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Four years observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific

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ABSTRACT

In order to understand the long-range atmospheric transport of terrestrial organic matter over the open ocean, marine aerosol samples were collected on a biweekly basis from 1990 to 1993 in a remote island, Chichi-Jima, in the western North Pacific. The samples were analyzed for lipid class compounds using a capillary gas chromatography (GC) and GC/mass spectrometry (GC/MS). A homologous series of n-alkanes (C_{20}-C_{40}), alcohols (C_{13}-C_{34}), fatty acids (C_9-C_{34}) and α,ω-dicarboxylic acids (C_7-C_{28}) were detected in the aerosol samples. Distributions of n-alkanes (0.17-14 ngm^{-3}, av. 1.7 ngm^{-3}) are characterized by a strong odd-carbon number predominance (CPI ratios, av. 4.5) with a maximum at C_{29} or C_{31}, indicating that n-alkanes are mainly derived from terrestrial higher plant waxes. Fatty alcohols (0.19-23 ngm^{-3}, av. 2.0 ngm^{-3}) show an even-carbon number predominance with a maximum generally at C_{26} or C_{28}, again indicating a contribution from terrestrial higher plants. On the other hand, fatty acids (2.5-38 ngm^{-3}, av. 14 ngm^{-3}) show a bimodal distribution with two maxima at C_{16} and C_{24} or C_{28}. Lower molecular weight fatty acids (generally < C_{20}) that are mainly derived from marine organisms showed higher concentrations in summer. In contrast, higher molecular weight fatty acids (C_{21}-C_{34}) derived from terrestrial higher plants, together with C_{25}-C_{35} alkanes, C_{20}-C_{34} alcohols and C_{20}-C_{28} dicarboxylic acids, generally showed higher concentrations in winter to spring seasons. This seasonal trend is most likely interpreted as atmospheric transport of terrestrial organic matter from Asian continent in winter/spring, when westerly winds dominate over the western North Pacific. Backward trajectory analyses supported the long-range atmospheric transport of higher plant- and soil-derived organic matter from the Asian continent over the Pacific Ocean. This study also suggested that the atmospheric transport is the main pathway for the terrestrial lipid compounds that are abundantly present in the deep-sea sediments in the Central Pacific.

1. Introduction

Lipid class compounds of terrestrial higher plant origin have been reported in the pelagic deep-sea sediments from the Pacific [Prahl et al., 1989; Kawamura, 1995; Ohkouchi et al., 1997a] and Atlantic Oceans [Farrington and Tripp, 1977; Poynter et al., 1989; Santos et al., 1994; Madureira et al., 1995, 1997]. Kawamura [1995] reported that concentrations of terrestrial biomarkers such as n-alkanes, fatty alcohols and fatty acids in the surface sediments decrease from the western to the central Pacific at a longitudinal transect of ca. 40°N. This result suggests that terrestrial organic materials are transported long distances in the atmosphere from Asian continent over the Pacific Ocean and are settled down to the deep ocean floor after wet/dry deposition. On the other hand, latitudinal distributions of land-derived biomarkers in the surface sediments from Central Pacific at 175°E transect showed that their concentrations are greater in the higher latitudes, although fatty acids were relatively abundant in the low latitudinal sediments [Ohkouchi et al., 1997a]. The sedimentary lipids that are mostly derived by a long-range atmospheric transport have successfully been used as tracers to reconstruct the changes in the atmospheric circulation in the geological past [Prahl et al., 1989; Poynter et al., 1989; Madureira et al., 1977; Ohkouchi et al., 1997b; Ikehara et al., 2000].

Lipid class compounds have been studied in the marine aerosol particles collected over the open ocean including the Atlantic [Simoneit et al., 1977; Conte et al., 2002], Pacific [Gagosian et al., 1981, 1982; Gagosian and Pelter, 1986; Peltzer and Gagosian, 1989; Kawamura and Gagosian, 1990], and Mediterranean Sea [Sicre et al., 1987]. Although these studies have demonstrated that a long-range atmospheric transport is an important pathway for the continent-derived organic materials over the ocean, the observations are often limited to a short period of time, certain oceanic regions and/or certain organic species. For example, aerosol studies in the western North Pacific where Asian dusts are often transported in spring have rarely been conducted for lipid class compounds [Kawamura, 1995]. In order to understand the linkage between terrestrial biomarkers in the atmosphere and those in the pelagic sediments, it is needed to obtain the data set of long-term observation on the terrestrial biomarkers in the remote marine aerosol particles. Such understanding may also be important to reconstruct the changes in the atmospheric transport and the atmospheric circulation patterns in the geological past.

In order to understand the atmospheric transport of continent-derived lipid compounds over the remote marine atmosphere, we collected marine aerosol samples for four years at a remote island, Chichi-Jima, in the western North Pacific. This island is located in the boundary of westerly and trade wind regimes. The aerosol samples were analyzed for lipid class compounds (alkanes, fatty alcohols, fatty acids and dicarboxylic acids) using a gas chromatography (GC) and GC/mass spectrometer (GC/MS). Here, we present four-year variations of the lipid compounds in the marine aerosols and discuss the source regions and the pathways for a long-range atmospheric transport of terrestrial organic matter over the western North Pacific. Meteorological data were used to interpret the concentrations of terrestrial biomarkers.

2. Sample and Method

Aerosol sampling was conducted on a biweekly basis from April 1990 to November 1993 at Satellite Tracking Center of National Aeronautic and Science Develop Agency (NASDA, elevation: 254 m) in Chichi-Jima Island (27°04’N; 142°13’E), western North Pacific. The high volume air sampler was set on the top of the base (5 m above the ground) for the parabola antenna and was operated without a wind sector control. Figure 1 shows a map of the western North Pacific and location of the island. This island is located ca. 2000 km away from the Asian continent and at ca. 1000 km south of Tokyo. In this region, wind systems are characterized by westerlies during winter to spring whereas trade winds dominate in summer to autumn. Figure 2 shows variations of wind direction at 700 hPa over Chichi-Jima Island over the four year sampling period.

Aerosol particles were collected on a pre-combusted (500 °C, 3 hrs) quartz fiber filter (Pallflex 2500 QAT-UP, 20 x 25 cm) with a flow rate of 1 m^3min^{-1}. Sampling periods ranged from 4 to 6 days. Before the sampling, filter was placed in a clean glass jar with a Teflon-lined cap during the transport and storage. After the sampling, the filter was recovered into the glass jar, transported to the laboratory and stored at –20 °C prior to analysis. Total aerosol mass was measured by weighing the filter before and after the aerosol sampling. The relative humidity changed from 60 % to 90 % (ave. 78 %) during the sampling periods. The aerosol mass was not corrected for the contribution of sea salt. However, the moisture was removed before the weighing when the frost appeared on the wall inside the glass jar during the storage in a freezer. Seventy aerosol samples were used in this study.

Aliquots (one fifth or one tenth) of the filters were extracted under a reflux with 100 ml 0.1 M KOH in methanol containing 5 % pure water. The extracts were concentrated using a rotary evaporator and then divided into neutral and acidic fractions as follows. The neutral fraction was first extracted from the alkaline solution with n-hexane/methylene chloride (10:1) mixture. The extracts were then separated into four sub-fractions using a silica gel column chromatography, that is, aliphatic hydrocarbons (N1), aromatic hydrocarbons (N2), aldehydes and ketones (N3) and alcohols (N4) by elution with n-hexane, n-hexane/methylene chloride (2:1) mixture, methylene chloride and methylene chloride/methanol (95:5) mixture, respectively [Kawamura, 1995]. The remaining alkaline solution was acidified with 6 M HCl and the carboxylic acids were extracted with methylene chloride. The acid fraction was methylated with 14 % BF_3/methanol. The carboxylic acid methyl esters were divided on a silica gel column into three fractions (A1: monocarboxylic acid methyl esters, A2: dicarboxylic acid dimethyl esters, A3: hydroxyacid methyl esters) by eluting with n-hexane/methylene chloride (1:2) mixture, methylene chloride/ethyl acetate (98:2) mixture, and methylene chloride/methanol (95:5) mixture, respectively.

In this study, four fractions (n-alkanes, fatty alcohols, fatty acids and dicarboxylic acids) were analyzed using a capillary gas chromatograph (Carlo Erba Mega 5160) equipped with a cool on-column injector, fused silica capillary column (HP-5, 30 m x 0.32 mm i.d. x 0.25 μm) and FID detector. Alcohol fraction was silylated with BSTFA to derive trimethyl silyl (TMS) ethers prior to GC injection. For the determination of the alkanes and alcohols, the GC oven temperature was programmed from 70 °C to 120 °C at 30 °C/min and to 320 °C (20 min) at 6 °C/min. For the fatty acid methyl esters and dicarboxylic acid dimethyl esters, the GC oven temperature was programmed from 50 °C (1 min) to 320 °C (20 min) at 6 °C/min. Structural identification of these compounds was performed using a GC/MS (ThermoQuest, Voyager) with similar GC column conditions. Authentic n-C_{29} alkane, n-C_{20} alcohol, and n-C_{16} fatty acid methyl ester were used as external standards for quantification. The recoveries of n-alkane (C_{29}), n-alcohol (C_{20}) and n-fatty acid (C_{16}) were better than 80 %. Analytical errors of the procedures were within 15 %. Blank filters were also analyzed and the data were used for the blank correction. Laboratory procedural blanks showed that blank levels were less than 1 % of the samples (e.g., < 50 ng for C_{16} fatty acid whose blank level per sample was the highest).

Total carbon and nitrogen contents of the aerosols were also measured using elemental analyzer [Sempéré and Kawamura, 1994]. Samples were not treated with HCl because carbonate contents were found to be negligible in the marine aerosols. Similar result was also obtained for the marine aerosols collected at Bermuda (Turekian et al., 2002).

3. Results

In the marine aerosol samples from Chichi-Jima, we detected homologous series of n-alkanes (C_{20}-C_{40}), n-alcohols (C_{13}-C_{34}), fatty acids (C_9-C_{34}) and α,ω-dicarboxylic acids (C_7-C_{28}). Table 1 presents the concentration ranges and average and median concentrations of lipid class compounds. Results of aerosol mass, total carbon and total nitrogen in the aerosols are also given in the table. Although concentrations of these components are highly variable, they show characteristic seasonal trends as follows.

3.1. Concentrations of aerosol mass, carbon and nitrogen

Figure 3 gives four year variations of aerosol mass, total carbon (TC) and total nitrogen (TN) in the atmosphere over Chichi-Jima Island. Concentrations of the aerosol mass largely fluctuated from ca. 10 μgm^{-3} to ca. 300 μgm^{-3} with a median of 35 μgm^{-3} (Table 1 and Figure 3a). The average concentration (53 μgm^{-3}) is about one half of that of the continental air from Tokyo (e.g., 54-220 μgm^{-3}, av. 107 μgm^{-3}) [Kawamura et al., 1995], with the lowest value of one fifth.

As illustrated in Figure 4a, aerosol mass concentrations show seasonal changes with relatively high values in spring and very high values in late summer to autumn samples (August, September and November). The former peak may be associated with a long-range atmospheric transport of Asian dusts by westerly winds [Duce et al., 1980]. The maximum in the late summer to autumn may be caused by enhanced sea-to-air emission of sea salts induced by tropical cyclones (Typhoon), which originate in the low latitudes and develop on the way to the north in the northwestern Pacific including Chichi-Jima Island. Figure 5 shows averaged wind directions at surface and 850 hPa for 17-20 August 1991 (quartz fiber filter number, QFF 219). This demonstrates that very high concentrations of aerosol mass in the 1991 fall (see Figure 3a) was derived from the Typhoon, with which marine- and continent-derived materials can be transported from the south to the north near Chichi-Jima. This is also supported by the high concentrations of Na and Cl (data are not shown here). Similar results was also obtained for the QFF 220 sample (6-9 September, 1991) which showed high aerosol mass concentration (Figure 4a)

Total carbon contents in the aerosols ranged from 0.11 μgm^{-3} to 1.91 μgm^{-3} with an average of 0.63 μgm^{-3} (Table 1 and Figure 3b). These values are about 30 times lower than urban Tokyo aerosols (12-44 μgm^{-3}, av. 22 μgm^{-3}) [Kawamura and Ikushima, 1993] and 80 times lower than Beijing aerosols (24-85 μgm^{-3}, average of 49 μgm^{-3}) [Sekine et al., 1992]. However, the TC concentrations are in a same level with or lower than those reported in the marine aerosols collected in April and May over the North Pacific (from Tokyo to Honolulu, 0.48-11 μgm^{-3}, av. 2.4 μgm^{-3}) [Uematsu et al., 1995]. Okita et al. [1986] reported the concentration of organics (1.4 μgm^{-3}) in the winter aerosol sample collected at Chichi-Jima (Dec. 14-20, 1981), which is within the range of the TC concentrations in our study. Higher concentrations were observed in winter to spring whereas lower values were generally seen in summer/autumn season (see Fig. 4b). The elevated TC concentrations in winter/spring periods should be associated with the enhanced atmospheric transport of Asian dusts from arid regions in China [Duce et al., 1980] and from urban areas in the Asian countries. However, relatively high TC contents were sometimes observed in the fall of 1991 (see Fig. 3b), which can again be explained by atmospheric transport from the south including Southeast Asia due to the meteorological data (see Figure 5). This point will be later discussed in details (see section 4.4.).

Total nitrogen contents ranged from 0.04 μgm^{-3} to 0.93 μgm^{-3}, with an average of 0.18 μgm^{-3} (Table 1 and Figure 3c). These values are one or two orders magnitudes lower than those reported in Tokyo (5.7-19.4 μgm^{-3}) [Sempéré and Kawamura, 1994], but are in a same level or a bit lower than those reported in the North Pacific (0.10-1.6 μgm^{-3}, av. 0.40±0.35 μgm^{-3}) [Uematsu et al., 1995]. TN contents in the Chichi-Jima aerosols generally show a seasonal trend with higher values in spring and lower values in fall. The monthly averaged concentrations of TN show a gradual increase from the winter to spring with the highest value in April (Figure 4c). Nitrate which is formed by photo-oxidation of NO_x is an important constituent of total nitrogen in the marine aerosols [Uematsu et al., 1995]. Thus, NO_x emitted from Asian countries by fossil fuel combustion and their atmospheric transport over the western North Pacific should be responsible to the enhanced TN in spring. On the contrary, TN contents generally decreased in summer/autumn. This may be the result of changing wind pattern from westerly to easterly over the western North Pacific (see Figure 2).

3.2. n-Alkanes and UCM hydrocarbons

Figure 6 presents a typical gas chromatogram of aliphatic hydrocarbons isolated from the aerosol sample. Normal alkanes were detected in a range of C_{20}-C_{43}. Their molecular distributions are characterized by an odd-carbon-numbered predominance with a maximum at C_{29} or C_{31}. Such a molecular distribution suggests that n-alkanes were most likely derived from higher plant waxes, in which C_{27}, C_{29}, C_{31} and C_{33} are dominant species [Gagosian et al., 1982]. Lower molecular weight alkanes such as C_{20}-C_{26} and higher alkanes such as C_{35}-C_{43} show the weaker odd/even predominance (Figure 6). Such molecular distributions suggest that these n-alkanes are in part derived from the incomplete combustion of fossil fuels and petroleum residue (Simoneit, 1984); i.e., the n-alkanes in crude oils have no odd/even predominance (CPI=1) [Tissot and Welte, 1984].

The CPI (Carbon Preference Index, concentration ratios of odd-carbon n-alkanes over even-carbon n-alkanes) ratios for C_{25}-C_{35} n-alkanes in the Chichi-Jima aerosols are plotted in Figure 7 for 4 years. The CPI indices ranged from 1.8 to 14.6, with an average of 4.5 and a median of 3.8. The values (av. 4.5) are much higher than those reported in urban aerosols from several cities in China (0.91-1.8, av. 1.3, Fu et al., 1997) and Tokyo (1.1-2.8, av. 1.5) [Kawamura et al., 1995]. However, they are similar to or higher than those (1.6-3.2) reported in the tropical North Pacific [Gagosian et al., 1982]. These results indicate that n-alkanes in the Chichi-Jima aerosols are mainly derived from higher plant waxes whereas the contribution from petroleum residue is generally minimal. As seen in Figure 7, seasonal trend of the CPI ratios is not clear. However, higher values >5 were often obtained in the winter/spring aerosols whereas very high CPI ratios were sporadically observed in May, August and September. High CPI ratios (>5) were reported in the aerosols collected in the mountain forests from Japan [Kawamura et al., 1995].

Total concentrations of n-alkanes are in a range of 0.11-14.1 ngm^{-3}, with an average of 1.75 ngm^{-3} and median of 1.1 ngm^{-3} (Table 1). These values are ca. two orders of magnitudes lower than those reported in the urban Tokyo atmosphere (31-323 ngm^{-3}, av. 95

ngm^{-3}) and the mountain forest air (14-34 ngm^{-3}) [Kawamura et al., 1995]. However, they are similar to those (0.3-0.6 ngm^{-3}) reported in the marine aerosols from off the coast of Peru [Schneider and Gagosian, 1985]. In contrast, the concentrations are higher than those (0.02-0.16 ngm^{-3}) reported in the aerosols from Enewetak Atoll (11°20'N; 162°20'E, see Figure 1), Marshal Islands, tropical North Pacific [Gagosian et al., 1986]. The higher values in Chichi-Jima than Enewetak Atoll are reasonable, because the former island is much closer to Asian continent (ca. 2000 km southeast of Asia) than the latter (ca. 5000 km southeast of Asia). There is no correlation between the total n-alkane concentrations and their CPI values (C_{25}-C_{35}).

Unresolved complex mixture of hydrocarbons (UCM) was detected as a hump in the aliphatic hydrocarbon fraction separated from the Chichi-Jima aerosol samples (Figure 7). This mixture is composed of positional isomers of branched/cyclic hydrocarbons with different carbon numbers, which cannot be resolved even with a high-resolution capillary gas chromatography. UCM hydrocarbons are abundantly present in the crude oils that are degraded by bacterial activities in the oil reservoirs [Peters and Moldowan, 1993] and are emitted to the atmosphere by incomplete combustion of fossil fuels [Boyer and Laitinen, 1975; Simoneit and Mazurek, 1981]. A cracking process during the incomplete combustion of fossil fuels also produces UCM. The UCM hydrocarbons have been reported in aerosol and rainwater samples from the urban atmosphere [Simoneit, 1984; Simoneit et al., 1988; Kawamura and Kaplan, 1991; Kawamura et al., 1995].

The presence of UCM in the Chichi-Jima aerosols demonstrates that the western North Pacific region is influenced by polluted air from Asian countries. However, their concentrations (av. 5.4 ngm^{-3}, med. 3.4 ngm^{-3}, Table 1) are two or three orders of magnitudes lower than those of urban air (e.g., 270-3000 ngm^{-3}, av. 880 ngm^{-3}) [Kawamura et al., 1995]. Four year observation of UCM hydrocarbons did not show a clear seasonal trend (data are not shown here). It is likely that there is an oceanic background for this material that would be more or less uniform year-round. Interestingly, the UCM concentrations showed a negative correlation with the CPI indices of n-alkanes (see Figure 8). Such a negative correlation has been reported in urban aerosols from Tokyo [Kawamura et al., 1995], although their CPI ratios were less than 3 (av.) in the urban atmosphere.

3.3. n-Alcohols and sterols

Figure 9 shows a capillary gas chromatogram of alcohol fraction isolated from Chichi-Jima aerosols. Normal C_{13}-C_{34} alcohols were detected in the aerosol samples. Their distributions are characterized by an even carbon number predominance, with C_{24}, C_{26}, C_{28} and C_{30} being dominant species. The most abundant alcohol was generally C_{26} or C_{28} but some aerosol samples showed a maximum at C_{30} or C_{32}. Although several samples show a peak at n-C_{16}, its concentrations are generally low. Molecular distributions of n-alcohols suggest that they are most likely derived from waxes of terrestrial higher plants [Simoneit et al., 1977; Gagosian et al., 1981]. Concentration range of total n-alcohols was 0.18-19.7 ngm^{-3} with an average of 2.2 ngm^{-3} (Table 1). Their concentrations are lower than those (8-1200 ngm^{-3}) reported in the continental aerosols from China [Simoneit et al., 1991], but higher than those (0.07-0.25 ngm^{-3}) reported in the remote marine aerosols from Enewetak Atoll, tropical North Pacific [Gagosian et al., 1981]. The n-alcohol concentrations in the Chichi-Jima aerosols are consistent with that (4.4 ngm^{-3}) reported for the marine aerosols collected in the western North Pacific near Japanese Islands [Kawamura, 1995].

Cholesterol (C_{27}) and β-sitosterol (C_{29}) were also detected in the marine aerosols. Their concentration ranges were 0.0-0.89 ngm^{-3} (av. 0.053 ngm^{-3}) and 0.0-0.38 ngm^{-3} (av. 0.066 ngm^{-3}), respectively (Table 1). The concentrations of cholesterol are higher than those (0.0002-0.028 ngm^{-3}) reported in the marine aerosols from Enewetak Atoll [Gagosian et al., 1982]. Although β-sitosterol has not been reported from Enewetak Atoll, this compound was found in the rain samples from the island at approximately one-third the concentration of cholesterol [Zafiriou et al., 1985]. Presumably they both had atmospheric dust sources. Although the sterols are less abundant than n-alcohols (Table 1), their concentrations showed some seasonal trend. The cholesterol concentrations increase from winter to spring and reached a maximum in May. Cholesterol has been proposed as a source marker of marine organisms whereas β-sitosterol is derived from terrestrial higher plants [Gagosian, 1986]. The sterols have been reported in continental aerosols from the west coast of United State and central Africa, with C_{29} sterol being more abundant than C_{27} species in the warmer climatological regions [Simoneit et al., 1983].

3.4. Monocarboxylic acids

Homologous series of fatty acids (C_{12}-C_{34}) have been detected in the marine aerosols. Molecular distributions of saturated fatty acids indicate a strong even carbon number predominance with two maxima at C_{16} and C_{24} or C_{28}. Similar bimodal distribution has been reported in continental aerosols from different locations [Simoneit and Mazurek, 1982; Simoneit et al., 1988] and in remote marine aerosols [Gagosian et al., 1981; Schneider and Gagosian, 1985; Kawamura and Gagosian, 1990]. Unsaturated fatty acids such as oleic acid ($C_{18:1}$) and linoleic acid ($C_{18:2}$) that are abundant in plants were also detected in the marine atmosphere as relatively minor species. However, summer aerosol samples sometimes showed abundant presence of unsaturated fatty acids [Kawamura et al., in prep.]. Lower molecular weight (LMW) fatty acids (C_{12}-C_{19}) are derived from marine phytoplankton as well as terrestrial plants. In contrast, higher molecular weight (HMW) fatty acids (C_{20}-C_{32}) are characteristic of terrestrial higher plant waxes [Kolattukudy, 1976] and not generally found in marine organisms at least as major components [Gagosian, 1986].

Concentrations of LMW fatty acids ranged from 1.9 ngm^{-3} to 54.6 ngm^{-3} with an average of 10.4 ngm^{-3} whereas those of HMW fatty acids ranged from 0.38 ngm^{-3} to 24.3 ngm^{-3} with an average of 3.5 ngm^{-3}. Fatty acids are the most abundant lipid class compounds detected in the marine aerosols (Table 1). On average basis, they are roughly ten times more abundant than n-alkanes and n-alcohols and three times more abundant than UCM hydrocarbons (Table 1). Concentrations of fatty acids in the marine aerosols from

Chichi-Jima are much lower than those obtained in the continental aerosols from Japan (31-1110 ngm^{-3}, av. 330 ngm^{-3}) [Kawamura, 1991], China (14-11,000 ngm^{-3}) [Simoneit et al., 1991], and western United States (22-670 ngm^{-3}) [Simoneit and Mazurek, 1982]. The concentrations in the Chichi-Jima aerosols are much lower than those reported from North Atlantic (80-230 ngm^{-3}, av. 130 ngm^{-3}) [Marty et al., 1979], but are consistent with those obtained from Pacific Ocean (7-54 ngm^{-3}, av. 24 ngm^{-3}) [Kawamura and Tanaka, 1994, unpublished data]. The atmospheric concentrations of fatty acids are higher than those obtained in the Southern Ocean (0.3-2.6 ngm^{-3}) [Kawamura and Niwai, 1996].

In the monocarboxylic acid fraction, dehydroabietic acid was detected with a concentration range of 0.00-0.51 ngm^{-3}. This resin acid has been reported in the continental aerosols and in the smoke particle from biomass burning of conifer [Simoneit, 2002].

3.5. Dicarboxylic acids

A homologous series of α,ω-dicarboxylic acids (C_7-C_{28}) were detected as dimethyl esters in the aerosol samples. Their distributions are generally characterized by the predominance of azelaic acid (C_9), although the diacids smaller than C_7 were not measured. Previous studies using dibutyl derivatization technique, indicated that oxalic acid (C_2) is the most abundant in the range of C_2-C_{10} in both continental [Kawamura and Ikushima, 1993] and marine aerosols [Kawamura and Sakaguchi, 1999]. However, lower molecular weight diacids (C_2-C_6) were not determined here because of the methyl ester derivatization technique employed, where a loss of the dimethyl esters is significant due to the evaporation [Kawamura and Ikushima, 1993]. It is of interest to note that azelaic acid is generally more abundant than higher molecular weight diacids (>C_{10}). Because the C_9 diacid is the typical photochemical oxidation product of unsaturated fatty acids that have a double bond predominantly at C-9 position [Kawamura and Gagosian, 1987], this result suggests that the marine aerosols are heavily influenced by photochemical processes in the atmosphere. Unsaturated fatty acids are abundant organic species in seawater surfaces.

In contrast, longer chain dicarboxylic acids (>C_{10}) generally showed even carbon number predominance in a range of C_{20}-C_{28} with a maximum at C_{22} or C_{24}. Although C_{16} and C_{18} diacids are abundant in fresh soil organic matter, they are sometimes less abundant than the HMW diacids (C_{20}-C_{28}) in the marine aerosols from the central to eastern North Pacific [Kawamura and Gagosian, 1990]. Similar distribution has been reported in the marine aerosols collected in the western North Pacific near Japanese Islands [Kawamura, 1995] as well as in the Chinese loess samples [Kawamura and Gagosian, 1990]. Long-chain dicarboxylic acids have also been reported in the arctic aerosols, in which their concentrations reached a maximum in the late April to early May due to a long-range atmospheric transport of Asian soil dusts [Kawamura et al., 1996]. These diacids are mainly derived from microbial ω- and $\omega-1$ oxidation of fatty acids in soils [Kawamura and Gagosian, 1990] and, to a lessor extent, from direct ablation from plant waxes. Thus, the presence of these diacids in the marine aerosols indicates that soil dusts are transported over the western North Pacific through the atmosphere. This is consistent with the conclusion inferred from the molecular distributions of long-chain n-alkanes, alcohols and fatty acids.

3.6. Chain length distributions of terrestrial lipids

Although the terrestrial biomarkers showed similar molecular distributions (e.g., odd number predominance for n-alkanes) throughout the 4-year observation period, some differences were found in their chain-length distributions (e.g., maximum at C_{29} or C_{31} in the case of n-alkanes). In order to understand such difference in the distributions, average chain length (ACL: the concentration-weighted mean carbon chain length) was calculated for the lipid class compounds [Peltzer and Gagosian, 1989]. Figure 10 presents four-year variation of ACL indices of the long-chain n-alkanes, alcohols, fatty acids, and dicarboxylic acids in the marine aerosols from Chichi-Jima. ACL of the terrestrial biomarkers showed a range of 29 to 31 (n-alkanes), 26 to 28 (n-alcohols), 24 to 28 (n-fatty acids) and 22 to 25 (dicarboxylic acids). These indices seem to have some seasonal trends; the ACL values of n-alkanes and n-alcohols apparently increase from spring to autumn (see Figure 10a,b) whereas those of fatty acids and dicarboxylic acids increase vice versa although fluctuation is significant (Figure 10c,d). These changes in the composition of terrestrial biomarkers may be involved with the changes in the source regions and transport pathways.

4. Discussion

4.1. Winter/spring maximum of terrestrial biomarkers

As illustrated in Figure 11, concentrations of terrestrial lipid components (long-chain n-alkanes, n-alcohols, n-fatty acids and dicarboxylic acids) over Chichi-Jima fluctuate significantly with an amplitude of nearly two orders of magnitude. However, these variations seem to have a seasonal trend with higher concentrations in winter/spring. For example, concentrations of C_{27}-C_{35} n-alkanes that are mostly of terrestrial higher plant origin generally increase in winter/spring and decrease toward summer/autumn season, except for the year of 1991 when the concentrations are relatively high in the summer/autumn (Figure 11a), a point to be discussed later. Similar seasonal pattern can also be seen in the 4-year variations of long-chain n-alcohols, fatty acids and dicarboxylic acids (see Figure 11b,c,d). Such seasonal trend suggests that atmospheric transport of terrestrial organic materials over the western North Pacific are enhanced during winter/spring season probably due to the strong westerly winds (see Figure 2). Similar seasonal trend of the long-chain fatty acids has been reported in Enewetak Atoll, equatorial North Pacific, far south from our sampling site (see Figure 1), although their concentrations are much lower than the present results [Gagosian et al., 1982].

Correlation coefficients were found to be fairly high (>0.83) among the concentrations of four terrestrial biomarkers with a maximum (r=0.93) for the combination of long-chain alkanes and fatty acids. Such a good covariance suggests that terrestrial organic materials are transported over the island from the similar source regions and sources, however the source regions should have been changed depending on seasons and meteorological conditions. Figure 12 plots concentrations of long-chain n-alkanes, n-alcohols, fatty acids and dicarboxylic acids as a function of their ACL indices. Higher concentrations were found for n-alkanes and alcohols when the ACL values are around 30 and 27.5, respectively (see Figure 12a,b). On the other hand, concentrations of long-chain fatty acids and dicarboxylic acids were found to increase with an increase in the ACL indices (Figure 12c,d). These results may suggest that major sources for these compounds are associated with specific regions, although their molecular distributions do not provide a clear information on the source regions.

In order to understand the source regions of the terrestrial biomarkers, backward air mass trajectory analyses were conducted for 10-20 days for the sampling periods of the aerosols studied [Yamazaki et al., 1989; Murayama et al., 1998; Yamazaki et al., 1999]. The trajectory analysis generally showed that, in winter/spring seasons when the concentrations of terrestrial lipids are high, most of the air masses originated from Asia and Siberia including arid regions (e.g., Gobi desert) in China and Mongolia (see Figure 13a). On the contrary, the trajectories calculated for the periods of the samples collected in summer/autumn seasons showed that the air masses are of marine origin in the Central Pacific or far east (Figure 13b), except for some aerosol samples of 1991. These results suggest that terrestrial organic materials are transported from Asian continent over the western North Pacific through the atmosphere in winter/spring seasons under the meteorological conditions dominated by strong westerly winds.

Figure 14 plots the concentrations of terrestrial biomarkers in the 70 aerosol samples studied as a function of wind direction at 700 hPa over Chichi-Jima in the western North Pacific. The concentrations of long-chain n-alkanes, n-alcohols, fatty acids and dicarboxylic acids are generally higher when winds come from the west and lower when winds come from the east (Figure 14a-d). Similar trends were also obtained when the concentrations were plotted against the wind direction at 850 hPa, although trends are weaker. These results suggest that atmospheric transport of the terrestrial organic matter over Chichi-Jima is largely associated with westerly winds. Combination of the concentrations of terrestrial lipids and the meteorological data can explain the reason why terrestrial biomarkers are abundantly present in the mid-latitudinal pelagic sediments of Pacific Basin and their concentrations in the sediments decrease from the west to the east in the central Pacific [Kawamura, 1995].

β-Sitosterol and dehydroabietic acid of terrestrial higher plant origin also showed the similar results (see Fig. 14e,f). However, the concentrations of dehydroabietic acid that is reported in the smoke from biomass burning of conifer [Simoneit, 2002] are sometimes high when the winds came from the east or south, suggesting a long-range atmospheric transport by the trade wind. Higher concentrations of this compound are sometimes involved with aerosol samples collected in 1991 and 1992 when forest fires were active in Southeast Asia [Kita et al., 2000].

4.2. Compositional changes of terrestrial biomarkers in westerly and trade wind regimes

Although n-alkanes are characterized by a maximum at C_{29} or C_{31}, their chain-length distributions seem to have a seasonal trend. As shown in Figure 15a, monthly averaged ACL values decrease from February (av. 29.8) to May (29.5) and then increase toward August (30.3) and September (30.3). This excursion in the n-alkane composition may suggest that source areas of the terrestrial organic matter may be shifted from one region to another with seasons. Generally, the results of air mass trajectory analyses suggested that the winter/spring aerosols were transported from Asian continent under the influence of westerly winds (see Figure 13a). In contrast, the summer/autumn samples are more influenced by trade winds, whose pathways may include the central Pacific and sometimes Central America [Gagosian et al., 1981; Merrill et al., 1985]. However, the trajectories in August and September showed that the source regions of the air parcels with higher ACL values are the central North Pacific (see Figure 13b), but they did not reach to the Central America even in 20 days in backward. Rather, air mass trajectories in the summer/autumn, especially in 1991, suggest that the air parcels often came from Southeast Asia, as discussed later. Relatively high standard deviation of the ACL values obtained in September (Figure 15a) seems to be involved with the diversity of the wind directions and thus source regions.

Gagosian and Peltzer [1986] analyzed n-alkanes in the aerosol samples collected in Enewetak Atoll, Central Pacific, and reported a shift of the ACL values from 27 in spring to 29.5 in summer. They considered that, together with the trajectory analysis, this shift is caused by the changes of wind direction pattern from westerly in spring to easterly in summer and concluded that the air masses in the summer are delivered from tropical Central American regions. Simoneit et al. [1991] analyzed continental aerosols from China and reported that higher molecular weight n-alkanes (C_{31}) of the aerosols predominate in the warmer climate of southern China. Hence, it could be hypothesized that the higher plants growing in the tropical region biosynthesize higher molecular weight epicuticular wax in response to higher ambient temperatures to maintain the hardness of the leaf surfaces. However, there is no data set of plant wax n-alkanes that supports this climatological adaptation by plant community.

To substantiate the above hypothesis, we collected plant leaf samples from ca. 10 broad-leaf plant species growing at tropical (6°S, Bidadari Island, Indonesia), subtropical (27°N, Chichi-Jima Is, western North Pacific), and temperate (43°N, Sapporo, Japan) regions. The leaf samples were analyzed for n-alkanes using the method described in the experimental section. Figure 16 shows typical chain-length distributions of n-alkanes extracted from the broadleaf higher plant waxes, which were collected from three latitudinal regions. Normal C_{23}-C_{37} alkanes in the leaf waxes were characterized by a strong odd carbon number predominance with a maximum at C_{29} or C_{31}. The averaged ACL values of n-alkanes increase from 28.9 (43°N) to 29.6 (27°N) and then to 31.5 (6°S). Although not being conclusive, these results support an idea that the ACL values are higher when n-alkanes are biosynthesized in the tropical (warmer) regions. It is also of interest to note that

CPI values in the subtropical and temperate plants ranged from 9.5 to 28.7 with an average of 23.7 and median of 24.0 whereas the n-alkanes in the tropical plant leaves showed lower CPI values (ca. 5.3).

Monthly averaged ACL values of n-alcohols in the marine aerosols also show a seasonal trend (see Figure 15b). The ACL values of n-alcohols generally decrease from 27.3 (January) to 26.5 (May) and then increase toward autumn (27.4). Such trend seems to be consistent to the case of n-alkanes (see Figure 15a). Fatty acids also show a decrease in their ACL values from 26.5 (February) to 25.4 (May), although the values scatter in the summer/autumn. Their averaged ACL values seem to slightly increase in fall, although relatively low values are seen as well in the summer and autumn samples (Figure 15c). Such a trend is generally similar to that of n-alkanes (Figure 15a), except for the results in summer/fall seasons. These results suggest a change in the source region for the terrestrial organic matter, which may be associated with the shift of atmospheric circulation pattern from the westerly to easterly regime. Although we cannot specify the source regions at this point, these results suggest that chain-length distributions of terrestrial lipids may be useful to trace the changes in source region and wind system.

4.3. Relative abundances of terrestrial alkanes, alcohols and fatty acids

Although concentrations of higher plant-derived biomarkers (n-alkanes, alcohols and fatty acids) generally co-varied in the marine atmosphere of western North Pacific, their amplitudes are not consistent as seen in Figure 11. Figure 17 illustrates the triangular plots for the relative abundances (%) of three terrestrial biomarkers in the marine aerosol samples from Chichi-Jima Island. The aerosol samples collected during summer/autumn (July to October) under the trade wind regime are generally plotted in the upper part of the triangle (Group B, see Figure 17), indicating that long-chain fatty acids are relatively more abundant in those seasons. In contrast, the aerosols collected in winter/summer (November to June) are plotted in the lower part of the triangle (Group A, see Figure 17). Because the latter samples are mostly collected under the condition of westerly winds, Asian continent should be the major source region for the terrestrial organic matter transported over the western North Pacific. Although it is not clear why fatty acids are enriched in the aerosols (Group B) collected under the trade wind regime, they may be involved with the specific vegetation in the source region whose biological situation may be different from Asian Continent. As seen in Figure 17, several samples that are expected to fall in Group A or B were plotted in the opposite group. Trajectory analyses, however, demonstrated that most samples are categorized by wind patterns; for example, the QFF 194 sample collected in 1-4 October 1990 includes air mass trajectories from Asia (see a closed square plotted in the lower part of Group A in Figure 17).

Ohkouchi et al. [1997a] analyzed terrestrial biomarkers (long-chain n-alkanes, n-alcohols, and n-fatty acids) in the pelagic sediments collected at 175°E transect (15°S to 48°N) and plotted their relative abundances in the same triangular figure. As shown in Figure 18, the sediment samples collected in the lower latitudes (15°S to 15°N) where trade winds dominate are plotted in the upper part of the triangle and categorized as trade wind regime (Category B). In contrast, the sediment samples collected in the mid- to high-latitudes (19°N-48°N) where westerlies dominate are plotted in the lower part of the triangle and categorized as westerly regime (Category A, see Figure 18). These results of the Pacific sediments seem to be consistent with the present aerosol samples that are collected over the western North Pacific (see Figure 17), although relative abundance of HMW fatty acids are greater in the pelagic sediments than those in the aerosol samples (see Figure 17 and 18). This may be due to the difference in the sampling location. Sediments were collected in the central Pacific between 15°S to 48°N whereas aerosols were collected on the island in the western North Pacific. These comparisons of terrestrial biomarkers between the marine aerosols and deep-sea sediments suggest that terrestrial biomarkers are transported long distances from Asian continent and Central America by westerly and trade winds over the Pacific Ocean and settled down in the pelagic deep-sea sediments.

4.4. Terrestrial organic matter transported from Southeast Asia during 1991 El Niño event

Concentrations of terrestrial biomarkers in the Chichi-Jima aerosols are generally low in the summer/autumn seasons (Figure 11). This is because the atmospheric condition over this island is governed by the trade winds in these seasons, as discussed above. However, exceptionally high concentrations of terrestrial biomarkers such as n-alkanes and alcohols were recorded in the aerosol samples collected in August and September 1991 (see Figure 11). The summer of 1991 was meteorologically characterized by weaker subtropical high pressure systems in the western Pacific, being different from the averaged years when the high pressure covers over the western North Pacific near Chichi-Jima. Consequently, tropical low systems (Typhoons) frequently developed over the northwestern Pacific. In order to search the source region for the sporadic input of the terrestrial materials, we conducted the backward air mass trajectory analysis in more details for the 1991 August/September samples. The trajectories demonstrated that the air masses associated with these samples are often originated from Southeast Asia including Indonesia, Kalimantan and Northern Australia (see Figure 19 and also Figure 5). Trajectory analyses confirmed that 3 of 5 samples (QFF 218, 219 and 221) in 1991August/September are involved with the trajectories from Southeast Asia. This is in contrast to other years during the observation; that is, only one such sample was found in 1992 and none was found in 1990 and 1993. High concentrations of both TC and terrestrial biomarkers were obtained in the aerosol samples collected 5-9 August (QFF 218) and 17-20 September (QFF 221) 1991 (see the trajectories in Figure 19 for the latter case), suggesting that they are transported from the regions in Southeast Asia. However, total nitrogen contents were relatively low throughout the 1991August/September period.

The year of 1991 was also characterized by a strong El Ninõ event, during which the air over the western equatorial Pacific became dry and hot and many forest fires occurred in Southeast Asia including Sumatra and Kalimantan [Kita et al., 2000], as well as the following year. During the forest fires and biomass burning, lipid class compounds that are originally present as leaf-waxes could be significantly emitted as a smoke particle via volatilization without severe oxidative degradation (Abas et al., 1995; Oros and Simoneit, 2001). These smokes produced by smoldering and flaming process may be uplifted by convection and transported long distances over the Pacific Ocean when wind direction turned to the northeast (Figure 5). It is of interest to note that β-sitosterol, a useful tracer of terrestrial plants (e.g., Gagosian, 1986), was detected abundantly in the marine aerosols collected during the El Ninõ/forest fire event of 1991 (see Figure 14e for QFF 221). Hence, terrestrial lipid class compounds may have been transported over Chichi-Jima Island in the western North Pacific during the 1991 event, as suggested by the air mass trajectory analysis (Figure 19). Such sporadic transport pathway could be involved with the changes in the atmospheric circulation pattern that is probably caused during the El Niño event.

Conte and Weber (2002) analyzed the marine aerosol samples collected at Bermuda in the Atlantic Ocean and found extremely high concentrations of plant biomarkers. They reported that high concentrations of terrestrial biomarkers are associated with the back air trajectories originating from Central America, where forest fires frequently occur and influence the regional air quality.

4.5. Atmospheric flux of terrestrial biomarkers to the sediments

In order to evaluate the importance of atmospheric input of terrestrial organic materials to the deep-sea sediments, we estimated a dry deposition flux for the lipid class compounds over the western North Pacific Ocean. For the estimation ,we used the averaged concentrations of n-alkanes (C_{27}-C_{35}, 1.6 ngm^{-3}), n-alcohols (C_{20}-C_{34}, 2.0 ngm^{-3}) and fatty acids (C_{21}-C_{34}, 3.5 ngm^{-3}) and the dry deposition velocity of 0.1 cm/sec for aerosol particles [Slinn and Slinn, 1980]. We obtained the air-to-sea fluxes of 5 μgm^{-2}yr^{-1}, 6.3 μgm^{-2}yr^{-1} and 11 μgm^{-2}yr^{-1}, respectively (Table 2). These minimum estimates of fluxes from the dry deposition calculation are one order of magnitude higher than the seawater-to-sediment fluxes in the northern North Pacific based on the sediment analysis [Kawamura, 1995]. However, the air-to-sea fluxes are equivalent to or a little larger than those obtained at Enewetak Atoll [Zafiriou et al., 1985]. These results indicate that the fluxes of terrestrial plant lipids involved with atmospheric transport are high enough to explain the abundant presence of terrestrial biomarkers in the deep-sea sediments in the North Pacific.

The higher fluxes obtained from the aerosols than the sediments may suggest that the terrestrial lipids are in part subjected to microbial degradation in the water column during the settling process and/or in the water-sediment interface after deposition. This comparison of the aerosols and sediments may also suggest that the atmospheric input of terrestrial organic matter in the 1990s was more enhanced compared to the last several thousands years (the late Holocene) by a global change. Alternatively, the higher values of the atmospheric fluxes may be due to the sampling location of Chichi-Jima, which is closer to the Asian continent than the sampling sites for the sediments used for the flux calculation in the central North Pacific [Kawamura, 1995]. Gagosian and Peltzer [1986] estimated annual wet and dry deposition fluxes of C_{21}-C_{36} n-alkanes at Enewetak Atoll and reported that rainfall deposition flux is ca. 10 times higher than that of dry deposition (25 $\mu g m^{-2} yr^{-1}$). These results and consideration again suggest that atmospheric transport of terrestrial organic materials from Asia and their subsequent deposition on the surface ocean are significant enough to contribute to the underling sedimentary organic matter in the Pacific Basin.

5. Summary and conclusion

1. Four year observations of long-chain n-alkanes, n-fatty alcohols, fatty acids and dicarboxylic acids in the marine aerosols from the western North Pacific showed a strong seasonal change in their concentrations with maxima in winter/spring seasons. Because these lipid biomarkers are of terrestrial higher plant and/or soil origin, atmospheric transport of continental materials over the western North Pacific should be enhanced in this

season.

2. Backward air mass trajectory analyses for the aerosol samples generally demonstrated that the air masses are delivered from Asia during winter/spring whereas they are originated from the Central Pacific during summer/autumn. This study indicated that long-range atmospheric transport is the major pathway to carry the terrestrial organic materials from Asia to the western North Pacific in the winter/spring season.
3. Although concentrations of terrestrial lipids are not abundant in the summer/autumn season, these biomarkers (especially, n-alkanes) showed the longer averaged chain length (ACL) in summer/autumn. This shift of the ACL values could be interpreted by the change in the source regions from the mid latitudes in Asian continent to the low latitudes.
4. Relative abundances of terrestrial n-alkanes, fatty alcohols and fatty acids in the aerosols are characterized by higher abundance of fatty acids under the influence of trade winds and vice versa under the influence of westerly winds. Triangular plots of the aerosol lipid data showed the results similar to the pelagic sediments recovered from the Central Pacific (15°S to 48°N) [Ohkouchi et al., 1997a], suggesting that abundant terrestrial organic materials are long-range transported to the Central Pacific through the atmosphere.
5. Sporadic transport of terrestrial materials over the western North Pacific was suggested to have occurred during 1991 summer/autumn. Back trajectory analysis demonstrated that the source region is Southeast Asia where forest fires had frequently and extensively occurred during the 1991 El Niño event.
6. Flux calculation of terrestrial organic materials showed that long-range atmospheric transport and subsequent deposition of continent-derived biomarkers are a major source of the terrestrial organic matter in the deep-sea sediments of the western North Pacific. These terrestrial biomarkers could further be used for the reconstruction of past atmospheric transport of continental materials and atmospheric circulation associated with paleoclimatology.

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Table 1. Concentrations of lipid class compounds, as well as total mass, carbon and nitrogen contents in the marine aerosols collected in Chichi-Jima Island, western North Pacific.

Components		Concentrations		Average	Median
	Carbon Range	Min.	Max.		
Aerosol mass (μgm^{-3})		11.6	292	52.8	34.7
Total carbon (μgm^{-3})		0.11	1.91	0.63	0.52
Total nitrogen (μgm^{-3})		0.04	0.93	0.18	0.11
n-Alkanes (ngm^{-3})	C_{20}-C_{36}	0.11	14.1	1.8	1.1
CPI of n-alkanes	C_{25}-C_{35}	1.8	14.6	4.5	3.8
n-Alcohols (ngm^{-3})	C_{13}-C_{34}	0.18	19.7	2.2	1.1
LMW alcohols	C_{13}-C_{19}	0.00	0.77	0.20	0.14
HMW alcohols	C_{20}-C_{34}	0.06	19.4	2.00	0.97
Cholesterol (ngm^{-3})	C_{27}	0.00	0.89	0.053	0.030
β-Sitolesterol (ngm^{-3})	C_{29}	0.00	0.38	0.066	0.046
Fatty acids (ngm^{-3})	C_{12}-C_{32}	2.4	60.2	13.8	11.4
LMW fatty acids	C_{12}-C_{19}	1.89	54.6	10.4	8.2
HMW fatty acids	C_{20}-C_{32}	0.38	24.3	3.5	2.3
Dehydroabietic acid	C_{20}	0.00	0.51	0.07	0.03
α,ω-Dicarboxylic acids (ngm^{-3})	C_8-C_{28}	0.00	11.7	3.1	2.5
LMW diacids	C_8-C_{19}	0.00	12.7	2.88	2.39
HMW diacids	C_{20}-C_{28}	0.00	4.54	0.83	0.51
UCM hydrocarbons (ngm^{-3})		0.22	59.1	5.4	3.4

Table 2. Calculated annual fluxes of total carbon and nitrogen, and lipid class compounds in the western North Pacific.

Components	Carbon Range	Flux ($\mu g m^{-2} y^{-1}$)
Total carbon		1700
Total nitrogen		560
n-Alkanes	C_{27}-C_{35}	5.0
n-Alcohols	C_{13}-C_{34}	6.9
LMW alcohols	C_{13}-C_{19}	0.6
HMW alcohols	C_{20}-C_{34}	6.3
Cholesterol	C_{27}	0.17
β-Sitolesterol	C_{29}	0.21
Fatty acids	C_{12}-C_{32}	43
LMW fatty acids	C_{12}-C_{19}	33
HMW fatty acids	C_{21}-C_{32}	11
Dehydroabietic acid	C_{20}	0.22
α,ω-Dicarboxylic acids	C_{8}-C_{28}	10
LMW diacids	C_{8}-C_{19}	9.1
HMW diacids	C_{20}-C_{28}	2.6
UCM hydrocarbons		17

Fluxes were calculated based on the analyses of marine aerosols over Chichi-Jima Island. See the text for the details.

Figure Captions

Fig. 1. Map of sampling location (Chichi-Jima Island) in the western North Pacific.

Fig. 2. Variations of wind direction at 700 hPa over Chichi-Jima in the western North Pacific (see a map in Fig. 1).

Fig. 3. Four-year variations of (a) aerosol mass, (b) total carbon and (c) total nitrogen in the marine aerosols collected from Chichi-Jima Island, western North Pacific.

Fig. 4. Monthly averaged concentrations of (a) aerosol mass, (b) total carbon and (c) total nitrogen in the marine aerosols collected from Chichi-Jima Island, western North Pacific. High values of aerosol masses in summer/autumn are influenced by the activity of the tropical low (Typhoon) in 1991 (see the text).

Fig. 5. Averaged wind directions and speeds (m/sec) over Chichi-Jima Island (850 hPa) for 17-20 September 1991 (aerosol QFF 221). Chichi-Jima is indicated with a closed circle.

Fig. 6. A capillary gas chromatogram of aliphatic hydrocarbon fraction isolated from the marine aerosol sample (QFF 207, March 4-7, 1991).

Fig. 7. Four-year variation of CPI index for n-alkanes (C_{25}-C_{35}) in the aerosols from the western North Pacific.

Fig. 8. Relationship between the concentrations of UCM hydrocarbons and CPI index of n-alkanes (C_{25}-C_{35}).

Fig. 9. A capillary gas chromatogram of alcohol fraction isolated from the marine aerosol sample (QFF 207, March 4-7, 1991).

Fig. 10. Four-year variation of averaged chain length (ACL) for (a) n-alkanes, (b) n-alcohols, (c) n-fatty acids, and (d) dicarboxylic acids in the marine aerosols from the western North Pacific.

Fig. 11. Four-year variation of terrestrial lipid concentrations, (a) n-alkanes (C_{27}-C_{35}), (b) n-alcohols (C_{20}-C_{34}), (c) monocarboxylic acids (C_{21}-C_{34}) and (d) dicarboxylic acids (C_{20}-C_{28}) in the marine aerosol samples from Chichi-Jima Island.

Fig. 12. Concentrations of terrestrial biomarkers as a function of the ACL index. (a) n-alkanes (C_{25}-C_{35}), (b) n-alcohols (C_{20}-C_{32}), (c) n-fatty acids (C_{21}-C_{32}), and (d) dicarboxylic acids (C_{20}-C_{28}).

Fig. 13. Typical backward air mass trajectories of (a) winter/spring season (10 days backward trajectories starting from 12UTC, 23 February 1992, QFF 399), (b) summer/autumn season (20 days backward trajectories starting from 12UTC, 22 August 1993, QFF 432). Initial positions of air parcels are placed at Chichi-Jima Island and ±0.5 degree in latitude and longitude. Air parcels are placed vertically at 850, 925 and 1000 hPa. Totally 27 trajectories are drawn on each map.

Fig. 14. Polar coordinate plots for the concentrations of terrestrial biomarkers against wind direction at 700 hPa over Chichi-Jima Island in the western North Pacific. (a) n-alkanes (C_{25}-C_{35}), (b) n-alcohols (C_{20}-C_{32}), (c) n-fatty acids (C_{21}-C_{32}), and (d) dicarboxylic acids (C_{20}-C_{28}), (e) β-sitosterol, and (f) dehydroabietic acid. Sampling date/month/year for the data points with the filter numbers are 1-4 September 1990 (QFF 194), 19-22 October 1990 (QFF 195), 6-9 September 1991 (QFF 220), 17-20 September 1991 (QFF 221), 21-25 February 1992 (QFF 399).

Fig. 15. Seasonal changes in average chain length (ACL) of (a) n-alkanes (C_{27}–C_{33}), (b) fatty alcohols (C_{24}-C_{30}) and (c) fatty acids (C_{22}-C_{32}) in the marine aerosols in the western North Pacific.

Fig. 16. Chain-length distributions of n-alkanes in higher plant leaf wax with average chain length (ACL, C_{27}-C_{33}). (a) a deciduous broadleaf (birch), collected in October from Hokkaido, Japan (43.1°N, 141.3°E), (b) an evergreen broadleaf (theaceae), collected in September from Chichi-Jima Island, Japan (27.4°N, 142.1°E), and (c) an evergreen broadleaf (unknown species), collected in October from Bidadari Island, Indonesia (6°S, 106.7°E).

Fig. 17. Triangular plots of terrestrial biomarkers: n-alkanes (C_{25}-C_{35}), n-alcohols (C_{20}-C_{34}) and n-fatty acids (C_{21}- C_{34}) in the marine aerosol samples collected from Chichi-

Jima Island, western North Pacific. Summer/autumn seasons mean July to October whereas winter/spring seasons mean November to June.

Fig. 18. Triangular plots of terrestrial biomarkers in the marine sediments from the central Pacific at 175°E transect (Ohkouchi et al., 1977a). Sediment samples collected from mid latitudes (15°N-48°N) fall in Category A whereas those from low latitudes (12°S-12°N) fall in Category B.

Fig. 19. Air mass trajectory for the aerosol sample collected at Chichi-Jima (17-20 September 1991, QFF 221) during El Ninõ event (1991, August). Trajectory analyses were conducted as same as Figure 13 except for the 20 days trajectories starting from 12UTC, 19 September 1991.

Fig. 1 (Kawamura et al.)

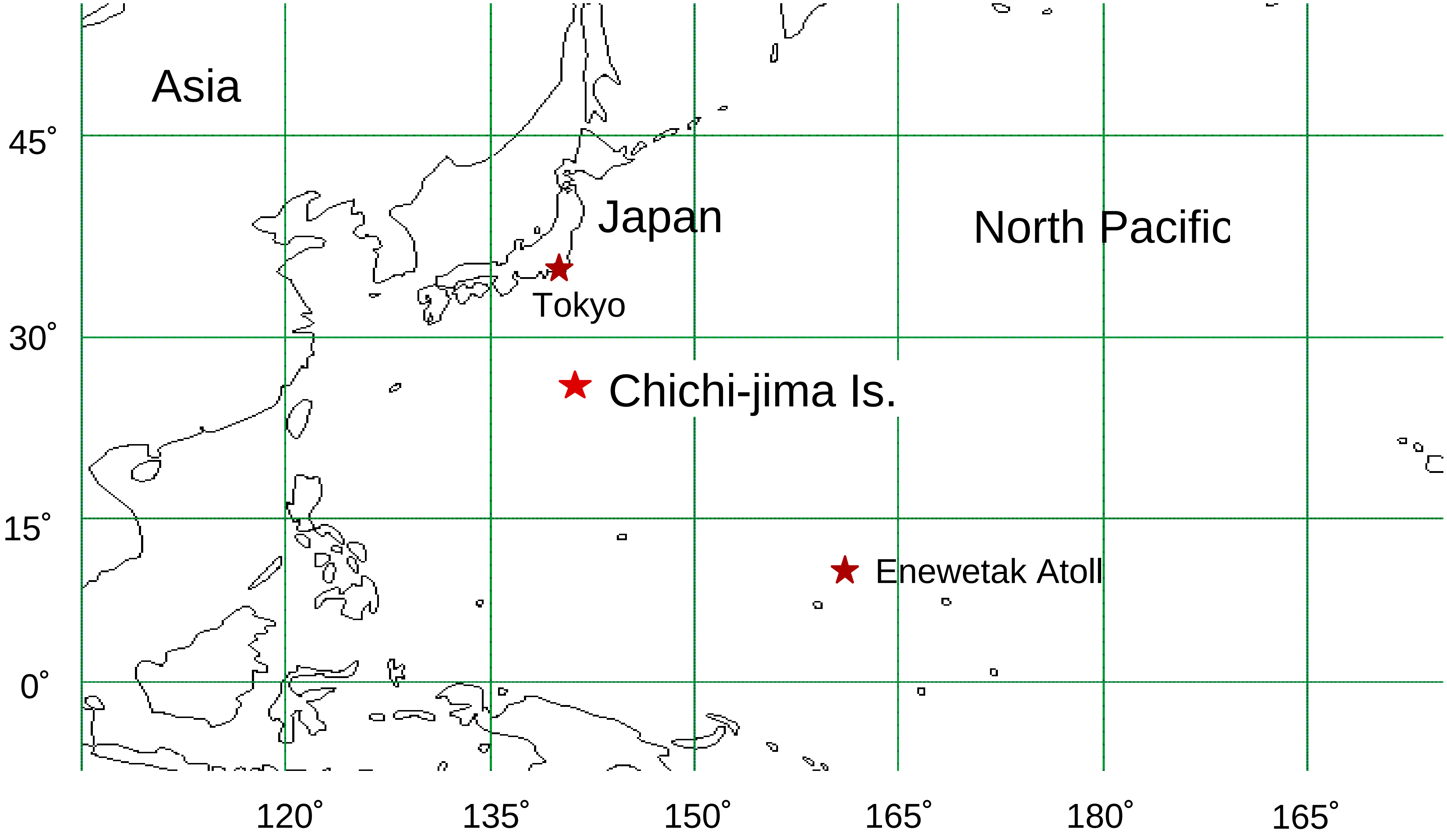
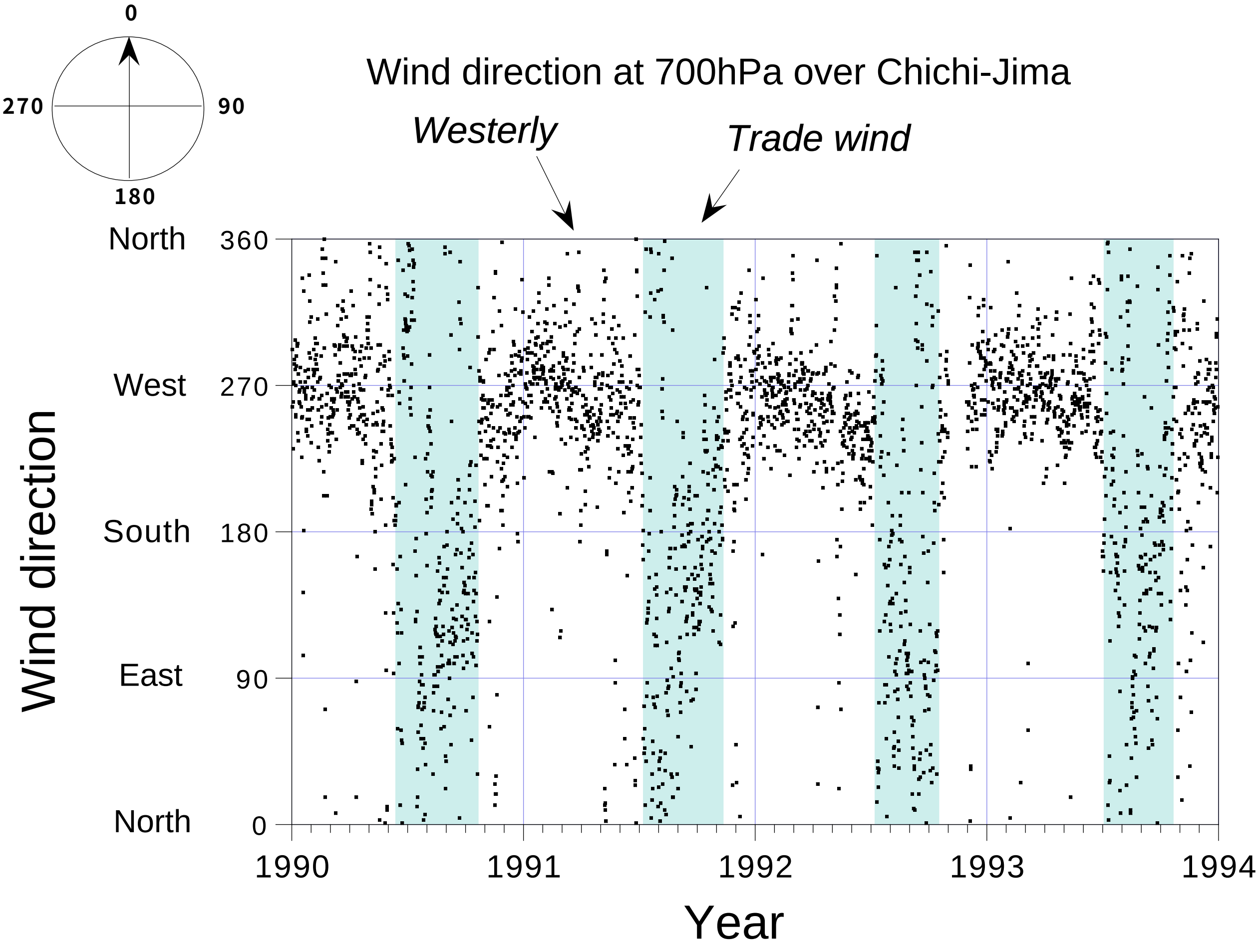
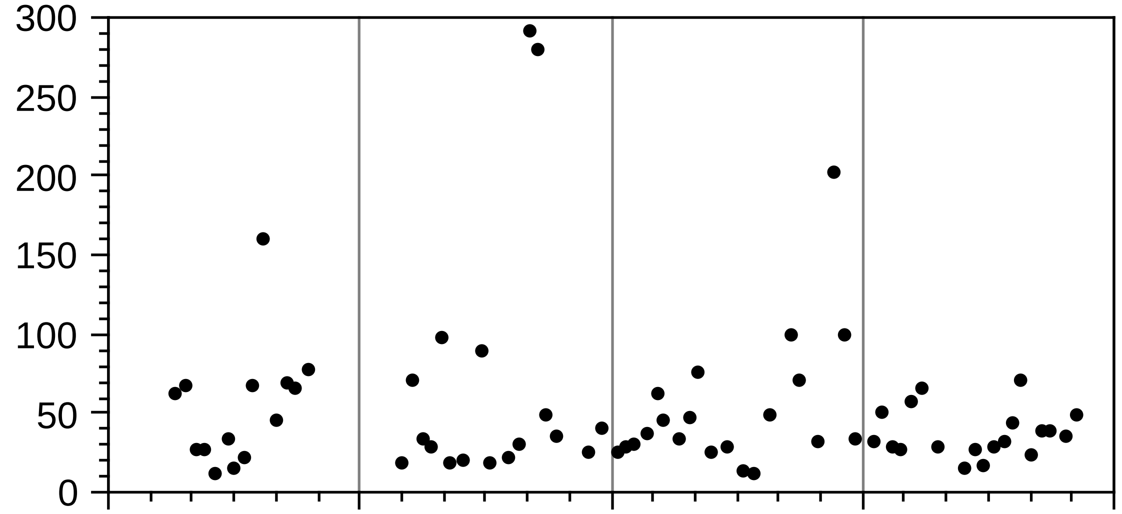


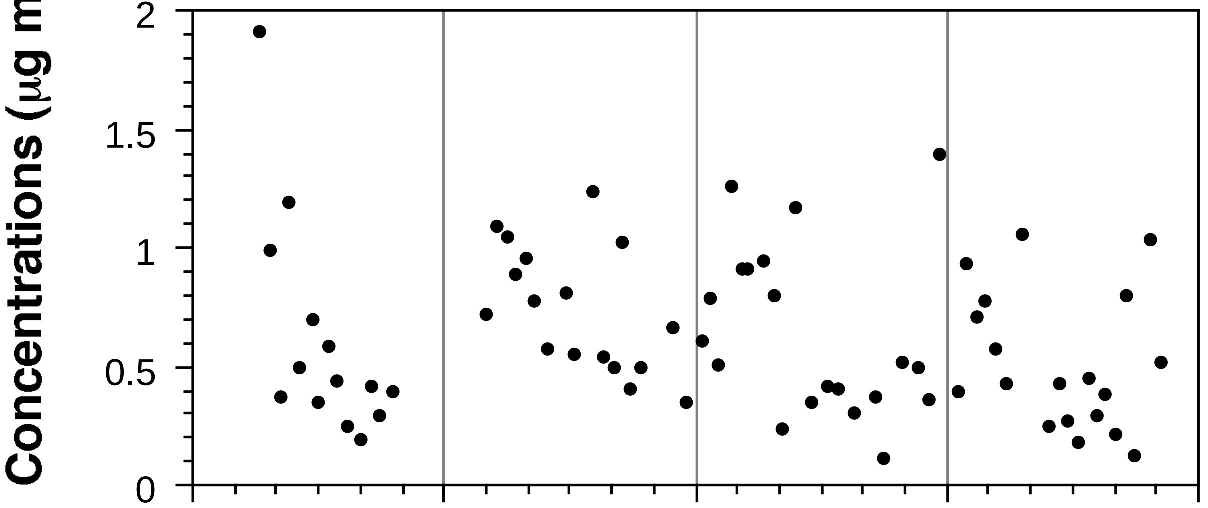
Fig. 2 (Kawamura et al.)



(a) Aerosol mass



(b) Total carbon



(c) Total nitrogen

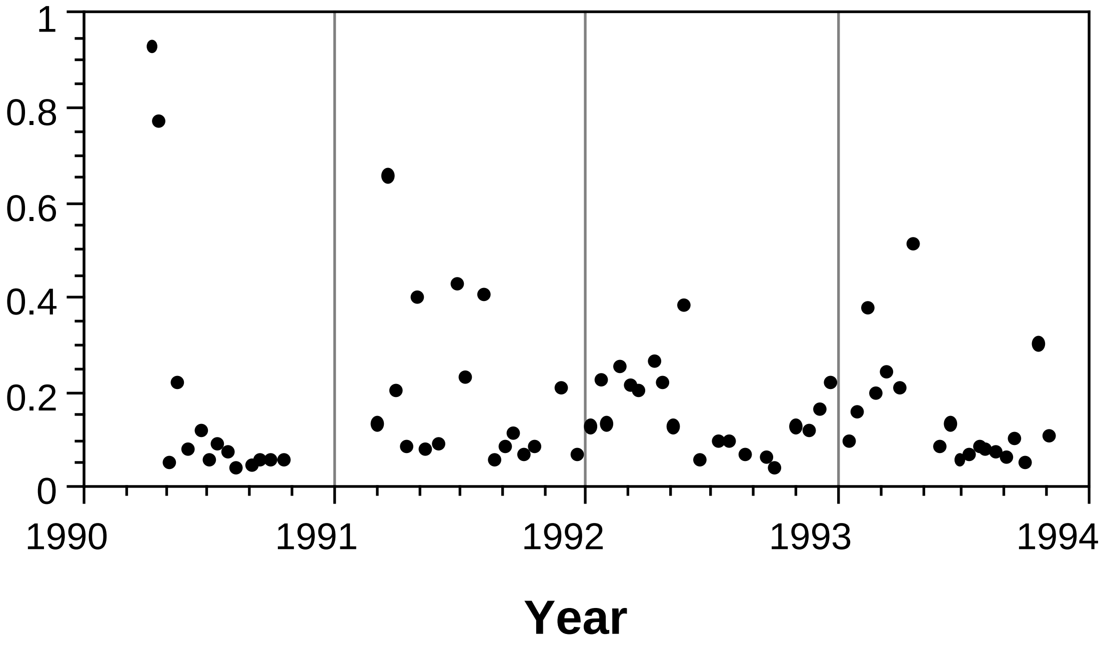


Fig. 4 (Kawamura et al.)

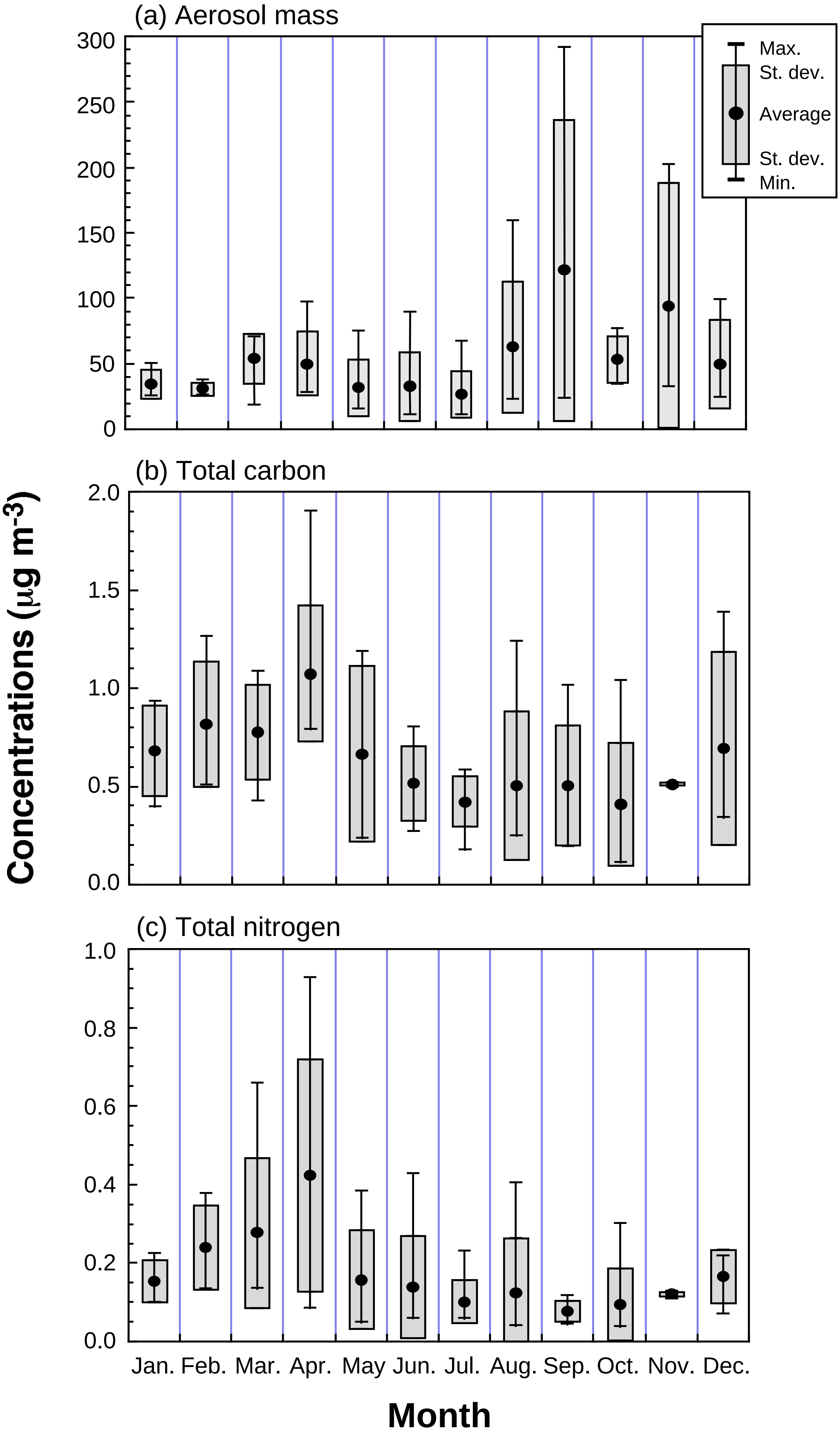


Fig.5 (Kawamura et al.)

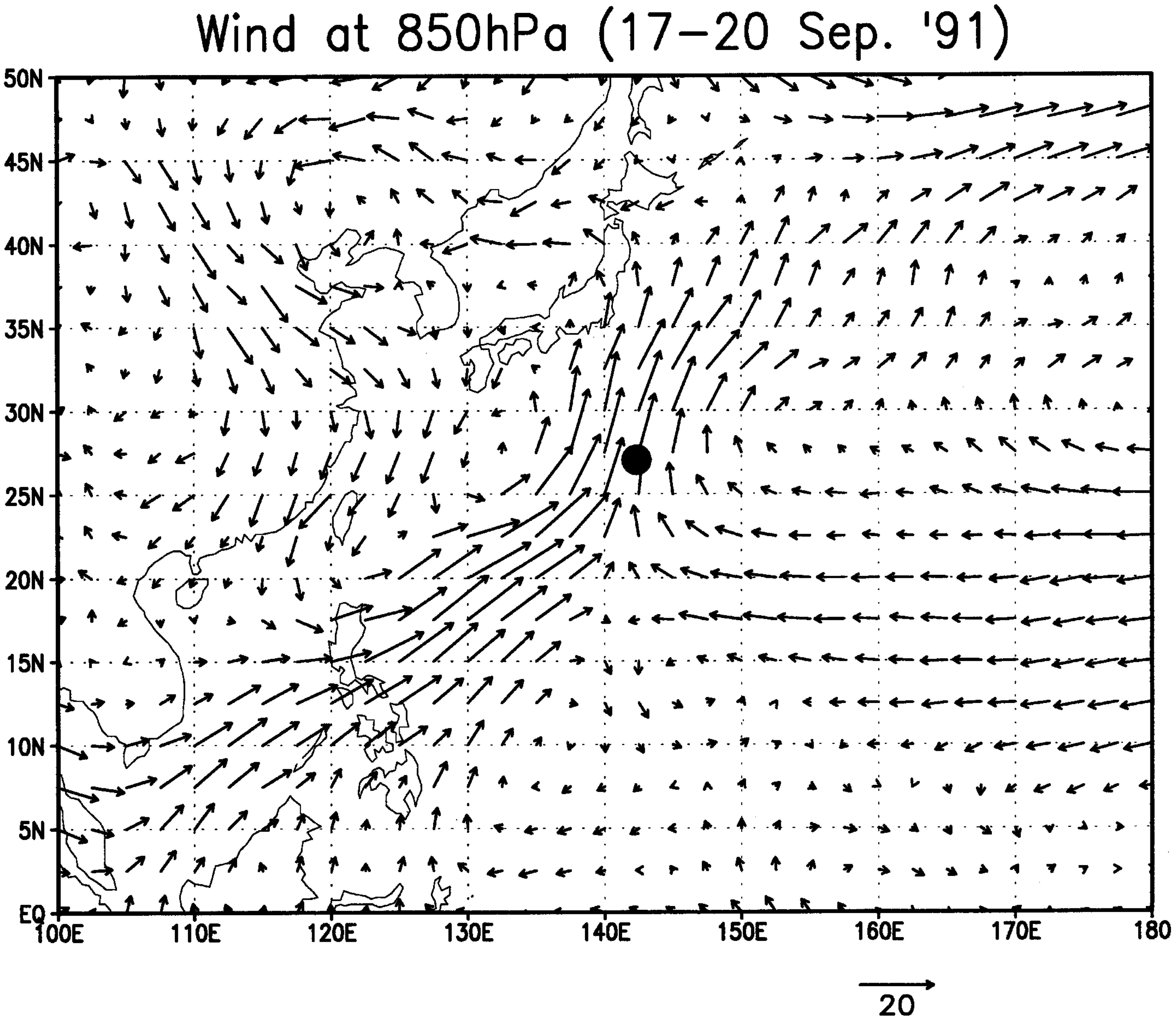


Fig.6 (Kawamura et al.)

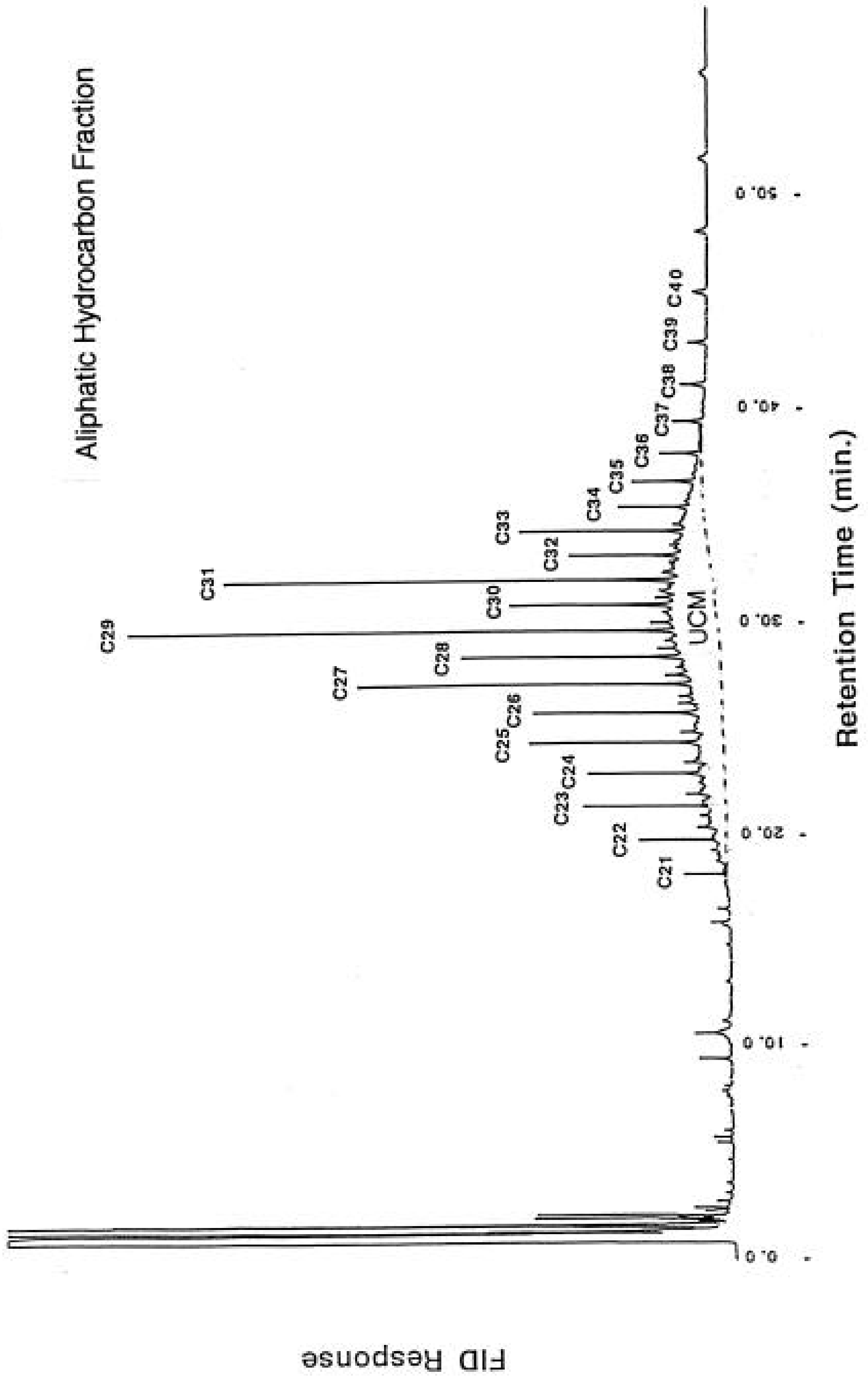


Fig. 7 (Kawamura et al.)

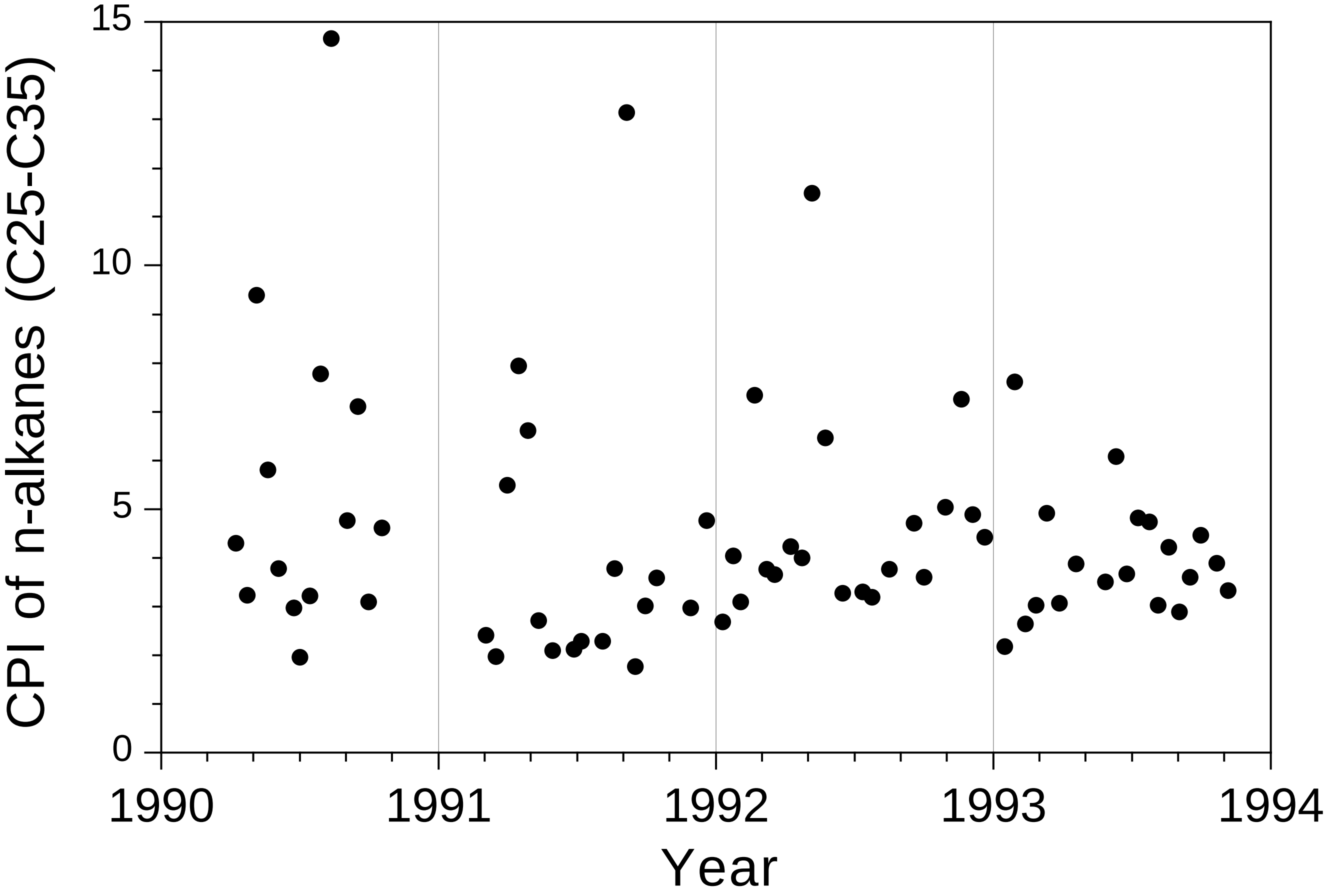


Fig. 8 (Kawamura et al.)

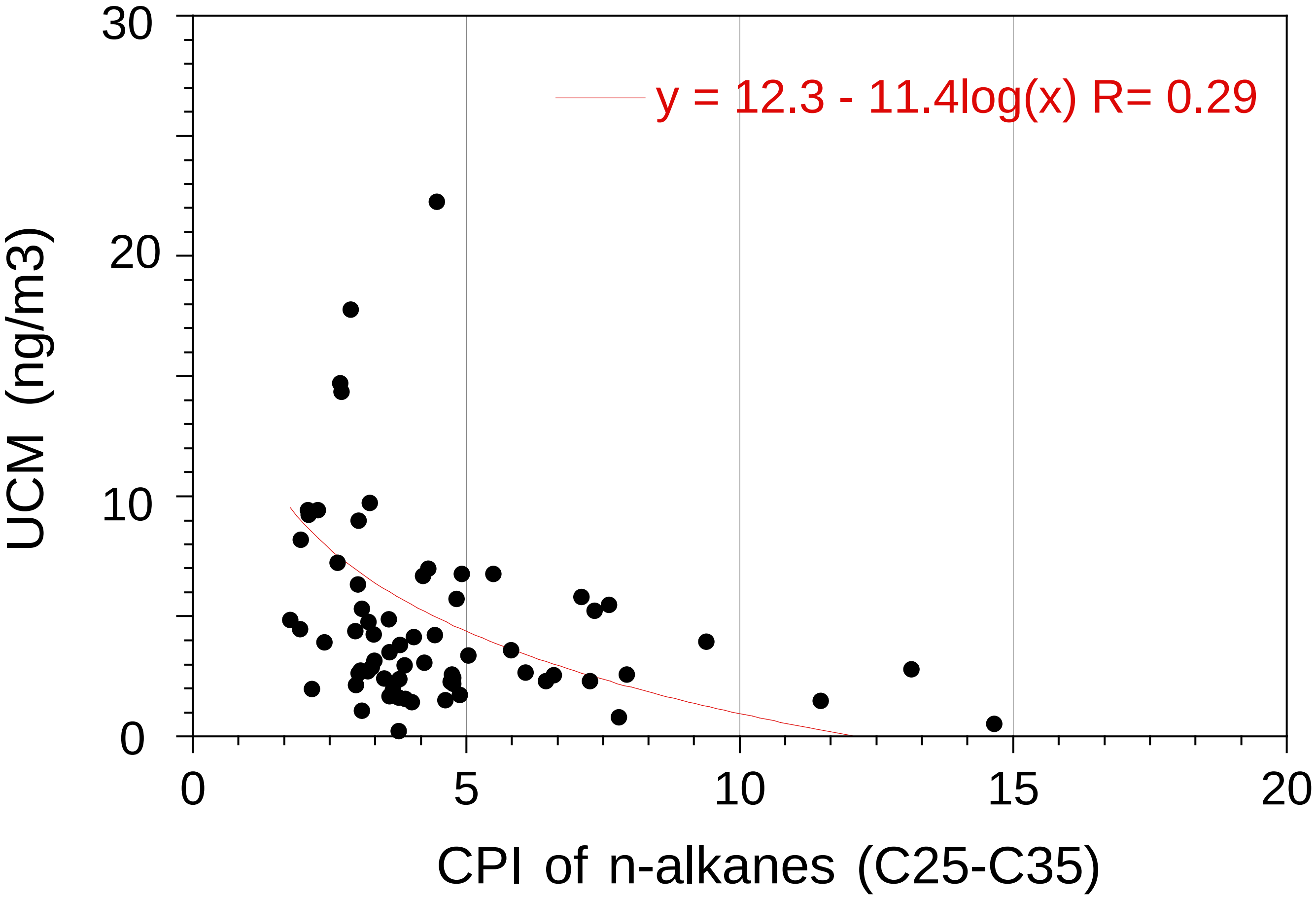


Fig.9 (Kawamura et al.)

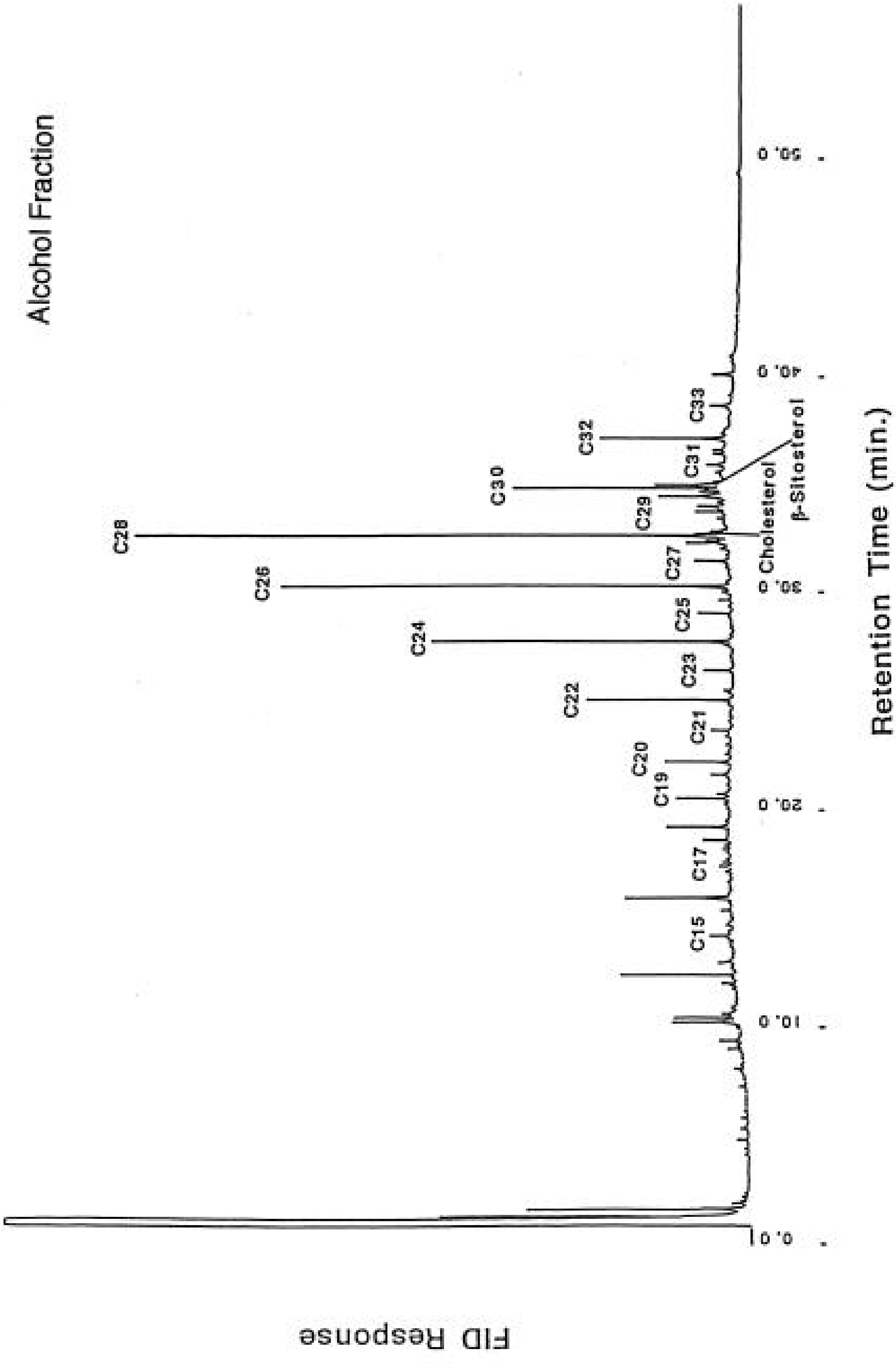


Fig. 10 (Kawamura et al.)

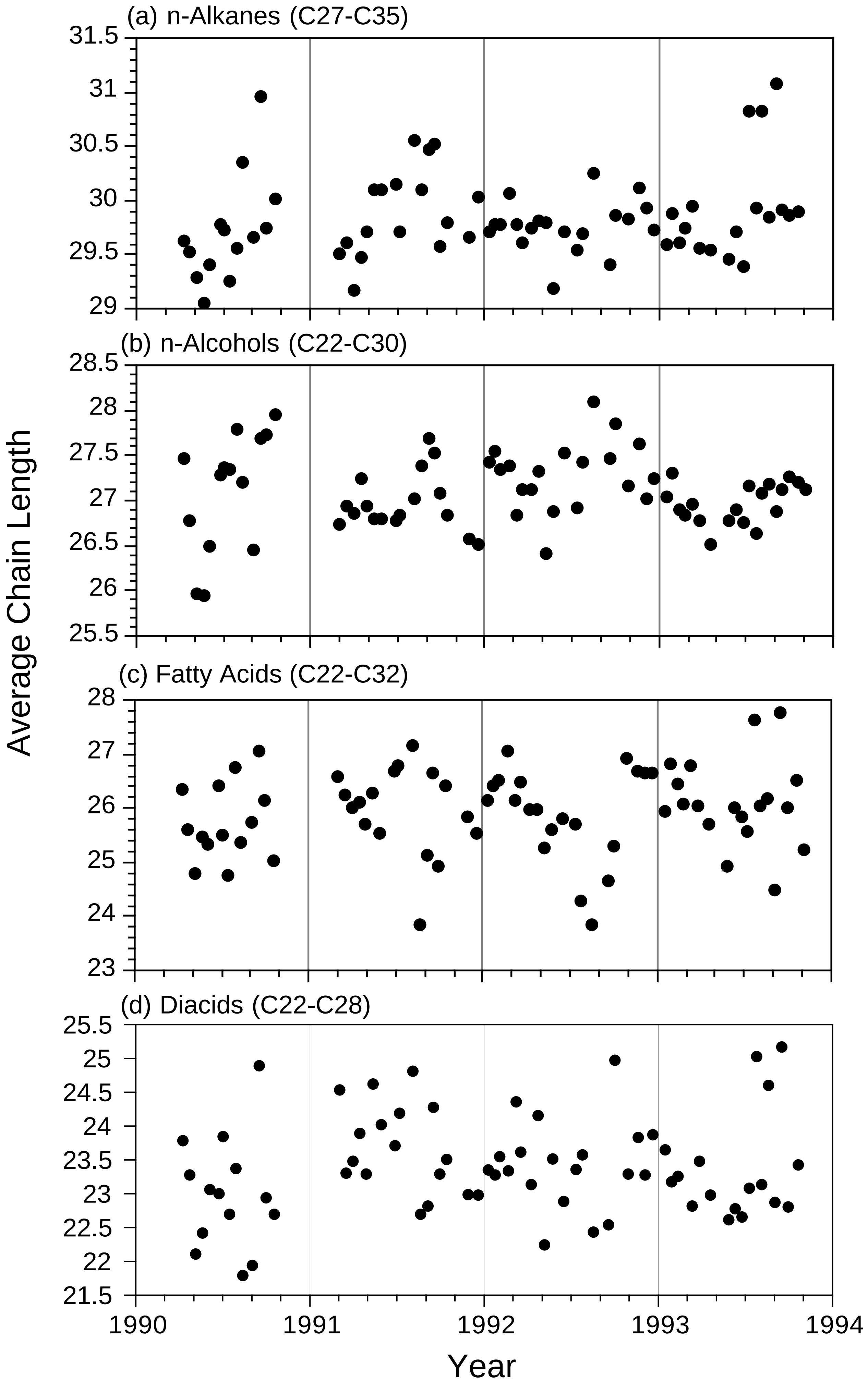


Fig. 11 (Kawamura et al.)

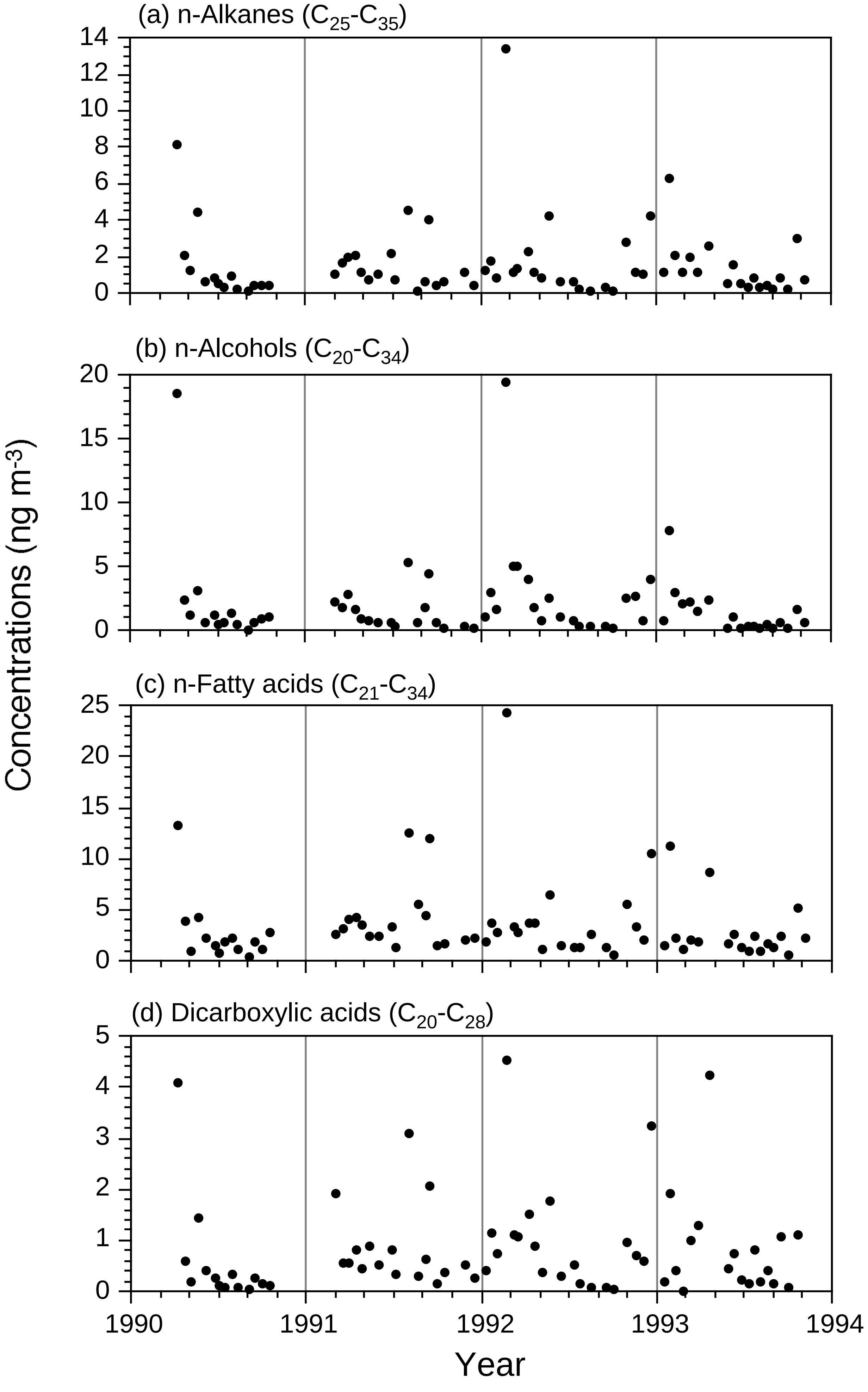
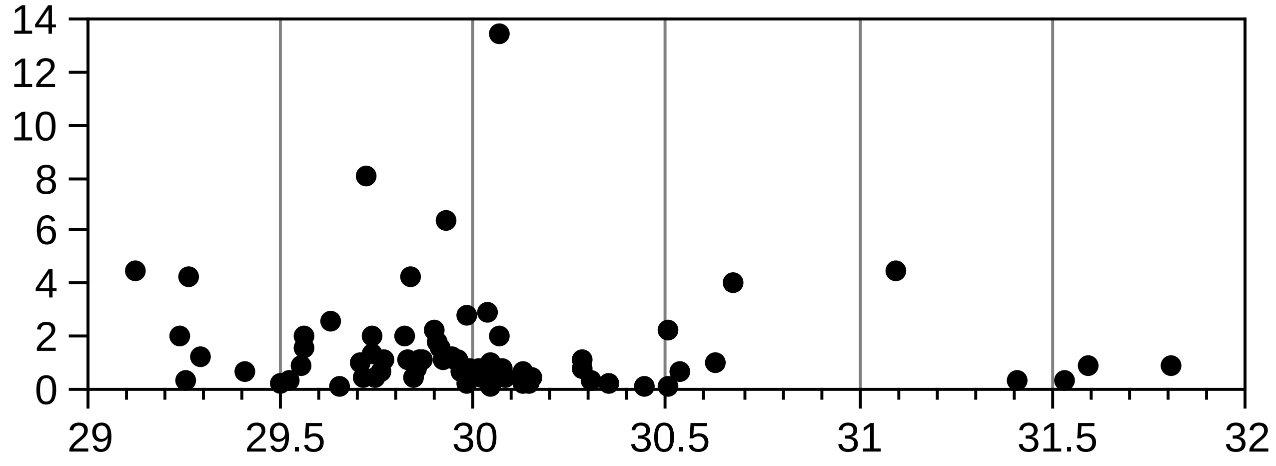
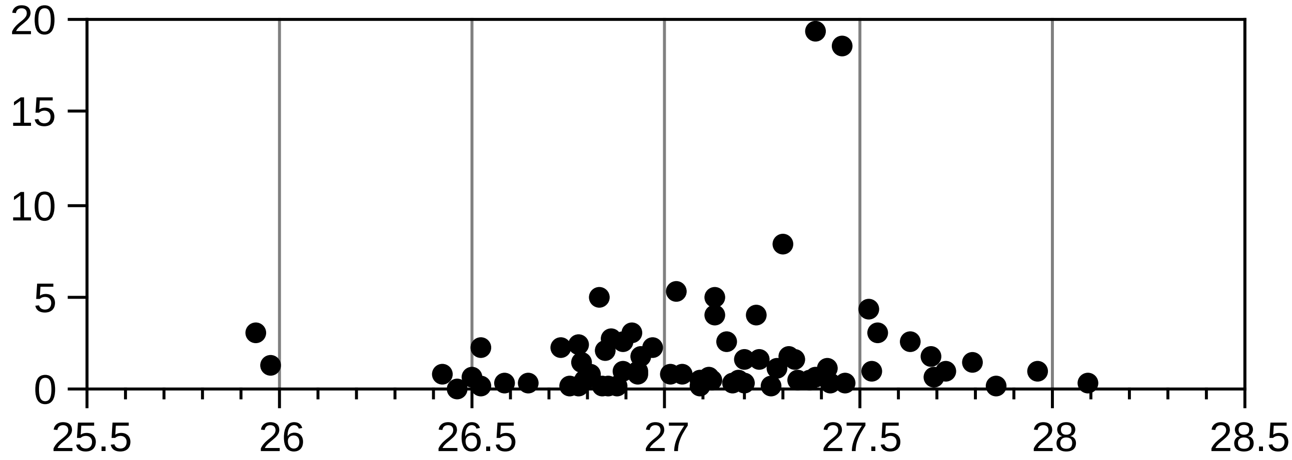


Fig.12 (Kawamura et al.)

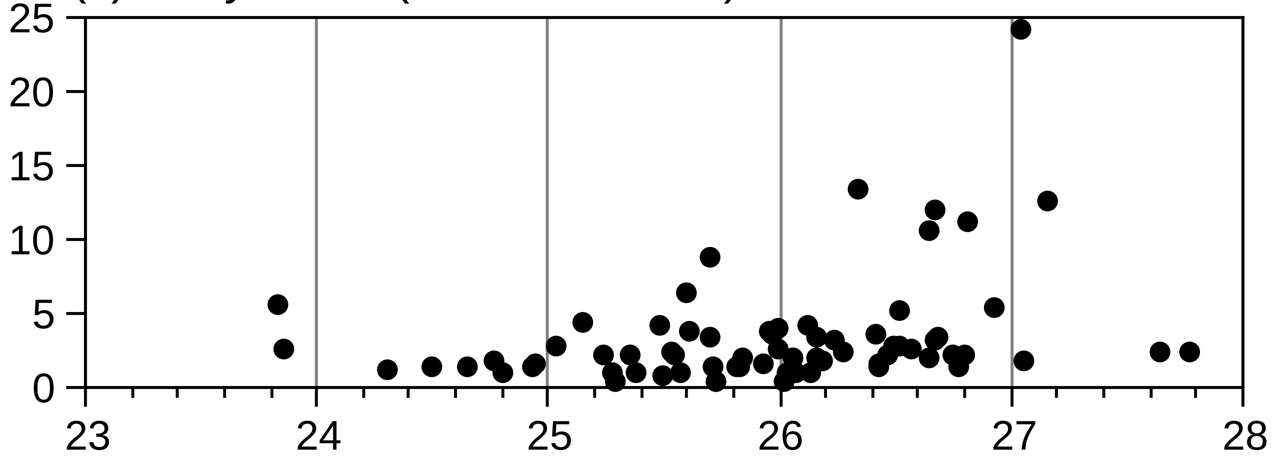
(a) n-Alkanes (ACL: C27-C35)



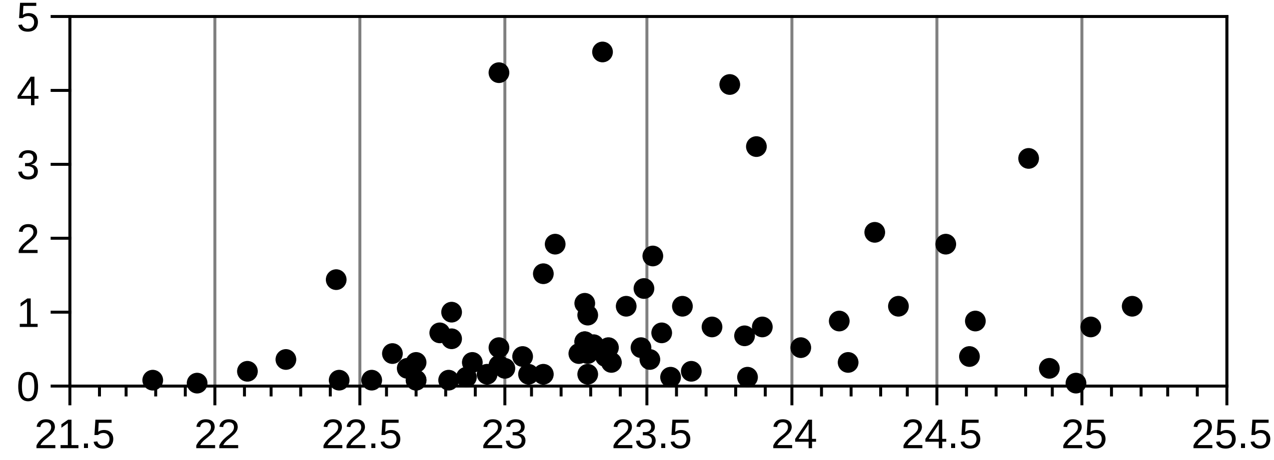
(b) n-Alcohols (ACL: C22-C30)



(c) Fatty Acids (ACL: C22-C32)



(d) Diacids (ACL: C20-C28)



1992.02.23.12UTC (10 days backward trajectories)

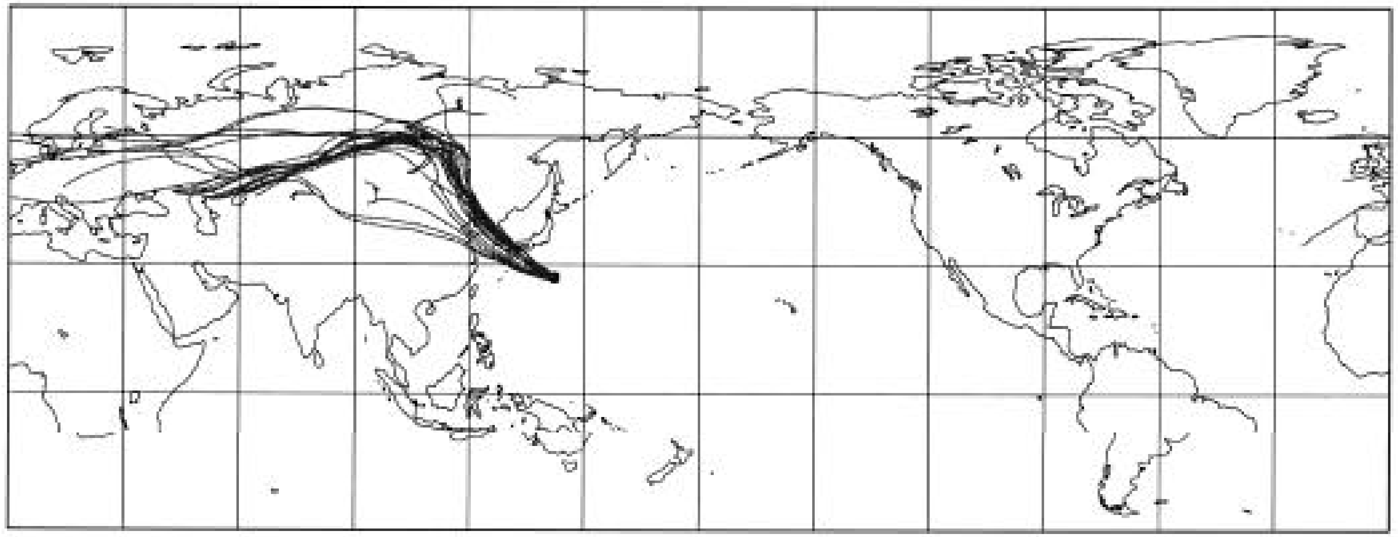
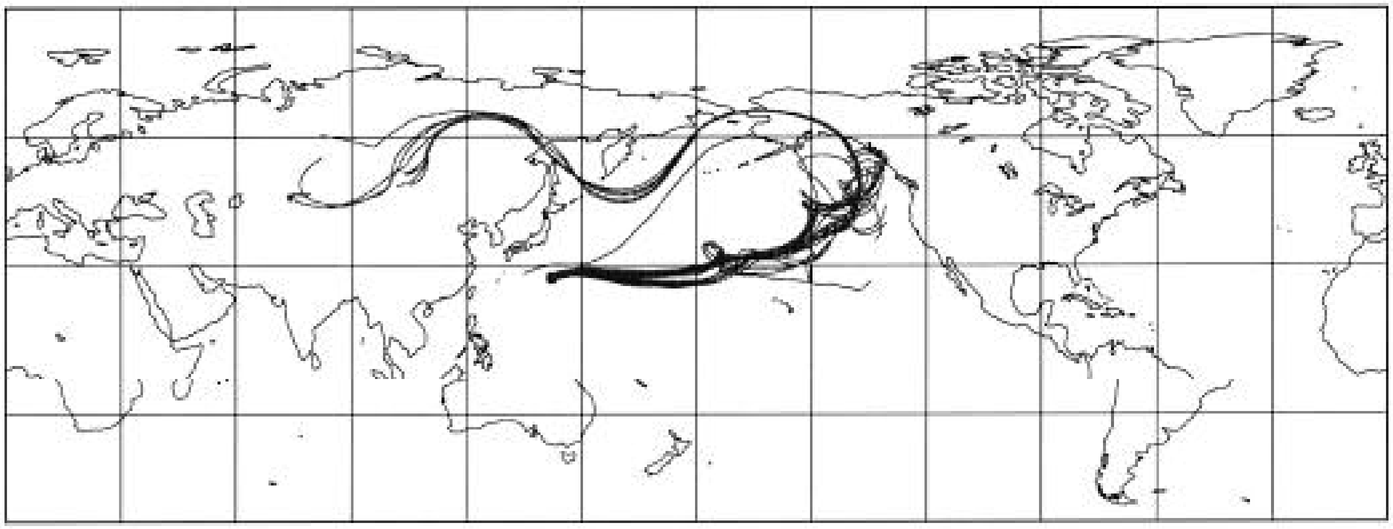


Fig.13a (Kawamura et al.)

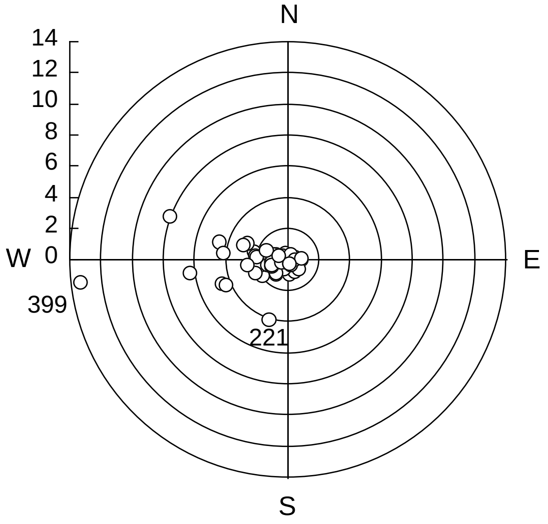


1993.08.22.12UTC (20 days backward trajectories)

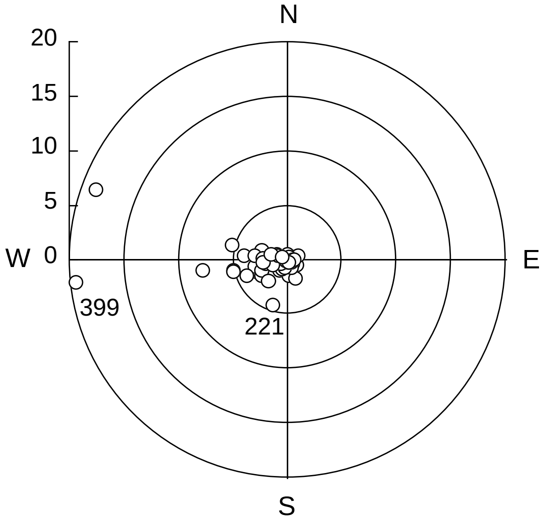
Fig.13b (Kawamura et al.)

Fig. 14 (Kawamura et al.)

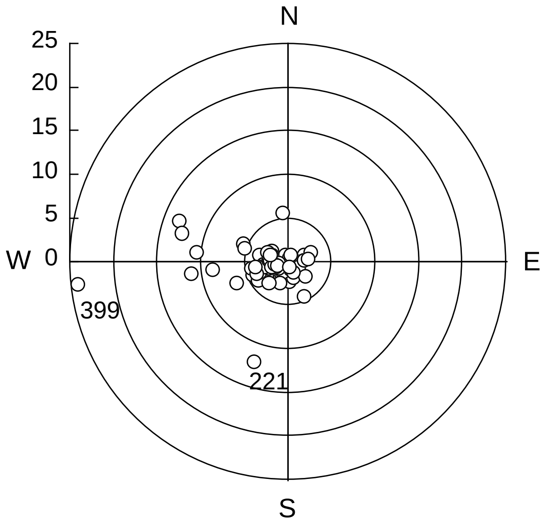
(a) n-Alkanes



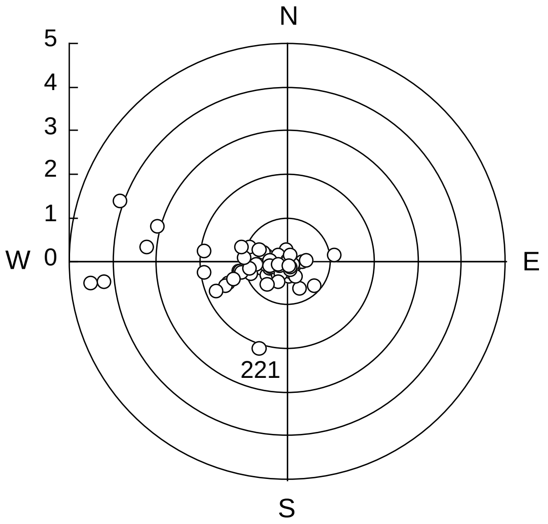
(b) n-Alcohols



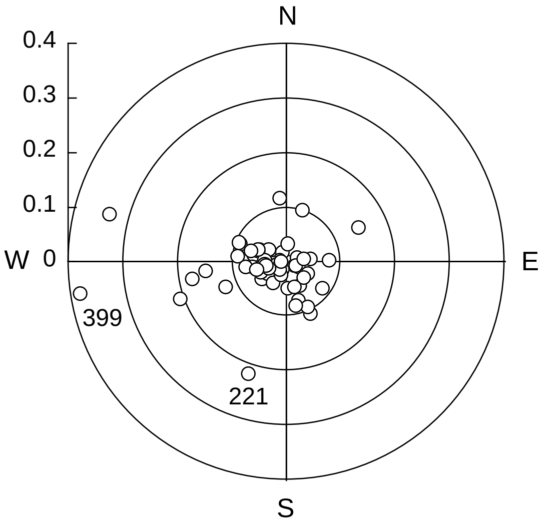
(c) Fatty Acids



(d) Diacids



(e) β-Sitosterol



(f) Dehydroabietic acid

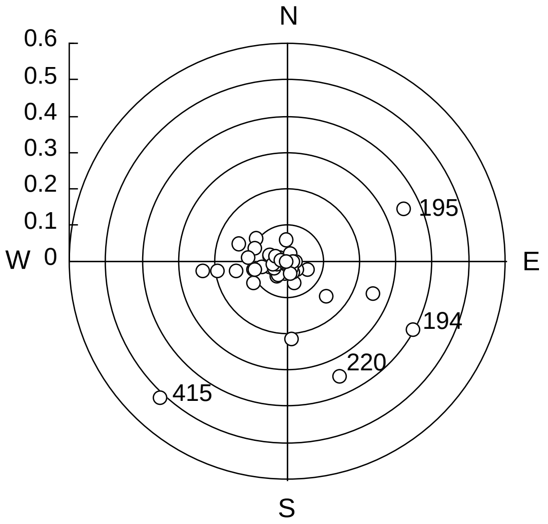


Fig. 15 (Kawamura et al.)

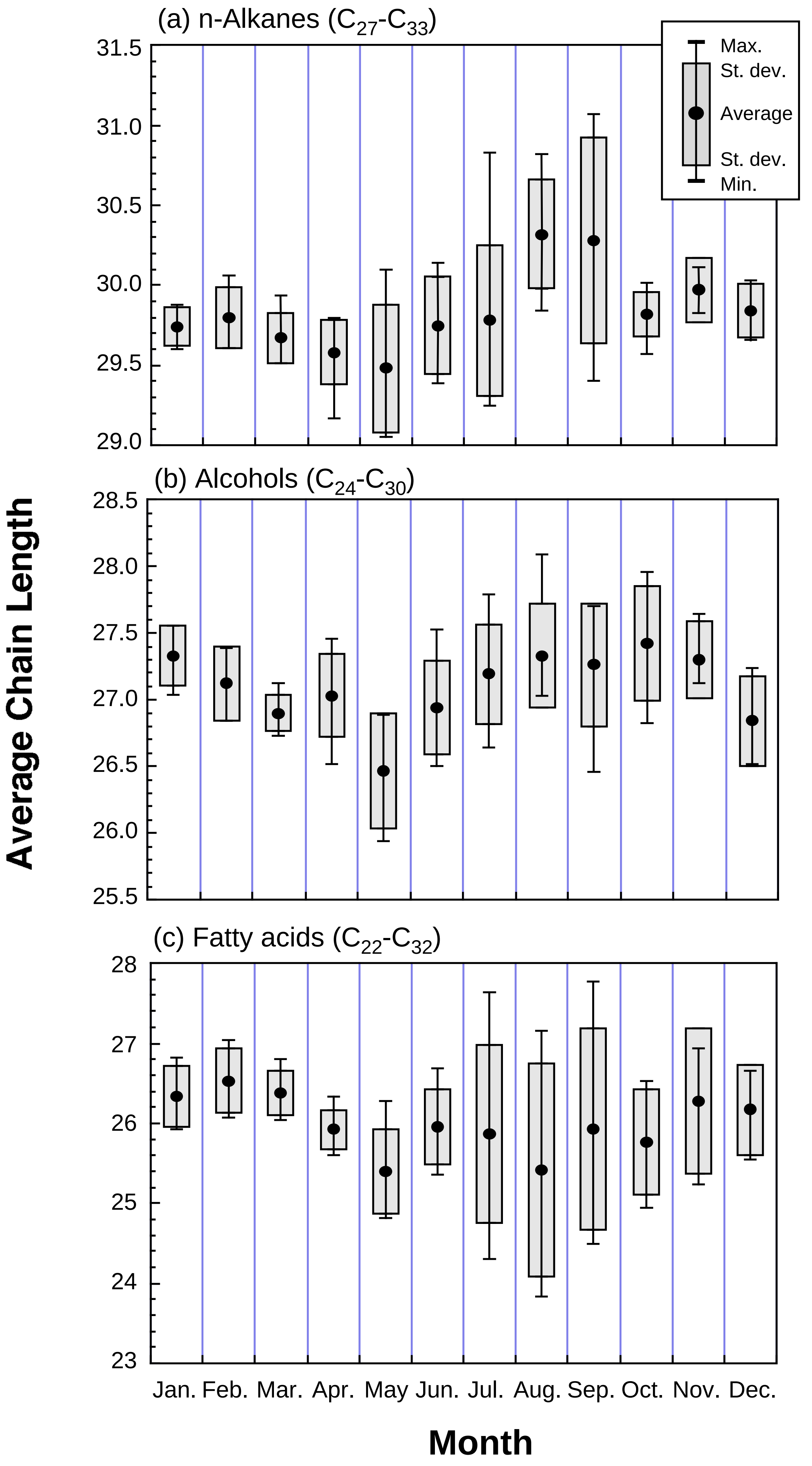


Fig. 16 (Kawamura et al.)

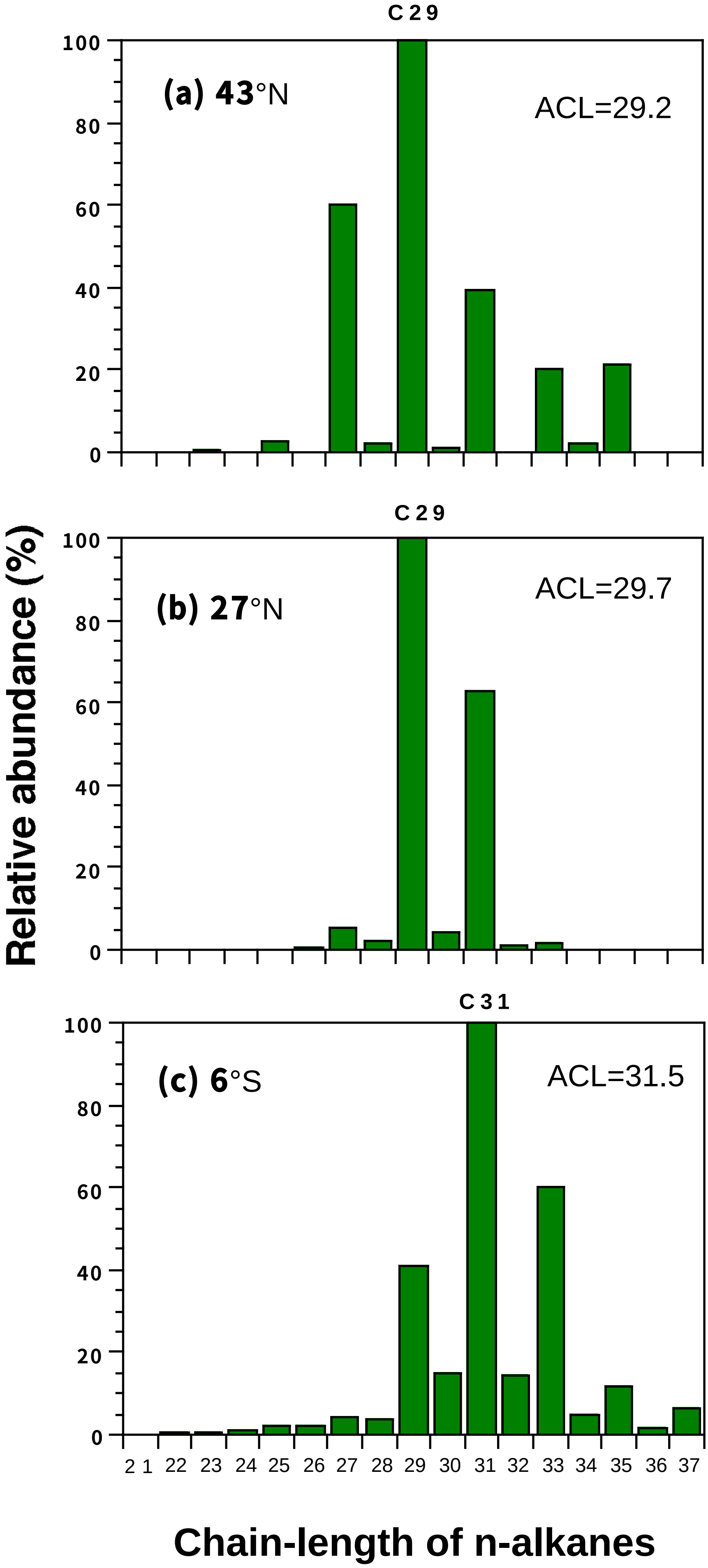


Fig.17 (Kawamura et al.)

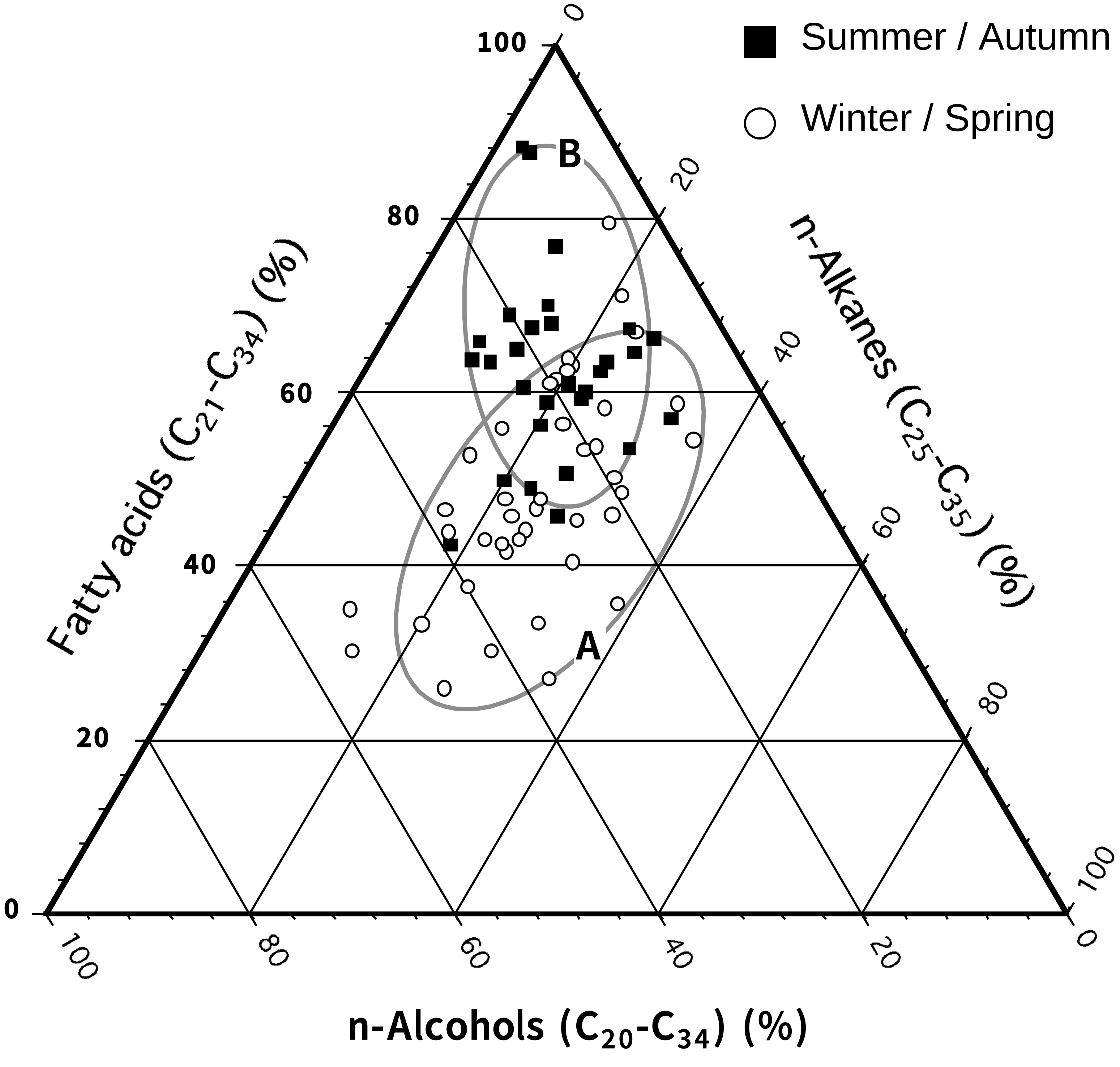
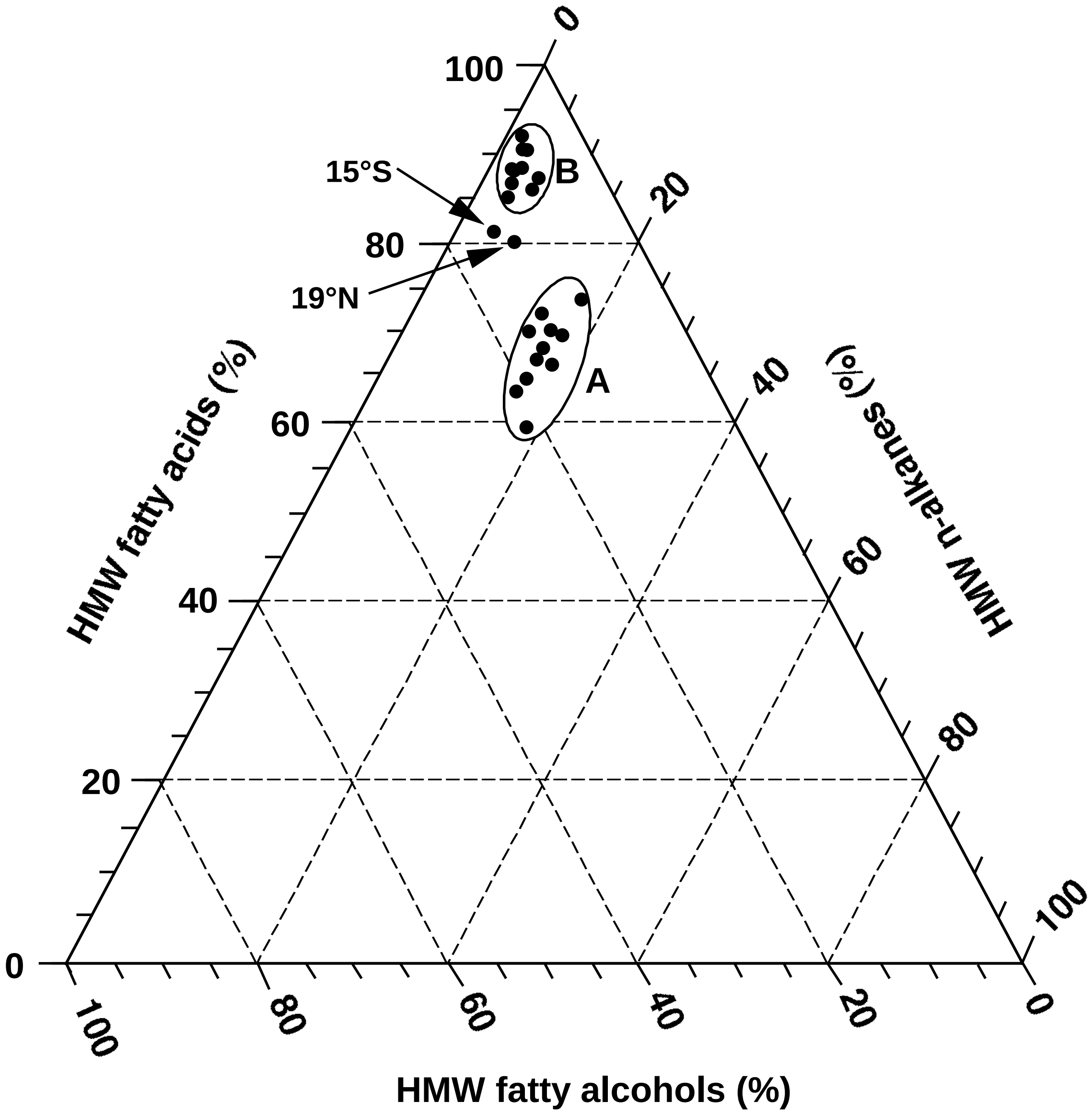


Fig. 18 (Kawamura et al.)



1991.9.19.12UTC (20 days backward trajectories)

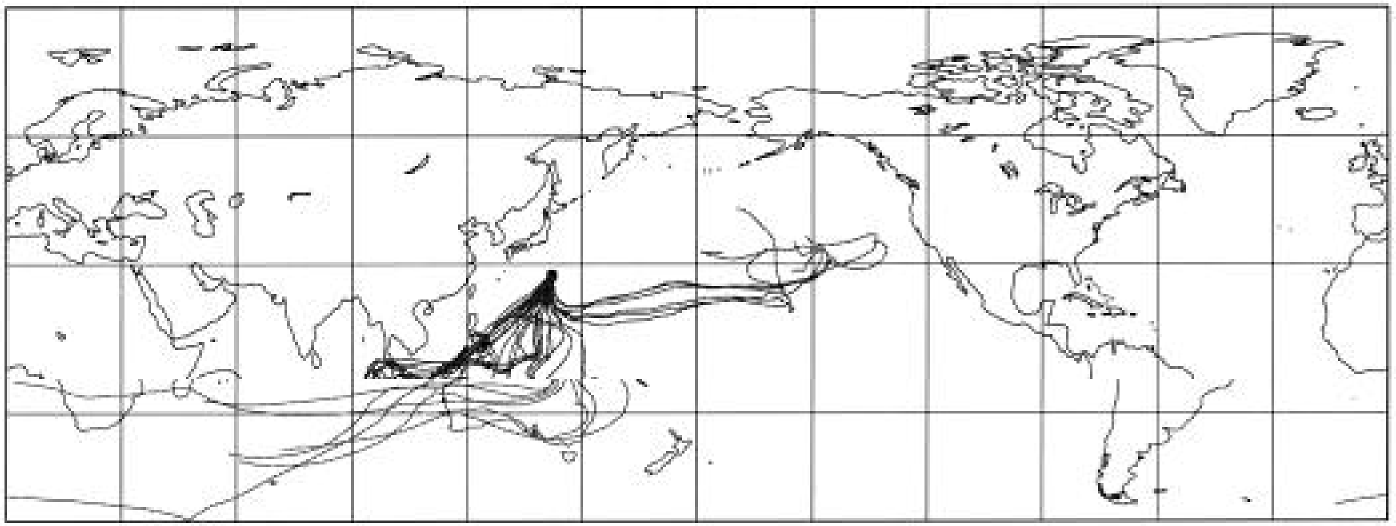


Fig.19 (Kawamura et al.)