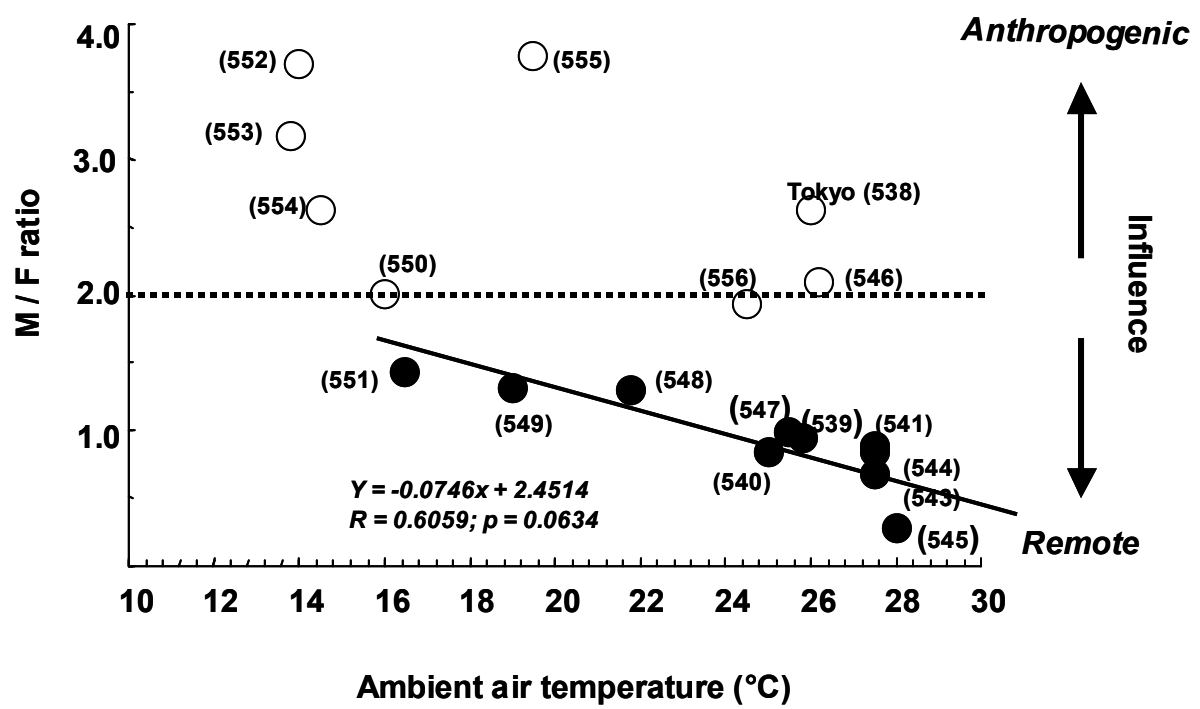


Fig. 12

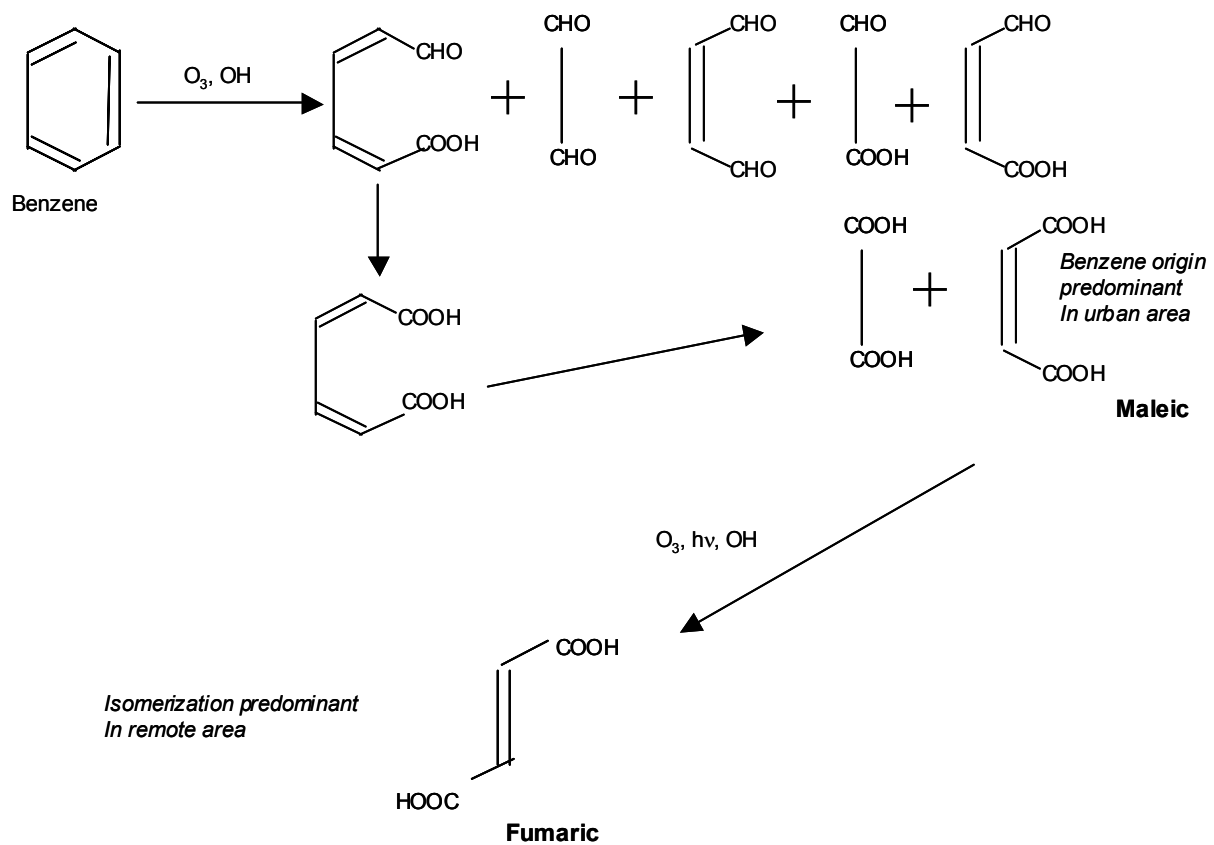


Fig. 13

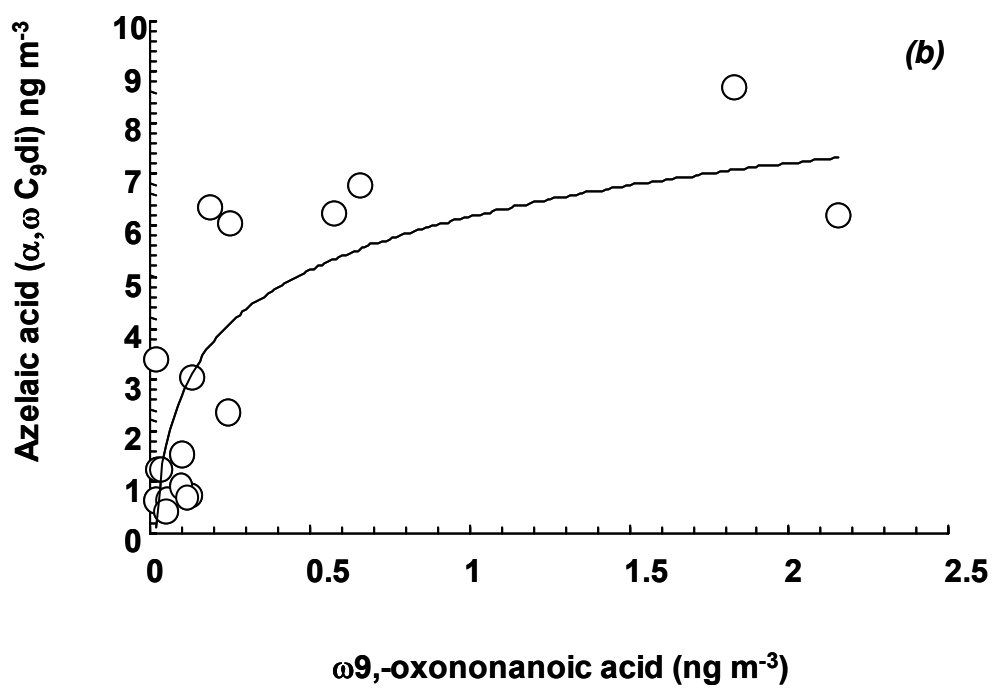
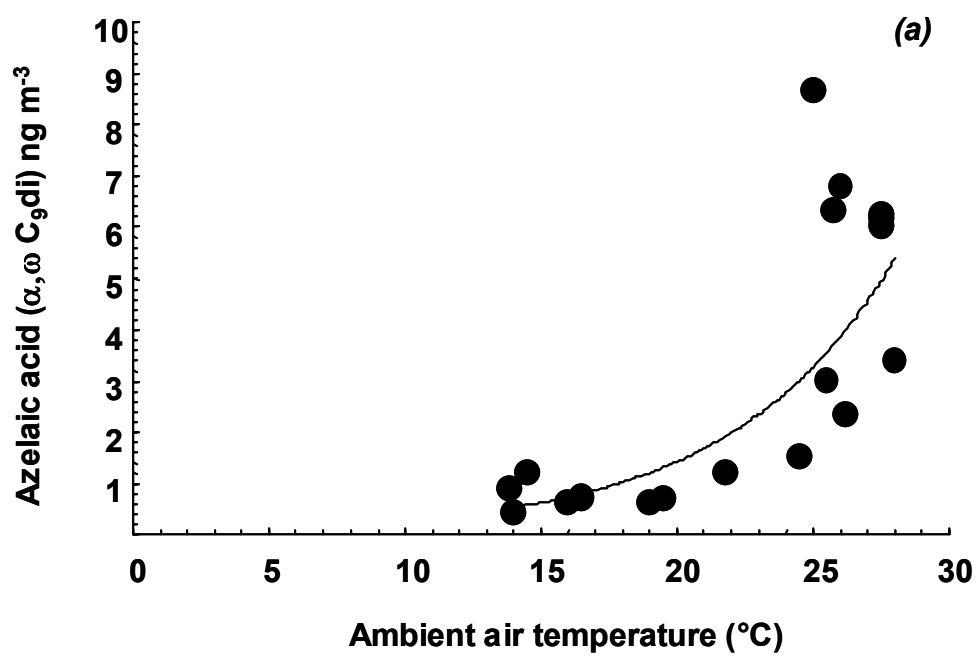


Fig. 14