<Revised JOCH1684-A to *Journal of Atmospheric Chemistry*>

Running head:
Water-soluble organic compounds in marine aerosols

Article type:
Research article (an observational and interpretative study of the composition of atmospheric aerosols)

Title:
Water-soluble dicarboxylic acids, ketoacids and dicarbonyls in the atmospheric aerosols over the Southern Ocean and western Pacific Ocean

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Abstract

Water-soluble dicarboxylic acids (DCAs), ketoacids, and α-dicarbonyls in the marine aerosol samples collected over the Southern Ocean and western Pacific Ocean were determined. Oxalic acid was the most abundant species, followed by malonic acid and then succinic acid. It is suggested that aerosol concentrations of the organics over the Southern Ocean in this work represent their global background levels. Over the Southern Ocean, total concentrations of DCAs ranged from 2.9 to 7.2 ng m^{-3} (average: 4.5 ng m^{-3}), ketoacids from 0.14 to 0.40 ng m^{-3} (av.: 0.28 ng m^{-3}), and dicarbonyls from 0.06 to 0.29 ng m^{-3} (av.: 0.11 ng m^{-3}). Over the western Pacific, total concentrations of DCAs ranged from 1.7 to 170 ng m^{-3} (av.: 60 ng m^{-3}), ketoacids from 0.08 to 5.3 ng m^{-3} (av.: 1.8 ng m^{-3}), and dicarbonyls from 0.03 to 4.6 ng m^{-3} (av.: 0.95 ng m^{-3}). DCAs over the western Pacific have constituted a large fraction of organic aerosols with a mean DCAs-C/TC (total carbon) of 7.0% (range: 0.59 – 14%). Such a high value was in contrast to the low DCAs-C/TC (av.: 1.8%; range: 0.89 – 4.0%) for the Southern Ocean aerosols. Based on the relative abundances and latitudinal distributions of these organics, we propose that long-range atmospheric transport is more important over the western Pacific Ocean, in contrast, *in situ* photochemical production is more significant over the Southern Ocean although absolute concentrations of the organics are much lower.

Keywords: Global background; Latitudinal distributions; Photochemical reactions; Remote marine aerosols; Sources; Water-soluble organics.

1. Introduction

Water-soluble organic species in atmospheric aerosols have a potential contribution to the formation of cloud condensation nuclei because of their water-soluble and hygroscopic

properties (Kawamura and Usukura, 1993; Saxena et al., 1995; Ansari and Pandis, 2000; Kerminen et al., 2000). Also, they are involved in a series of chemical reactions occurring in gas phase, aerosols and cloud water (Chebbi and Carlier, 1996). Low molecular weight (LMW) dicarboxylic acids (DCAs) and related polar compounds (particularly small DCAs) constitute a substantial fraction in water-soluble organics and have been found to be ubiquitous in the atmosphere (Saxena and Hildemann, 1996). Measurement of these water-soluble organics in marine aerosols is important for the understanding of their long-range transport, photochemical production and transformation, and global background concentration levels. Water-soluble DCAs, ketoacids and dicarbonyls have been detected in the marine aerosols and rain water over the western and central Pacific (Kawamura and Usukura, 1993; Sempéré and Kawamura, 1996; Kawamura and Sakaguchi, 1999; Kawamura et al., 2003; Mochida et al., 2003a; Mochida et al., 2003b; Narukawa et al., 2003; Sempéré and Kawamura, 2003). Some DCAs have also been determined in the marine aerosols over the Indian Ocean and Atlantic Ocean (Baboukas et al., 2000; Neusüß et al., 2002), and in the cloud water off central California coast (Hegg et al., 2002). However, their atmospheric concentrations in the marine aerosols over the Southern Ocean have not been reported although they have been measured in the atmospheric aerosols over the Antarctica (Kawamura et al., 1996b).

A number of sources for LMW DCAs and related polar compounds have been proposed in the literature, including primary emissions such as vehicle exhausts and biomass burning (Kawamura and Kaplan, 1987; Narukawa et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002; Gao et al., 2003), and secondary photochemical production (Kawamura and Gagosian, 1987; Satsumabayashi et al., 1990; Stephanou and Stratigakis, 1993). Nevertheless, some uncertainties still remain on their origins and formation mechanism, especially in the remote marine atmosphere far from pollution sources.

This paper reports atmospheric concentrations of water-soluble DCAs, ketoacids, and α-dicarbonyls in the marine aerosols over the Southern Ocean and western Pacific Ocean. The relative abundances and latitudinal variations of these organics are analysed in detail to better understand their sources/formation pathways in the remote marine atmosphere. Principal component analysis (PCA) is also used to discuss the sources of these organic compounds.

2. Experimental

2.1. Aerosol sampling

Marine aerosols were collected on preheated (450^{o}C, > 3 hours) quartz fibre filters (20 × 25 cm^{2}) using a high volume air sampler (Shibata HVC 1000) at the upper deck of the R/V *Hakuho Maru* during the cruise KH94-4 (November 22, 1994 to February 11, 1995). The sampler was operated under the control of the wind sector (± 45^{o}) and wind speed (≥ 5 m s^{-1}) system to avoid a potential contamination from ship exhausts. Consequently the actual sampling time period for a filter varied. Typically the sampling finished within two days. The cruise track is shown in Fig. 1 together with surface wind conditions.

The exposed filter was placed in a clean glass jar (wide mouth 150 mL) with a Teflon-lined cap and stored in a dark freezer room at –20 ^{o}C before analysis (although the filters had been stored for 10 years, degradation of organics on the filters should be insignificant under such a low temperature). Field blanks were obtained by the method used for the real sampling, except for exposing a filter to the air for a few seconds.

The total aerosol mass collected on a filter was measured gravimetrically by the mass difference before and after sampling (without controlling relative humidity, but in a air-conditioned room).

Quartz fibre filters may adsorb organic vapours that would contain or form the speciated

organic compounds, causing positive artefacts. On the other hand, some of the measured organics especially dicarbonyls and ketoacids may partially evaporate from the filters, resulting in negative artefacts.

2.2. Chemical analysis

An aliquot of the filter sample was analysed for total carbon (TC) content using a Fisons NA-1500 elemental analyser. Nitrate and methane sulfonate (MSA) ions were determined by ion chromatography. Water-soluble DCAs, ketoacids, and α-dicarbonyls were determined using the methods reported previously (Kawamura and Ikushima, 1993; Kawamura, 1993). Briefly, an aliquot (typically one eighth) of a filter was cut in small pieces and extracted with ultra-pure organic-free water in an ultrasonic bath. The water extracts were then concentrated to nearly dryness by a rotary evaporator under vacuum, and then derivatised to butyl esters and/or dibutyl acetals by reacting with 14% BF_3 in n-butanol. Lastly the derivatives were determined using a HP 6890 gas chromatograph equipped with a fused silica capillary column (HP-5, 0.2 mm × 25 m × 0.52 μm) and an FID detector.

Once a filter was extracted using pure water, the water extract was derivatised immediately and the derivatised fraction was kept in a freezer at –30 ^{o}C prior to GC-FID analysis. Experiments have found that the recovery is ca. 80% for oxalic acid, and ca. 90% for malonic, succinic, glutaric and adipic acids.

Field blanks were also analysed using the same procedures. Relatively high blank values were found for phthalic and glyoxylic acids (although they are generally less than 10 percent of real samples). The reported concentrations of the detected water-soluble species have been corrected for the field blanks.

2.3. Air mass back trajectory

Backward air mass trajectories were conducted using the Fifth-Generation NCAR/Penn State

meso-scale model (MM5). The trajectory calculation was based on backward tracking of selected air parcels, assuming that they were moving along the ambient airflow. The flow pattern was updated every 6 hours.

3. Results and Discussion

3.1. General latitudinal profiles of atmospheric concentrations and carbon contents

Table 1 summarises atmospheric concentrations of the speciated DCAs, ketoacids, and α-dicarbonyls in the marine aerosols over the Southern Ocean (> 50^{o} S, 130^{o} E – 150^{o} E) and western Pacific Ocean (35^{o} N - 50^{o} S), together with concentrations of total aerosol mass and TC. TC concentrations over the Southern Ocean are significantly lower than those of the western Pacific. In contrast, the aerosol mass concentrations over the Southern ocean are, on average, more than twice higher than those of the western Pacific. This suggests that marine aerosols over the Southern Ocean have been strongly influenced by sea salts. In fact, average concentration of Na^{+} was found to be higher in the Southern Ocean aerosols than the western Pacific (Kawamura, unpublished data). In both regions, DCAs are far more abundant than ketoacids and dicarbonyls.

On the other hand, aerosol concentrations of nearly all the speciated organics over the Southern Ocean are significantly lower than those of the western Pacific. On average, total concentrations of DCAs in the Southern Ocean aerosols are more than ten times lower than those of the western Pacific samples; and total concentrations of ketoacids and dicarbonyls in the Southern Ocean aerosols are more than five times lower than the western Pacific samples. Given that greater negative artefacts caused by evaporation might be associated with the western Pacific samples (much higher temperature than the Southern Ocean), actual differences in the aerosol concentrations between the both regions would be even larger. Moreover,

concentrations of DCAs, ketoacids, and dicarbonyls over the Southern Ocean are also lower than those previously reported in the marine aerosols over the western and central Pacific (Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999; Mochida et al., 2003a; Mochida et al., 2003b; Sempéré and Kawamura, 2003) and Indian Ocean (Neusüß et al., 2002), and those reported from continental background (Limbeck and Puxbaum, 1999) and the Arctic aerosols (Kawamura et al., 1996a). Concentrations of the speciated organics over the Southern Ocean are similar to those of the sub-micron aerosol samples collected in the Antarctica (at Syowa Station in 1991), except for the summer sample in Antarctica which showed higher concentrations (Kawamura et al., 1996b). These results lead to a conclusion that the atmospheric concentrations of the speciated organics in the marine aerosols over the Southern Ocean in this work represent their global background levels.

Concentrations of the organics detected in the marine aerosols over the western Pacific are comparable to those reported previously over the Pacific Ocean (Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999), but significantly lower than those over the East China Sea and the Sea of Japan (Mochida et al., 2003a; Kawamura et al., 2004). This indicates that continental air masses over the Asian Continent have a great impact on the occurrence of the water-soluble organics in the marine atmosphere over the North Pacific. However, the concentrations over the western Pacific in this work are significantly higher than those observed in a previous cruise, which was conducted in the similar region but in a different season (September to October 1992) (Sempéré and Kawamura, 2003). The difference in the concentrations of the organics might be caused by different meteorological conditions and thus different source strength encountered during the two sampling campaigns.

Substantially higher concentrations of DCAs, ketoacids and dicarbonyls were detected in six samples (QFF655, 689, 663, 672, 662 and 674), which were collected in the regions near the

continents and under strong wind conditions from continents (see Fig. 1). In contrast, QFF682, collected under a strong wind condition from the ocean in the same region as QFF672 and 674, showed significantly lower concentrations of the water-soluble organics (comparable to those of the Southern Ocean). Similarly, QFF658, which was collected in a similar region as QFF689, also showed much lower concentrations. As seen in Fig. 1, although QFF658 was collected under a weak wind condition a strong wind from the ocean occurred before its collection. These observations suggest that atmospheric concentrations of the speciated organics over the western Pacific have been strongly influenced by the outflow of continental air masses, and that the relative strength of their marine sources may have been significantly weaker in this region. Backward air mass trajectories confirm that outflow of continental air masses had a great impact on the western Pacific atmosphere (see Fig. 5a for an example).

Interestingly, the organics detected around the Equator were found to be significantly less abundant than those in other regions of the western Pacific (see Fig. 2a). As seen in Fig. 1, the samples collected around the Equator have experienced relatively weak winds mostly from the ocean. Moreover, dicarbonyls are semi-volatile and can be quickly removed from the atmosphere by photolysis when solar radiation is strong (Munger et al., 1995). This is the most likely reason why dicarbonyls had very low aerosol concentrations around the Equator (similar to those over the Southern Ocean). Ketoacids can also undergo fast photolysis (Grosjean, 1989) and ketoacids and DCAs have been reported to show semi-volatile behaviour (Limbeck et al., 2001).

Carbon contents of the speciated organic compounds relative to aerosol TC are also lower over the Southern Ocean than those of the western Pacific, particularly for DCAs-C/TC (see Fig. 2b). Total DCAs-C/TC ratios over the Southern Ocean ranged from 0.89 to 4.0% with a mean of 1.8%. Whereas those of the western Pacific ranged from 0.59 to 14% with a mean of 7.0%. This

confirms that DCAs have constituted a significant fraction of organic aerosols in the marine atmosphere over the western Pacific. Similar results have been observed in the remote marine aerosols over the central Pacific (Kawamura and Sakaguchi, 1999). Since there are no important sources for elemental carbon in the Southern Ocean, water-insoluble organic compounds might have been more enriched in the aerosols in this region. Unsaturated fatty acids are a likely source of aerosol TC since they are major lipid components in the marine algae and are enriched in the micro-layers of sea surfaces (Marty et al., 1979). The levels of DCAs-C/TC over the western Pacific in this work are significantly higher than those (1.3 to 4.6%) observed in Tokyo (Sempéré and Kawamura, 1994), demonstrating that photochemical production of DCAs during the long-range atmospheric transport may be important in the Pacific.

Ketoacids-C/TC and dicarbonyls-C/TC over the western Pacific are similar to those previously reported for the above-mentioned cruise conducted in the similar region (Sempéré and Kawamura, 2003). However, the mean of DCAs-C/TC over the western Pacific in this work is about twice higher than that of the previous campaign.

Table 2 indicates that over both the Southern Ocean and western Pacific Ocean, either total concentrations of DCAs, ketoacids and dicarbonyls, or their carbon contents in aerosol TC show good correlations each other (though correlation between DCAs and dicarbonyls over the Southern Ocean is relatively poor). This suggests that these organic compounds are originated from similar sources and/or formation pathways. Most likely, this may have arisen from the fact that their chemical structures and hydrophilic properties are similar and they are involved in a series of chain reactions occurring in the atmosphere.

3.2. Relative abundances of individual compounds and their latitudinal distributions

3.2.1. Dicarboxylic acids

Normal saturated DCAs. Oxalic acid (C_2) was the most abundant species followed by malonic

acid (C_3) and then succinic acid (C_4), being consistent with the findings in most of previous studies. Over the Southern Ocean, oxalic acid constituted 42 to 67% of total DCA mass with a mean of 52%; malonic acid ranged from 11 to 21% (mean: 17%); succinic acid ranged from 7.0 to 15% (mean: 9.8%). In contrast, in some aerosol samples collected over the Antarctica succinic acid was more abundant than oxalic acid (Kawamura et al., 1996b). Over the western Pacific, oxalic acid was even more enriched, constituting 51 to 80% of total DCA mass with a mean of 65%; malonic acid comprised 14 to 26% (mean: 19%); succinic acid ranged from 1.2 to 14% (mean: 6.9%). The relative abundance levels of the three acids over the western Pacific are comparable to those in the marine aerosols reported previously in the Pacific region (Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999; Sempéré and Kawamura, 2003).

The latitudinal variations of their relative abundances (molar ratios to total DCAs) are shown in Fig. 3a. Clearly, oxalic acid shows lower ratios over the Southern Ocean than those of the western Pacific. In contrast, succinic acid virtually presents a reverse pattern. It has been suggested that larger DCAs and related compounds are the precursors of oxalic acid. For example, succinic acid may be derived from larger molecules and can further undergo photochemical decomposition to result in oxalic and malonic acids with malic acid as an intermediate. Malonic acid can also decompose to form oxalic acid (Kawamura et al., 1996b; Kawamura and Sakaguchi, 1999). Therefore, the observations suggest that water-soluble organics in the marine aerosols over the Southern Ocean may have been produced mainly through *in situ* photochemical reactions with relatively insignificant contribution from long-range atmospheric transport. Otherwise, the organic aerosols would have been more enriched with oxalic acid over the Southern Ocean after long-range transport. Backward air mass trajectories found that the air masses for the Southern Ocean samples originated from the Southern Ocean and Antarctica (see Fig. 5b for an example).

Their precursors over the Southern Ocean may be predominately derived by sea-to-air emissions of biogenic organic compounds including unsaturated fatty acids, phenolic compounds (Kawamura et al., 1996b) and olefins (Warneck, 2003). It has been suggested that in the remote marine atmosphere, water-soluble organic aerosol composition is mainly controlled by photochemical reactions (Kawamura et al., 1996b). Significantly higher concentrations of DCAs in the summer aerosols over the Antarctica than those over the Southern Ocean further support the hypothesis (during the transport of their precursors emitted from the Southern Ocean to the Antarctica, more water-soluble organics can be produced by photochemical reactions).

In general, longer-chain DCAs are significantly less abundant, where azelaic acid (C_9) is usually the most abundant in the range of C_7 to C_{12}. Similar results were obtained in this work. The latitudinal changes of the relative abundances of glutaric (C_5), adipic (C_6) and azelaic acids (Fig. 3b) are quite similar to succinic acid.

Branched DCAs. Three branched DCAs, i.e. methylmalonic (iC_4), methylsuccinic (iC_5) and methylglutaric (iC_6) acids, were detected, though they were significantly less abundant than the corresponding straight-chain DCAs. It is interesting to note that iC_4 was not detected when the average ambient temperature was below 2^o C but its concentration level was comparable to C_6 over the western Pacific. The relative abundances of iC_4 and iC_6 did not show large spatial changes although iC_5 was more abundant in some samples over the Southern Ocean (Fig. 3c).

Unsaturated DCAs. Unsaturated DCAs, i.e. maleic (M), fumaric (F), and methylmaleic (mM) acids, are thought to be the products of the photochemical oxidation of aromatic hydrocarbons including benzene and toluene. M may be further converted to F by photochemical isomerisation (Kawamura and Ikushima, 1993). They were also detected as minor species and their relative abundances were slightly higher over the Southern Ocean (Fig. 3d). As seen in Fig. 3d, M is usually more abundant than F, being consistent with the previous observations

conducted in the western Pacific (Sempéré and Kawamura, 2003). However, the molar ratios of F/M in this work are significantly lower than those reported for the central Pacific where F was much more abundant than M (Kawamura and Sakaguchi, 1999). M may be significantly converted to F in the equatorial central Pacific where solar radiations are stronger (Kawamura and Sakaguchi, 1999). Further, relatively longer residence time of the air parcels over the central Pacific than that of the western Pacific and Southern Ocean may also contribute to this.

Hydroxylated and keto DCAs. The DCAs having an additional functional group including malic (hC_4), oxomalonic (kC_3) and oxopimelic (kC_7) acids were detected as minor species. Their molar ratios to total DCAs were larger over the Southern Ocean than those of the western Pacific (Fig. 3e). These tri-functional organic compounds have been proposed as precursors of oxalic acid (Kawamura and Sakaguchi, 1999).

Aromatic DCAs. On average, phthalic acid (Ph) was the fifth most abundant species among the detected organics over the Southern Ocean, with a median concentration being higher than glutaric acid. Its median concentration over the western Pacific was comparable to glutaric acid. In contrast, the concentrations of iso-phthalic (i-Ph) and tere-phthalic (t-Ph) acids were generally very low. Previous study found that concentrations of Ph were even higher than malonic acid in most of the Antarctica aerosol samples (Kawamura et al., 1996b). Although the Southern Ocean aerosols showed higher relative abundances of the aromatic DCAs (Fig. 3f), they still had lower absolute concentrations of the organics than the western Pacific samples.

Diesters of phthalic acid are widely used as plasticisers in polyvinyl chloride and other plastics. Ph is a degradation product of the diesters and high concentrations of Ph have been reported in sewages and landfill leachates (Jonsson et al., 2003; Marttinen et al., 2003). Ph has also been found to be one of the major DCA species in motor exhausts (Kawamura and Kaplan, 1987). Ph has also been proposed (Kawamura and Sakaguchi, 1999) to be derived from

photochemical oxidation of polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and its alklated forms (from incomplete combustion of fossil fuels), as well as phenolic compounds that are present in sea surface slicks (Carlson, 1982). Laboratory experiments have confirmed the presence of Ph in the photo-degradation products of PAHs (Jang and Mcdow, 1997). On the other hand, both iso- and tere-Ph are thought to be from primary vehicular emissions (Fine et al., 2004).

3.2.2. Ketoacids and α-dicarbonyls

Glyoxylic acid ($C_2\omega$) predominated in ketoacids. On average, it constituted 77% of total mass of ketoacids detected in the Southern Ocean aerosols and 65% in the western Pacific aerosols. In fact, it was the fourth most abundant species of the speciated organics. The second most abundant ketoacid was pyruvic acid (Pyr) followed by 4-oxobutanoic acid ($C_4\omega$) over the Southern Ocean. However, over the western Pacific the second most abundant ketoacid was 9-oxononanoic acid ($C_9\omega$) followed by Pyr. $C_2\omega$ was also found as the most abundant ketoacid in the previous campaign conducted in the western Pacific (Sempéré and Kawamura, 2003). Nevertheless, in some of the Antarctica aerosol samples Pyr was more abundant than $C_2\omega$ (Kawamura et al., 1996b). The latitudinal changes of relative abundances of ketoacids are shown in Fig. 4a. $C_9\omega$ shows the largest spatial variations with significantly higher relative abundances over the western Pacific than those of the southern Ocean.

$C_2\omega$ is the smallest oxoacid and thought to be one of the important intermediates in the formation of oxalic acid (Kawamura et al., 1996a; Warneck, 2003). It has been proposed that $C_9\omega$ can be formed by the photo-oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993). Higher relative abundance of $C_9\omega$ over the western Pacific may be explained by the fact that compared to the Southern Ocean, more unsaturated fatty acids may be emitted to the air from the warmer sea water and then undergo

stronger photochemical reactions in this region. In addition, terrestrial plants in the equatorial region may also emit a significant amount of unsaturated fatty acids to the atmosphere.

The latitudinal distributions for the relative abundances of dicarbonyls are illustrated in Fig. 4b. Although glyoxal (Gly) is generally more abundant than methylglyoxal (MeGly) over the Southern Ocean, their relative abundances vary over the western Pacific.

3.3. Source studies using principal component analysis

To further investigate the possible sources of the speciated organics, the data sets of their atmospheric concentrations in the western Pacific aerosols (n= 16) and those for the Southern Ocean (n = 10) were subjected to PCA. PCA has been applied previously for the source studies of these organics (Kawamura and Sakaguchi, 1999; Mochida et al., 2003a). To reduce the number of variables, only the chemical species that have relatively higher concentrations and are representatives of a certain compound class were chosen for PCA. NO_3^- and MSA ions were also included to indicate anthropogenic and secondary marine sources, respectively (Seinfeld and Pandis, 1998). Because the number of samples is too small and most of the variables are highly noisy (due to very low concentrations) for the Southern Ocean data, the PCA results are not presented here. Previous research has found that careful choice of chemical species included in a receptor model is very important in order to obtain reliable results since highly noisy variables could substantially distort the solutions (Huang et al., 1999; Paatero and Hopke, 2003). In fact, over the Southern Ocean NO_3^- concentrations were found to be very low and below detection limit in half of the samples (Kawamura, unpublished data), further suggesting that influence of terrestrial polluted air masses is insignificant in this region and *in situ* photochemical production may be more important for the speciated organics.

The rotated component matrix of the western Pacific data set by PCA with varimax rotation is given in Table 3. Three components were retained as suggested by the scree test,

which can explain 92% of the variance. Component 1 (explaining 65% of variance) clearly indicates a long-range atmospheric transport source since it has high loadings of NO_3^- and all the major speciated organics. Component 2 (explaining 15% of variance) has high loadings of C_8 and C_9 DCAs as well as maleic and glyoxylic acids, possibly representing a source of *in situ* photochemical production. C_8 and C_9 DCAs are considered to be photo-oxidation products of biogenic unsaturated fatty acids (Stephanou and Stratigakis, 1993) and the unsaturated DCAs to be derived from the photo-oxidation of aromatic hydrocarbons as mentioned above. Recently Warneck (2003) proposed an in-cloud formation pathway of oxalic acid from olefins where glyoxylic is a key intermediate. A field study (Crahan et al., 2004) has provided a support for this mechanism. A very weak loading of MSA on this component suggests that their precursors in the western Pacific may have had principal terrestrial origins. Alternatively, formation conditions for the speciated organics are very different from those for MSA. Component 3 (explaining 12% of variance) represents a marine source, manifested by a high loading of MSA. Interestingly, malonic acid has a quite strong association with this component.

4. Summary and Conclusions

Water-soluble dicarboxylic acids, ketoacids, and α-dicarbonyls in the marine aerosols collected over the Southern Ocean and western Pacific Ocean samples have been determined. Their concentrations over the Southern Ocean were found to be significantly lower than those of the western Pacific and those in the summer sample from the Antarctica. The concentration levels over the Southern Ocean were also lower than those observed in other marine environments and continental background sites. We thus propose that aerosol concentrations of the water-soluble organics over the Southern Ocean reported in this work represent the global background levels. It is suggested that long-range atmospheric transport of polluted air masses

is more important in controlling the water-soluble organics over the western Pacific, in contrast, *in situ* photochemical production more significant over the Southern Ocean that is far away from the major continental pollution sources.

Concentrations of the speciated organics around the Equator were found to be significantly lower than those in the rest of the western Pacific. This can be explained by several factors including meteorological conditions, source strength, and atmospheric chemistry. It was found that oxalic acid was the most abundant water-soluble species detected, followed by malonic acid and then succinic acid. In general, the latitudinal distribution of oxalic acid had an opposite trend to most of other DCAs. The comparison with aerosol carbon contents showed that DCAs have comprised a significantly larger fraction of aerosol organics over the western Pacific than the Southern Ocean.

Acknowledgements

We thank Mr. Niwai Takeji for his help in the sample collection and the cruise staff for their support during the R/V *Hakuho Maru* cruise (KH94-4). We also thank Prof. Keisuke Suzuki for IC analysis and Mrs. Tomomi Watanabe for her technical support. This study is in part supported by Japanese Ministry of Education, Science, Sports and Culture through grant-in-aids 14204055. Financial support from the Japan Society for the Promotion of Science to H.W. is also acknowledged.

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Table1

Summary of atmospheric concentrations of dicarboxylic acids, ketoacids and α-dicarbonyls in the aerosols collected over the Southern Ocean and western Pacific Ocean

Species (Abbre.)	*Southern Ocean (> 50°S, 130° - 150°E, n = 10)*		*Western Pacific (35°N - 50°S, n = 16)*	
	Range	*Mean/Median*	*Range*	*Mean/Median*
Aerosol mass	22-170	83/79	17-78	39/31
TC	0.05-0.23	0.11/0.09	0.06-5.5	0.67/0.16
		Dicarboxylic acids		
Oxalic (C_2)	1.4-4.2	2.4/2.0	0.98-98	38/26
Malonic (C_3)	0.46-1.3	0.75/0.67	0.32-43	12 /8.1
Succinic (C_4)	0.20-0.73	0.44/0.42	0.12-17	5.0/2.0
Glutaric (C_5)	0.08-0.27	0.14/0.13	0.03-5.5	1.2/0.32
Adipic (C_6)	0.04-0.14	0.07/0.06	0.03-1.5	0.47/0.17
Pimelic (C_7)	0.01-0.06	0.03/0.02	0.01-1.1	0.20/0.06
Suberic (C_8)	BDL-0.07	0.02/0.02	BDL-0.94	0.17/0.05
Azelaic (C_9)	0.03-0.14	0.05/0.04	0.03-1.8	0.39/0.20
Sebacic (C_{10})	BDL-0.03	0.01/0.01	BDL-0.49	0.07/0.02
Undecanedioic (C_{11})	0.01-0.05	0.02/0.02	0.01-0.36	0.10/0.07
Dodecanedioic (C_{12})	BDL-0.19	0.03/ BDL	BDL-0.07	0.01/ BDL
Methylmalonic (iC_4)	BDL-0.05	0.01/ BDL	0.02-1.2	0.44/0.33
Methylsuccinic (iC_5)	BDL-0.13	0.04/0.05	BDL-4.0	0.53/0.13
Methylglutaric (iC_6)	BDL-0.01	0.01/0.01	BDL-0.45	0.14/0.03
Maleic (M)	0.02-0.17	0.05/0.04	0.02-1.7	0.45/0.12
Fumaric (F)	0.01-0.05	0.03/0.02	BDL-1.0	0.23/0.07
Methylmaleic (mM)	0.01-0.03	0.02/0.02	0.01-1.3	0.23/0.08
Phthalic (Ph)	0.08-0.45	0.20/0.16	0.02-2.7	0.55/0.34
Iso-phthalic (iPh)	BDL-0.22	0.03/0.01	BDL-0.20	0.06/0.03
Tere-phthalic (tPh)	0.01-0.12	0.04/0.02	BDL-0.95	0.11/0.02
Malic (hC_4)	0.02-0.06	0.04/0.04	0.01-0.57	0.19/0.09
Oxomalonic (kC_3)	0.02-0.06	0.04/0.04	0.01-1.2	0.25/0.16
4-Oxopimelic (kC_7)	0.01-0.06	0.03/0.03	0.01-2.2	0.43/0.16
Subtotal	**2.9-7.2**	**4.5/4.0**	**1.7-170**	**60/39**
		Ketoacids		
Glyoxylic ($C_2\omega$)	0.08-0.36	0.22/0.21	0.02-3.9	1.3/0.46
3-Oxopropanoic ($C_3\omega$)	BDL-0.01	0.01/0.01	BDL-0.24	0.05/0.01
4-Oxobutanoic ($C_4\omega$)	BDL-0.03	0.02/0.02	BDL-0.31	0.05/0.02
9-Oxononanoic ($C_9\omega$)	BDL-0.02	0.01/0.01	BDL-1.0	0.29/0.19
Pyruvic (Pyr)	0.01-0.06	0.03/0.02	BDL-0.74	0.18/0.07
Subtotal	**0.14-0.40**	**0.28/0.25**	**0.08-5.3**	**1.8/0.75**
		α-Dicarbonyls		
Glyoxal (Gly)	0.03-0.24	0.07/0.06	0.02-1.1	0.24/0.10
Methylglyoxal (MeGly)	0.02-0.09	0.04/0.04	0.01-4.1	0.71/0.24
Subtotal	**0.06-0.29**	**0.11/0.09**	**0.03-4.6**	**0.95/0.35**
Total	**3.2-7.8**	**4.9/4.4**	**1.8-180**	**63/40**

Notes: The unit of aerosol mass and TC is μg m^{-3} and the unit of other species is ng m^{-3}; BDL = below detection limit.

Table 2

Correlations between total concentrations of the detected DCAs, ketoacids and dicarbonyls (a) and between their carbon contents in TC (b)（correlation coefficients over the Southern Ocean / correlation coefficients over the western Pacific）

(a)	DCAs	Ketoacids
Ketoacids	0.66 / 0.94	
Dicarbonyls	0.21 / 0.80	0.60 / 0.88

(b)	DCAs-C/TC	Ketoacids-C/TC
Ketoacids-C/TC	0.92 / 0.65	
Dicarbonyls-C/TC	0.45 / 0.72	0.67 / 0.71

Table 3

Rotated component matrix of principal component analysis on concentrations of selected chemical species in the western Pacific aerosols

Chemical species	*Component*		
	1 (65%)*	2 (15%)*	3 (12%)*
C_2	0.89	0.35	0.22
C_3	0.58	0.40	0.64
C_8	0.17	0.96	0.13
C_9	0.30	0.93	0.09
M	0.63	0.67	0.00
Ph	0.92	0.23	-0.19
$C_2\omega$	0.78	0.59	0.03
MeGly	0.90	0.23	-0.09
NO_3^-	0.91	0.16	0.21
MSA	-0.10	0.03	0.93

Notes: Rotation method is Varimax with Kaiser normalization. MSA = methane sulfonate. For other abbreviations, see Table 1. * The number in a parenthesis indicates the percentage of variance explained by this component.

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FIGURE CAPTIONS

Fig. 1

A figure showing the cruise track of KH94-4 and surface wind conditions. The numbers shown in the maps represent quartz fibre filter identification numbers used in the corresponding cruise periods. Arrows indicate wind directions with bold and regular arrows corresponding to the wind speeds above and below 7 m s^{-1}, respectively. (A) Legs 1 and 2: Leg 1 started from Tokyo, Japan in Nov. 22, 1994 and ended in Lyttelton, New Zealand in Dec. 9, 1994; Leg 2 started from the Southern Ocean in Dec. 19, 1994 and ended in Hobart, Australia in Jan. 4, 1995; (B) Legs 3 and 4: Leg 3 started from Hobart in Jan. 9, 1995 to the Southern Ocean and then back to Sydney, Australia in Jan. 28, 1995; Leg 4 started from Sydney in Feb. 1, 1995 and ended in Tokyo in Feb. 13, 1995.

Fig. 2

Latitudinal distributions for (a) total concentrations of dicarboxylic acids (DCAs), ketoacids and dicarbonyls; and for (b) their carbon contents in total carbon (TC).

Fig. 3

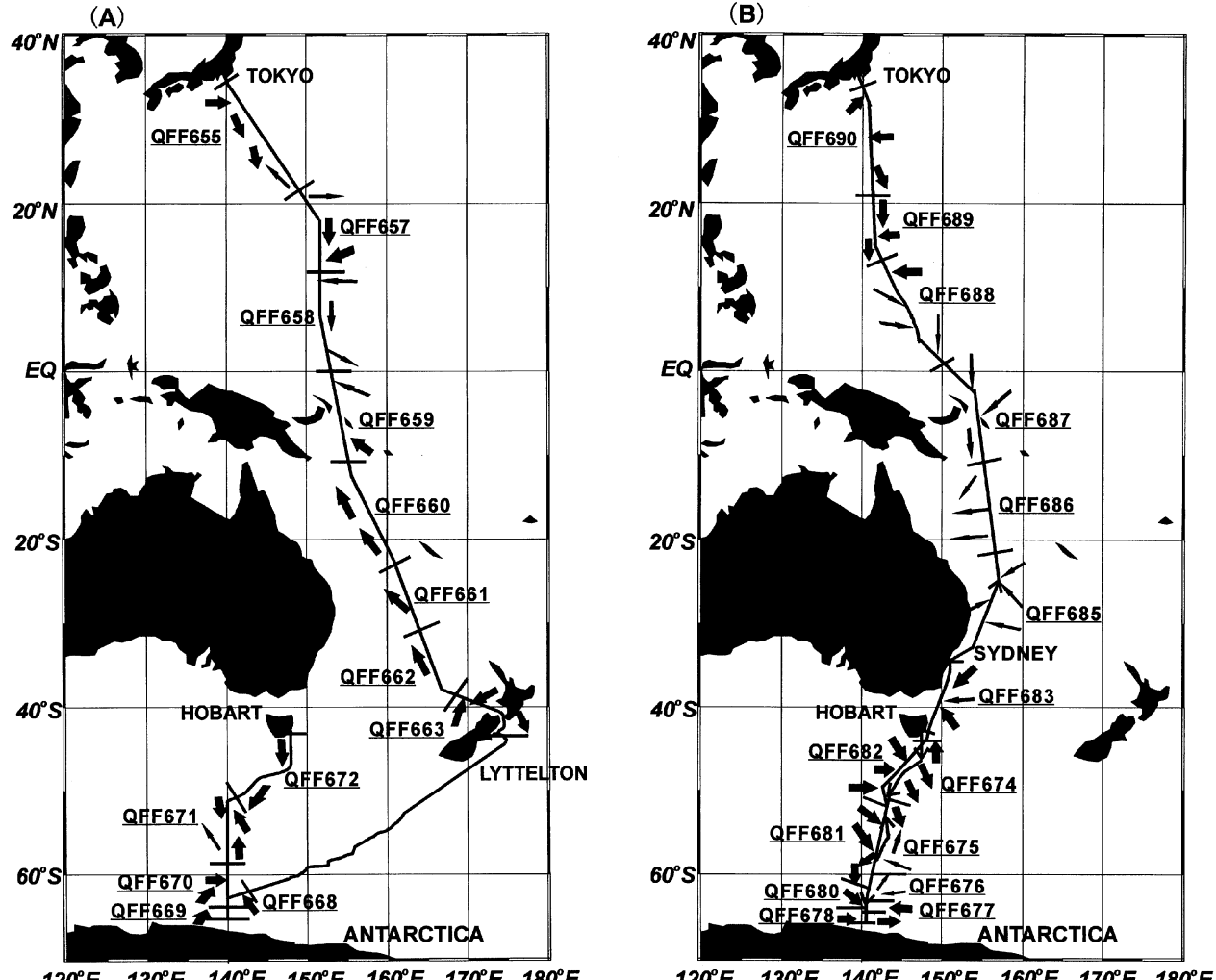
Latitudinal distributions of the relative abundances of individual dicarboxylic acids (For abbreviations, see Table 1).

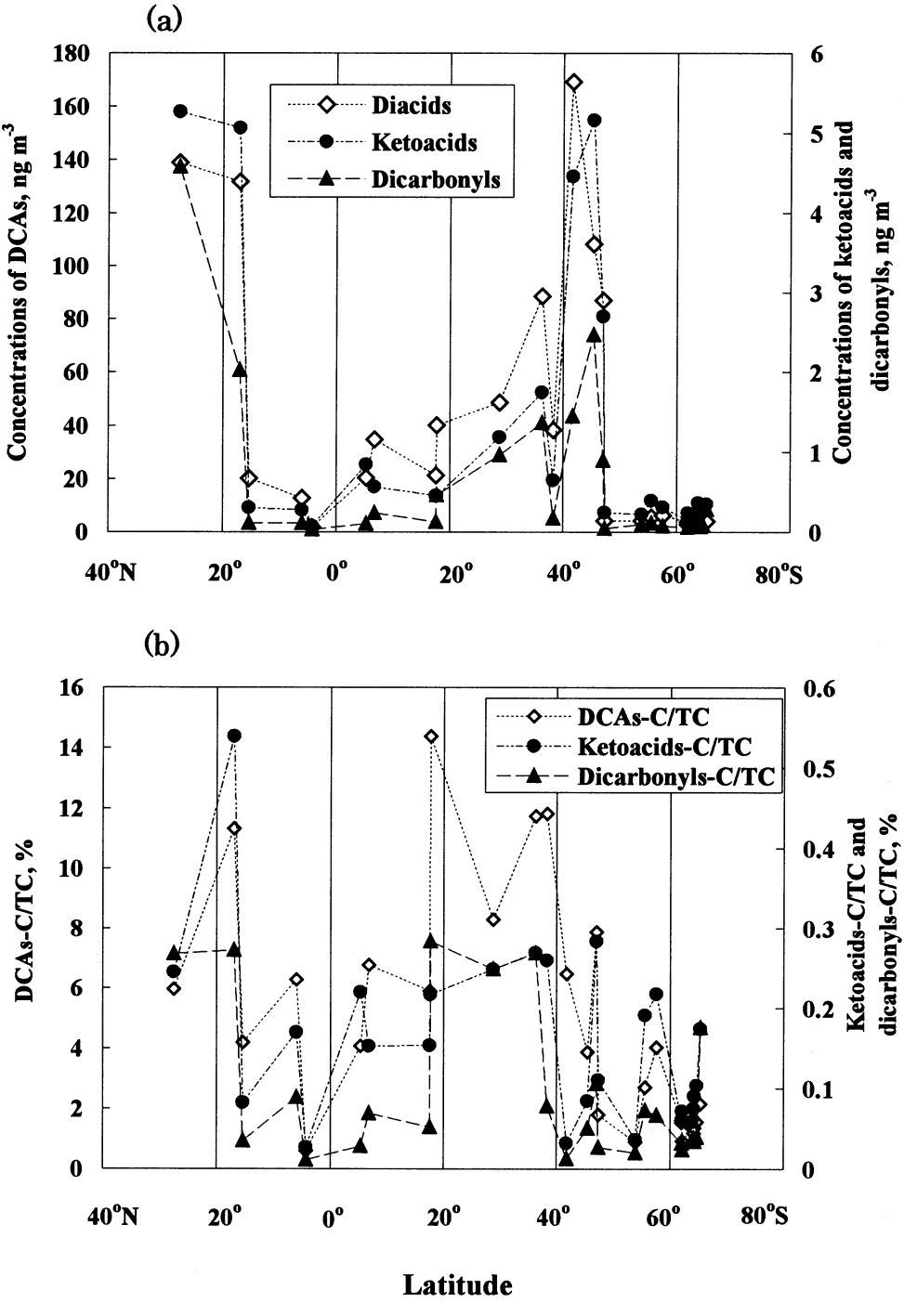
Fig. 4

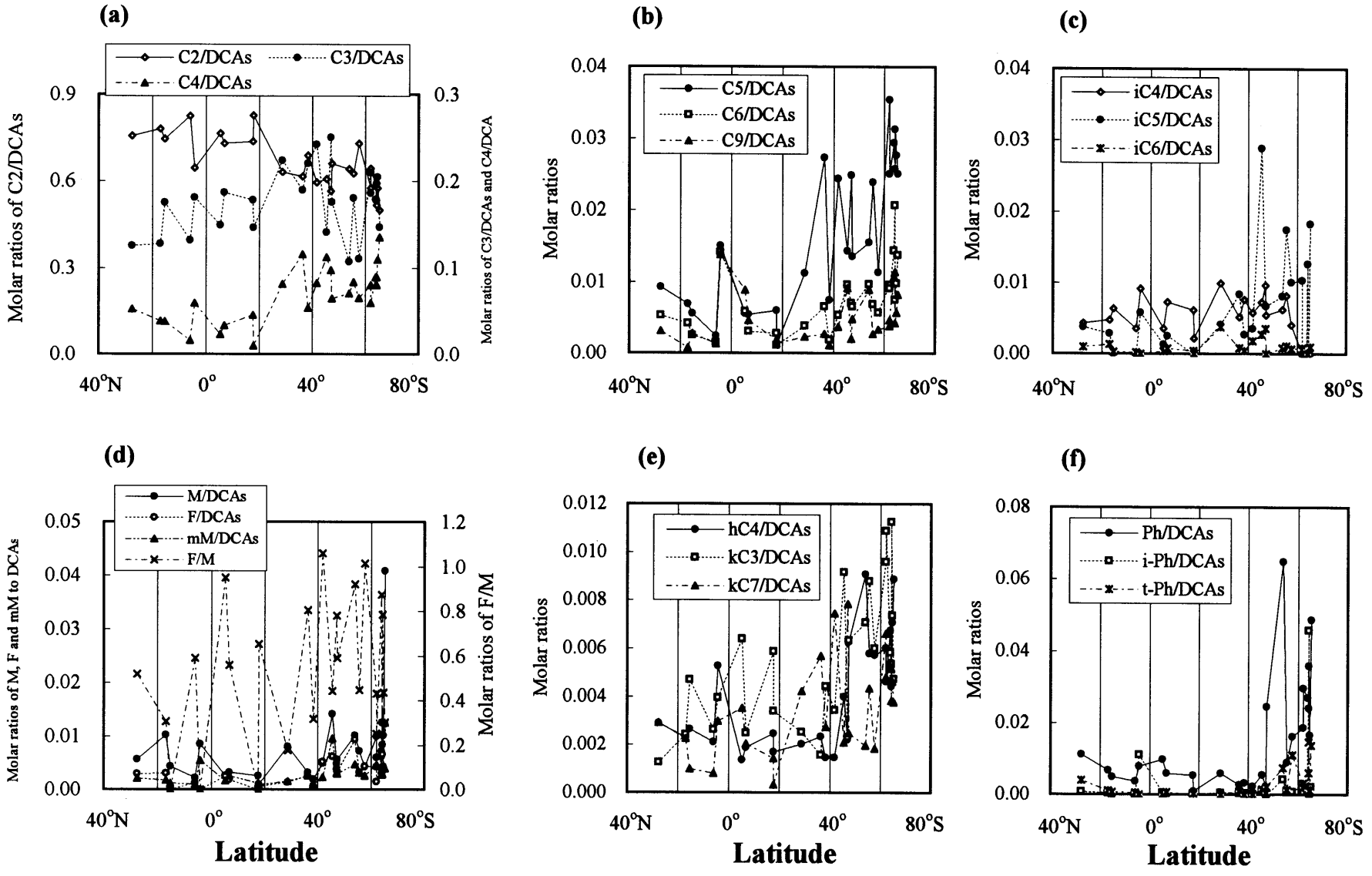
Latitudinal distributions of the relative abundances of individual ketoacids and dicarbonyls (For abbreviations, see Table 1).

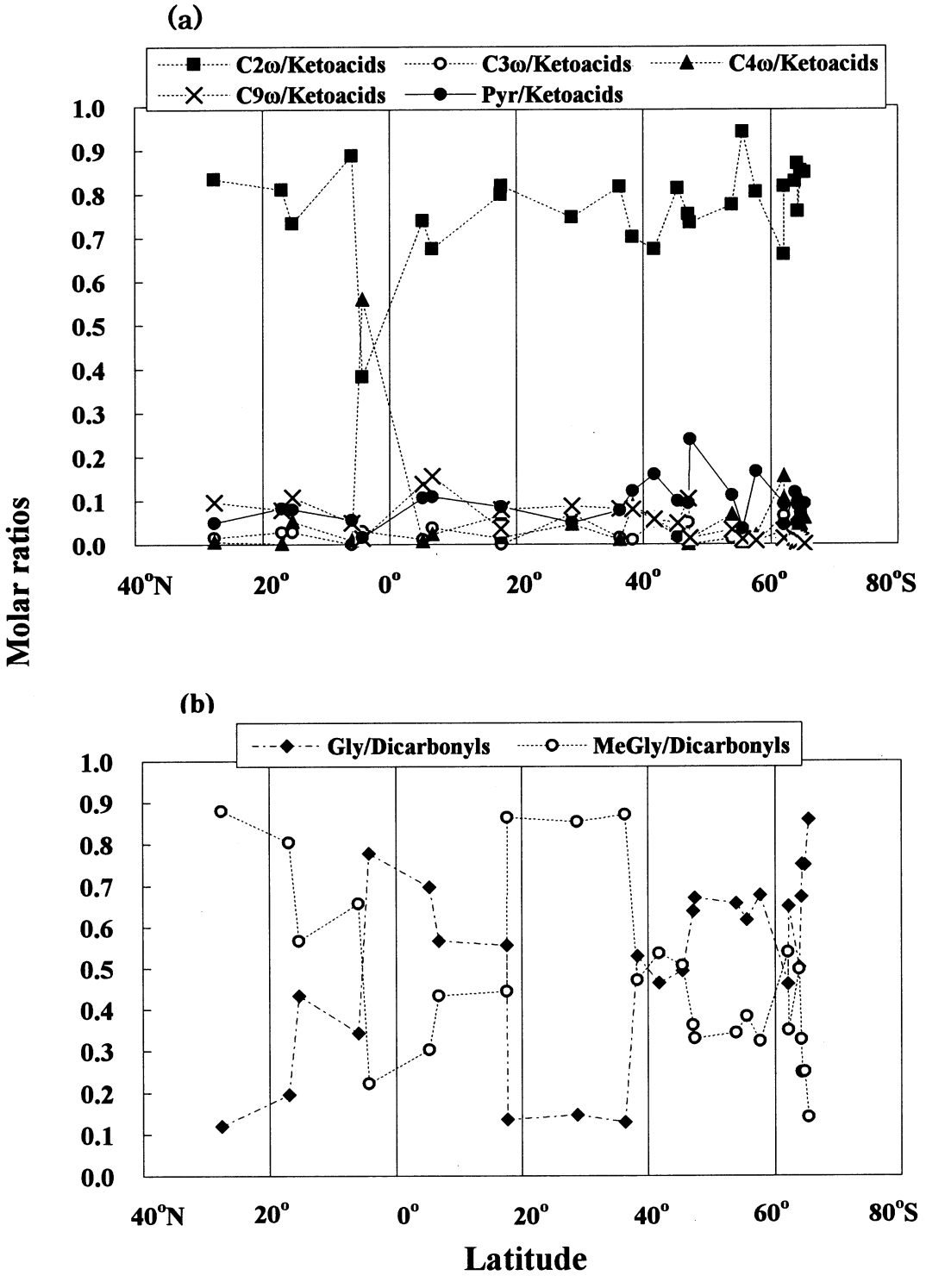
Fig. 5

Ten days' backward air mass trajectories for QFF689 (a sample from the western Pacific) and QFF670 (a sample from the Southern Ocean). The trajectory calculation was based on backward tracking of selected air parcels, assuming that they were moving with the ambient airflow. The flow pattern was updated every 6h.

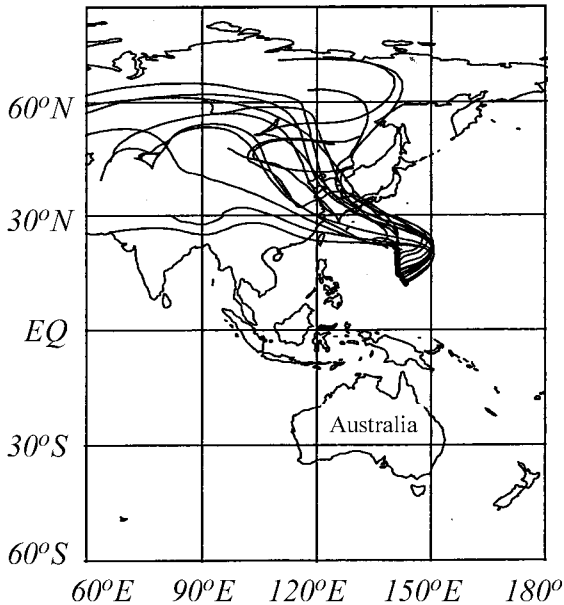

(A)
40°N
20°N
EQ
20°S
40°S
60°S
TOKYO
QFF655
QFF657
QFF658
QFF659
QFF660
QFF661
QFF662
QFF663
HOBART
QFF672
LYTTELTON
QFF671
QFF670
QFF669
QFF668
ANTARCTICA
120°E
130°E
140°E
150°E
160°E
170°E
180°E
(B)
40°N
20°N
EQ
20°S
40°S
60°S
TOKYO
QFF690
QFF689
QFF688
QFF687
QFF686
QFF685
SYDNEY
QFF683
HOBART
QFF682
QFF674
QFF681
QFF675
QFF680
QFF676
QFF678
QFF677
ANTARCTICA
120°E
130°E
140°E
150°E
160°E
170°E
180°E


(a)
Diacids
Ketoacids
Dicarbonyls
Concentrations of DCAs, ng m-3
Concentrations of ketoacids and dicarbonyls, ng m-3
180
160
140
120
100
80
60
40
20
0
6
5
4
3
2
1
0
40°N
20°
0°
20°
40°
60°
80°S
(b)
DCAs-C/TC
Ketoacids-C/TC
Dicarbonyls-C/TC
DCAs-C/TC, %
Ketoacids-C/TC and dicarbonyls-C/TC, %
16
14
12
10
8
6
4
2
0
0.6
0.5
0.4
0.3
0.2
0.1
0
40°N
20°
0°
20°
40°
60°
80°S
Latitude


(a)
C2/DCAs
C3/DCAs
C4/DCAs
Molar ratios of C2/DCAs
Molar ratios of C3/DCAs and C4/DCA
0.9
0.6
0.3
0.0
0.3
0.2
0.1
0.0
40°N
0°
40°
80°S
(b)
C5/DCAs
C6/DCAs
C9/DCAs
Molar ratios
0.04
0.03
0.02
0.01
0.00
40°N
0°
40°
80°S
(c)
iC4/DCAs
iC5/DCAs
iC6/DCAs
Molar ratios
0.04
0.03
0.02
0.01
0.00
40°N
0°
40°
80°S
(d)
M/DCAs
F/DCAs
mM/DCAs
F/M
Molar ratios of M, F and mM to DCAs
Molar ratios of F/M
0.05
0.04
0.03
0.02
0.01
0.00
1.2
1.0
0.8
0.6
0.4
0.2
0.0
40°N
0°
40°
80°S
Latitude
(e)
hC4/DCAs
kC3/DCAs
kC7/DCAs
Molar ratios
0.012
0.010
0.008
0.006
0.004
0.002
0.000
40°N
0°
40°
80°S
Latitude
(f)
Ph/DCAs
i-Ph/DCAs
t-Ph/DCAs
Molar ratios
0.08
0.06
0.04
0.02
0.00
40°N
0°
40°
80°S
Latitude


(a)
C2ω/Ketoacids
C3ω/Ketoacids
C4ω/Ketoacids
C9ω/Ketoacids
Pyr/Ketoacids
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
40°N
20°
0°
20°
40°
60°
80°S
Molar ratios
(b)
Gly/Dicarbonyls
MeGly/Dicarbonyls
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
40°N
20°
0°
20°
40°
60°
80°S
Latitude

(a) QFF689



(b) QFF670