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Fatty acid composition of particulate matter and photosynthetic products in subarctic and subtropical Pacific

Takeo Hama[1]

Institute for Hydrospheric-Atmospheric Sciences, Nagoya University, Chikusa-ku, Nagoya 464-8601, Japan

[1]Present address: Institute of Biological Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8572, Japan

Abstract. The fatty acid composition of lipid materials in particulate matter and photosynthetic products was determined using ^{13}C gas chromatography–mass spectrometry methodology in the subarctic and subtropical Pacific. Polyunsaturated fatty acids (PUFA) were measured as one of the major constituents of particulate and photosynthetically produced lipids in the subarctic Pacific. In the subtropical Pacific, on the other hand, a quite simple fatty acid composition was found, consisting mainly of saturated fatty acids (SFA) and monounsaturated fatty acids (MUFA); the production rate of PUFA could not be determined due to the low concentration in the subtropical area. The relationship between the fatty acid composition of particulate lipids and photosynthetically produced lipids indicated that PUFA observed in particulate lipids were mainly associated with phytoplankton. Non-living lipids, on the other hand, could be mainly constituted by SFA, due to the lability of PUFA to degradation. The difference in the contribution of phytoplankton lipids to particulate lipids is considered as an important factor affecting the difference in the fatty acid composition of particulate lipids between subarctic and subtropical Pacific.

Introduction

Lipid is one of the major organic constituents of all organisms, as well as carbohydrate and protein, and it is widely distributed in oceanic environments. The chemical structures of fatty acids, which are basic constituents of lipid material, vary in carbon chain length, and number and position of double bonds. Some fatty acids are specific to individual classes of organisms and attempts to trace organic materials from sea surface to sea bottom have been made using the fatty acid composition of particulate matter, sinking particles and sediments (e.g. Tanoue and Handa, 1980; De Baar *et al*., 1983; Wakeham and Canuel, 1988; Reemtsma *et al*., 1990; Harvey and Johnston, 1995).

Despite the abundance of cumulative knowledge on the compositional change in lipid material from sea surface to bottom, little information has been available on the geographical variability of fatty acid composition of particulate matter so far. Tanoue and Handa (1982) compared the fatty acid composition in particulate matter from various oceanic areas (7°N–64°S) and found high proportions of polyunsaturated fatty acids (PUFA) at the southern area of the Antarctic convergence. They suggested that water temperature and nutrient availability could regulate the fatty acid composition of particulate matter. Wakeham and Lee (1989), on the other hand, observed that PUFA accounted for a substantial part of the particulate lipids at the central North Pacific Gyre. Their results suggest that water temperature is not the sole related determinant in the contribution of PUFA in the particles.

Particulate matter filtered onto filter paper contains not only phytoplankton, but also non-phytoplankton microorganisms such as microzooplankon, some portion of living bacteria and non-living particles. The fatty acid composition of phytoplankton alone cannot be measured in natural environments and, therefore, the compositions of phytoplankton lipids are always 'blurred' by the presence of non-phytoplanktonic lipids. The degree of the 'blurring' effect of non-phytoplankton should depend on the phytoplankton biomass. In oligotrophic waters, however, the fatty acid composition of particulate lipids has usually been considered to reflect the composition of phytoplankton lipids (Ackman *et al*., 1968; Tanoue and Handa, 1982; Mayzaud *et al*., 1989; Wakeham and Lee, 1989), and the relationship between the fatty acid composition of particulate lipids and environmental factors has generally been discussed in relation to cultured phytoplankton.

Hama (1991) combined ^{13}C tracer and gas chromatography/mass spectrometry (GC/MS) methods to determine the fatty acid composition of photosynthetic products, which reflects phytoplankton metabolism, and indicated that some fatty acids in particulate lipids were mainly of non-phytoplankton origin. The ^{13}C/GC/MS method provides significant information on differences in fatty acid composition, both in particulate and photosynthetically produced lipids.

It has been impossible to estimate the fatty acid compositions of phytoplankton and non-phytoplankton particles separately, so the nature of non-phytoplankton lipid has not been determinable. Comparison of the fatty acid compositions of photosynthetically produced lipids and of particulate lipids by the new ^{13}C/GC/MS method can yield information on the 'freshness' of non-phytoplankton lipids.

In the present study, fatty acid compositions of photosynthetically produced lipids and particulate lipids were determined in the subarctic and subtropical Pacific, and related to physicochemical and biological parameters such as water temperature, nutrient concentration, chlorophyll (Chl) *a* concentration and primary productivity, in order to elucidate (i) the relationship between fatty acid compositions of phytoplanktonic and non-phytoplanktonic lipids and (ii) the differences in fatty acid compositions of photosynthetically produced lipids and particulate lipids between subarctic and subtropical Pacific.

Method

Ship observation

^{13}C uptake experiments were carried out in the subarctic region (45°N, 165°E) on 13 May (Station A) and 3 June 1991 (Station A′), and in the subtropical Station B (25°N, 165°E) on 20 May during a cruise (KH-91-3) of the 'Hakuho-Maru', Ocean Research Institute, University of Tokyo. Water samples were collected from the euphotic depth (6–7 layers) before dawn and transferred into three 6.5 l polycarbonate bottles. After adding [^{13}C]$NaHCO_3$ (final ^{13}C atom% in dissolved inorganic carbon was ~10%), the incubation bottles were suspended at a given depth (*in situ* method). Incubations were started around dawn and bottles were

recovered around the following dawn (24 h incubation). Subsamples (600 ml) were taken from each incubation bottle and filtered through pre-combusted (450°C, 4 h) glass fiber filters (Whatman GF/F) for the analysis of primary production rate. The remaining water was also filtered through glass fiber filters (Whatman GF/F) for the determination of fatty acid composition. Filters were stored at –20°C until analysis.

Analytical techniques

Lipid material was extracted with chloroform/methanol (1:2 v/v) with ultrasonic energy for 15 min and the extract separated by centrifugation. This procedure was repeated three times. Distilled water was added to the combined extract and the chloroform phase was used for lipid analysis (Hama and Handa, 1987). After addition of internal standard (21:0 acid), lipids were saponified with 0.5% KOH/CH_3OH at 65°C (Metcalfe *et al.*, 1966). Fatty acids were methylated by 14% BF_3/CH_3OH at 65°C.

The concentrations of fatty acids were determined by a gas chromatograph (Shimadzu GC-14A) equipped with a flame ionization detector, using a fused silica capillary column (HR-SS-10, 25 m × 0.25 mm i.d., Shinwa Chemical Industries Ltd) with N_2 as carrier gas. Oven temperature was programmed from 120 to 230°C at 3°C min^{-1} and held isothermally for 15 min.

The isotopic ratio of $^{13}C/^{12}C$ in each fatty acid was determined by a gas chromatograph/mass spectrometer (JEOL DX-302). The separation condition of fatty acid was identical with GC analysis shown above except for the program rate (4°C min^{-1}) of oven temperature. Chemical ionization (CI) spectra of each fatty acid were obtained with isobutane as a reagent gas and detailed analytical conditions were shown in Hama (1991). The ^{13}C atom% of fatty acid in the incubated samples was calculated from the differences in the relative intensities of isotope peaks between non-incubated and incubated samples (Kouchi, 1982; Hama *et al.*, 1987). The calculations of the ^{13}C atom% of fatty acids with a little incorporation of ^{13}C in the lower layer of the euphotic zone could not be carried out precisely due to a little difference in the mass spectra between non- and incubated samples. Analysis of the ^{13}C atom% of fatty acids, thus, was carried out for the samples from 0 to 50 m and 0 to 55 m in subarctic and subtropical regions, respectively. Further, some fatty acids with a concentration lower than 0.1 mg C m^{-3} were not able to be determined for ^{13}C atom% by GC/MS. Thus, the number of the fatty acids in the photosynthetic products were fewer than in particulate matter.

The concentration of particulate organic carbon and the $^{13}C/^{12}C$ isotope ratio, which were used for the calculation of primary productivity, were measured by an ANCA-MS instrument (Europe Scientific). Production rates of particulate organic carbon and of each fatty acid were calculated according to Hama *et al.* (1983) and Hama *et al.* (1987), respectively. Possible isotope discrimination of ^{13}C was not considered in this study because it has only a minor effect on the calculation of the production rate (Hama *et al.*, 1987).

Concentrations of inorganic nutrients were determined by an AutoAnalyzer AA-2 and Chl *a* by a fluorometric method using *N*,*N*-dimethylformamide (Suzuki and Ishimaru, 1990).

Results

General oceanography

Water temperatures and concentrations of inorganic nutrients in subarctic and subtropical stations are shown in Figure 1. Physicochemical conditions including water temperature and inorganic nutrient concentrations at Station A′ were almost the same as those at Station A, except for the extended mixing layer down to 50 m. Thus, data for physicochemical conditions at Station A′ are not shown. Surface water temperature in the subarctic Pacific was <5°C, whereas it was much higher at Station B. High concentrations of inorganic nutrients such as silicate, phosphate, nitrate and ammonium were measured in the surface layer of Station A and A′. In the surface layer of Station B, however, most of the inorganic nutrients were not measurable.

A relatively high concentration of Chl *a* (~0.7 mg m^{-3}) was found from the surface to 30 m at subarctic Station A and it decreased rapidly from 30 to 50 m. Almost comparable values were noticed after 20 days (Station A′), although the layer with the high concentration of Chl *a* now extended to 55 m. The concentration of Chl *a* at the surface water of the subtropical region was about one-tenth of that in the subarctic, ranging from 0.05 to 0.2 mg m^{-3} from 0 to 55 m. A subsurface Chl maximum (0.25 mg m^{-3}) was found at around 90 m depth.

Primary productivity

The primary production rate showed the highest value (10 mg C m^{-3} day^{-1}) at the water surface at Station A and it decreased to 5 mg C m^{-3} day^{-1} at 30 m (Figure 2). Low production rates, <1 mg C m^{-3} day^{-1}, were measured deeper than 50 m. After 20 days (Station A′), although the concentration of Chl *a* was almost comparable with Station A, primary production rates were ~1.5 times higher at 0–30 m depth. The Chl *a* specific production rate thus increased from 15 mg C (mg Chl *a*)$^{-1}$ day^{-1} (Station A) to 23 mg C (mg Chl *a*)$^{-1}$ day^{-1} at the surface. The depth-integrated primary production rate also increased form 350 to 370 mg C m^{-2} day^{-1} at this station.

Maximum production rates of 3–4 mg C m^{-3} day^{-1} were measured from 10 to 30 m depths at subtropical Station B. Production rates in the upper 30 m at Station B were from one-third to one-half those in the subarctic region. The Chl *a* specific production rates, on the contrary, were 4–6 times higher in the subtropical Pacific than the subarctic Pacific throughout the upper layer of the euphotic zone. The depth-integrated production rate at Station B was calculated as 230 mg C m^{-2} day^{-1}, which was lower than in the subarctic region.

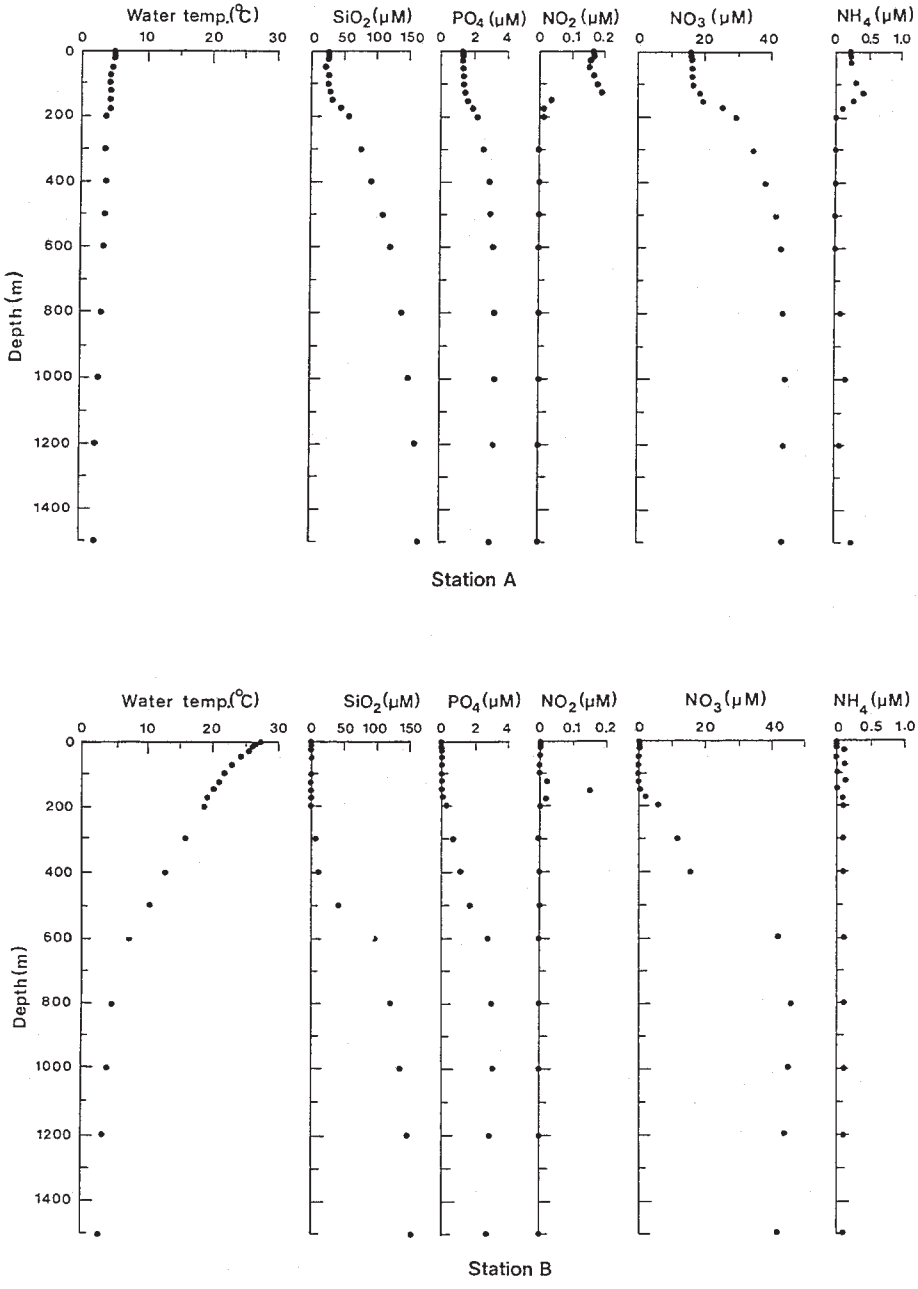

Fig. 1. Vertical profiles of water temperature and concentration of inorganic nutrients at subarctic (Station A) and subtropical (Station B) Pacific.

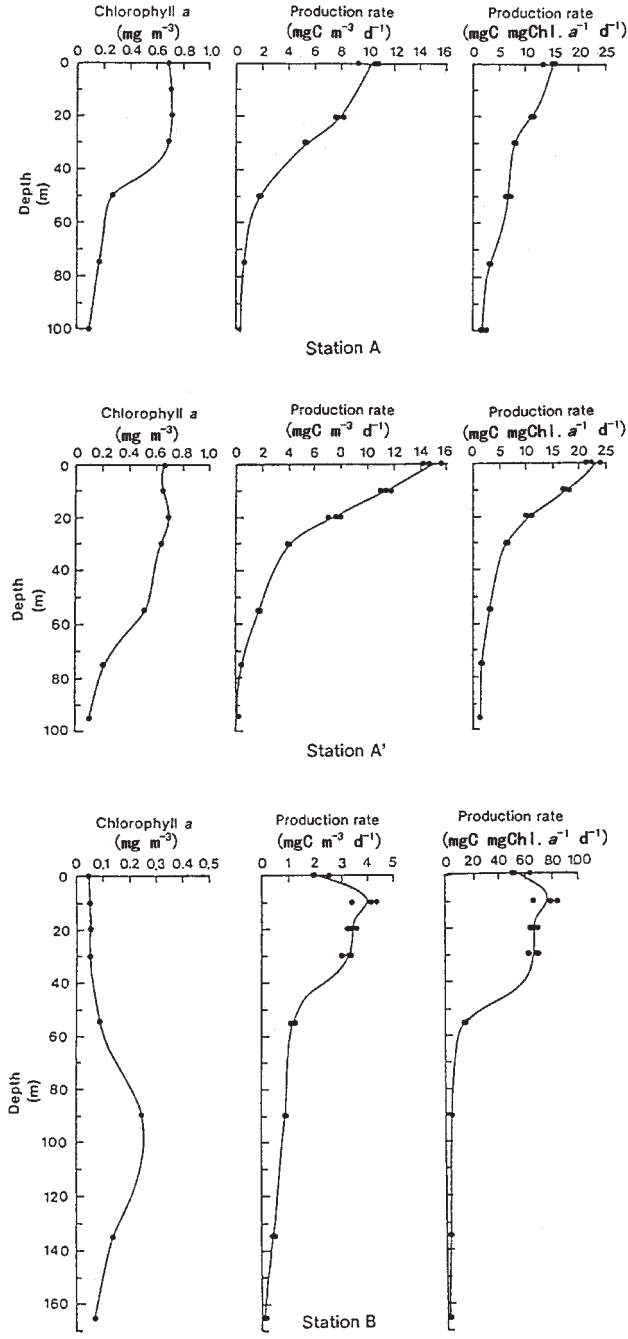

Fig. 2. Vertical profiles of the concentration of chlorophyll *a* and photosynthetic production rate of particulate organic carbon at Stations A, A′ and B.

Fatty acid composition of lipid in particulate matter

Tables I and II summarize the fatty acid composition of lipid extracted from particulate matter at the subarctic stations (Stations A and A′). The most abundant fatty acid in particulate matter was 16:0 throughout the euphotic zone in the subarctic region; its carbon ranged from 21 to 39% and from 18 to 39% of total fatty acid carbon at Stations A and A′, respectively. A higher contribution of 16:0 was observed in the deeper layer of the euphotic zone. Other saturated fatty acids (SFA), such as 14:0 and 18:0, accounted for 4.4–8.4% and 7.2–26.2% of the total fatty acids at Station A, respectively. The contribution of 14:0 tended to decrease with water depth, whereas that of 18:0 acid increased markedly with water depth. This variability was again observed after 20 days (Station A′).

At Stations A and A′, 16:1(n-7), 18:1(n-9) and 18:1(n-7) acids accounted for 4.1–9.1%, 3.1–8.8% and 1.6–3.6% of total fatty acids, respectively. Rather weak vertical trends were noticed in the contribution of 16:1(n-7) and 18:1(n-9), although they were not as distinct as those of 14:0, 16:0 and 18:0.

Table I. Concentration of fatty acid in particulate matter (mg C m^{-3}) at Station A. The percent of each fatty acid carbon to total fatty acid carbon is shown in parentheses

	0 m	20 m	30 m	50 m	75 m	100 m
14:0	0.66 (8.4)	0.50 (6.3)	0.51 (7.0)	0.24 (6.6)	0.12 (4.4)	0.19 (7.1)
iso 15:0	0.04 (0.5)	0.03 (0.4)	0.04 (0.6)	0.02 (0.6)	0.01 (0.5)	0.02 (0.6)
anteiso 15:0	0.04 (0.5)	–	0.03 (0.)	0.02 (0.6)	0.01 (0.5)	0.02 (0.6)
15:0	0.07 (0.8)	0.06 (0.7)	0.08 (1.1)	0.03 (1.0)	0.03 (1.1)	0.03 (1.0)
16:0	1.88 (23.7)	1.68 (21.2)	1.57 (21.6)	0.87 (23.8)	0.76 (27.3)	1.04 (39.1)
16:1(n-7)	0.58 (7.3)	0.44 (5.6)	0.48 (6.7)	0.30 (8.3)	0.14 (5.2)	0.11 (4.1)
16:2(n-3)	0.01 (0.1)	–	0.02 (0.3)	0.01 (0.4)	–	–
16:3(n-3)	–	–	0.03 (0.4)	0.01 (0.4)	–	–
16:4(n-1)	0.06 (0.8)	0.07 (0.8)	0.10 (1.4)	0.05 (1.3)	0.06 (2.1)	0.01 (0.4)
17:0	–	0.09 (1.1)	0.10 (1.4)	0.04 (1.2)	0.04 (1.4)	0.05 (1.8)
18:0	0.57 (7.2)	0.93 (11.7)	0.88 (12.1)	0.42 (11.5)	0.64 (22.9)	0.70 (26.2)
18:1(n-9)	0.38 (4.9)	0.36 (4.6)	0.51 (7.0)	0.21 (5.7)	0.25 (8.8)	0.17 (6.2)
18:1(n-7)	0.16 (2.1)	0.13 (1.6)	0.18 (2.5)	0.08 (2.3)	0.06 (2.0)	0.04 (1.7)
18:2(n-6)	0.22 (2.8)	0.16 (2.0)	0.20 (2.7)	0.06 (1.8)	0.04 (1.4)	0.03 (1.1)
18:3(n-3)	0.27 (3.4)	0.20 (2.5)	0.16 (2.2)	0.05 (1.4)	0.02 (0.8)	0.01 (0.4)
18:4(n-3)	0.71 (8.9)	0.65 (8.2)	0.49 (6.7)	0.25 (6.8)	0.02 (0.8)	0.06 (2.1)
18:5(n-3)	0.58 (7.4)	0.97 (12.2)	0.55 (7.6)	0.24 (6.5)	0.13 (4.8)	0.04 (1.3)
20:0	0.03 (0.3)	0.03 (0.4)	–	0.02 (0.6)	0.02 (0.7)	–
20:4(n-6)	0.03 (0.3)	–	0.04 (0.6)	–	0.02 (0.7)	0.02 (0.9)
22:5(n-3)	0.78 (9.9)	0.74 (9.4)	0.60 (8.2)	0.31 (8.6)	0.19 (7.0)	0.05 (1.8)
22:6(n-3)	0.86 (10.8)	0.90 (11.3)	0.69 (9.5)	0.40 (10.9)	0.22 (7.7)	0.09 (3.5)
Total	7.92	7.93	7.26	3.64	2.8	2.67
SFA[a]	3.28 (41.1)	3.31 (41.7)	3.21 (44.2)	1.66 (45.7)	1.65 (58.8)	2.04 (76.6)
SFA/Chl *a*	4.8	4.7	4.6	6.5	9.9	22
MUFA[b]	1.13 (14.3)	0.93 (11.8)	1.17 (16.1)	0.59 (16.3)	0.45 (15.9)	0.32 (11.9)
MUFA/Chl *a*	1.6	4.3	1.7	2.3	2.7	3.6
PUFA[c]	3.51 (44.3)	3.69 (46.5)	2.88 (39.7)	1.38 (38.0)	0.71 (25.2)	0.31 (11.5)
PUFA/Chl *a*	5.1	5.2	4.1	5.4	4.2	3.4

[a]Saturated fatty acid.
[b]Monounsaturated fatty acid.
[c]Polyunsaturated fatty acid.

A high contribution of PUFA was observed at subarctic stations In particular, 20:5(n-3) and 22:6(n-3) fatty acids were the major components, in total accounting for >17% of total fatty acids from 0 to 50 m depth. C_{18} PUFA, including 18:2(n-6), 18:3(n-3), 18:4(n-3) and 18:5(n-3), were the second most important PUFA at both stations.

Chlorophyll *a* specific concentrations of SFA, monounsaturated fatty acids (MUFA) and PUFA at Station A varied within the range 4.6–22, 1.6–3.6 and 4.1–5.2, respectively. Almost comparable ratios were obtained at Station A′.

In contrast to the rich fatty acid composition at the subarctic station, the composition at the subtropical station was quite simple, as summarized in Table III. SFA such as 16:0 and 18:0 were the major components, accounting for 27–38 and 29–49%, respectively, of total fatty acids throughout the euphotic zone; together, they accounted for 64–81% of total fatty acids. The contribution of 14:0 was almost comparable with that at Station A, ranging from 4.7 to 9.9%. SFA concentration normalized to Chl *a* concentration ranged from 13 to 87 and they are ~10 times higher than those at subarctic stations except the chlorophyll maximum layer.

MUFA such as 18:1(n-9), 18:1(n-7) and 16:1(n-7) accounted for 6.9–14% of the total fatty acids. Small amounts of PUFA (4.0–14% of total fatty acids) were

Table II. As Table I, but at Station A′

	0 m	10 m	20 m	30 m	55 m	75 m	95 m
14:0	0.64 (8.7)	0.68 (9.1)	0.63 (8.1)	0.51 (8.0)	0.47 (8.1)	0.14 (5.3)	0.13 (5.9)
iso 15:0	0.03 (0.4)	0.05 (0.7)	0.05 (0.6)	0.03 (0.5)	0.03 (0.5)	0.02 (0.6)	0.01 (0.4)
anteiso 15:0	0.04 (0.5)	0.04 (0.5)	0.04 (0.5)	0.04 (0.6)	0.03 (0.5)	0.01 (0.4)	0.02 (0.7)
15:0	0.06 (0.8)	0.06 (0.8)	0.06 (0.8)	0.07 (1.1)	0.06 (1.0)	0.04 (1.5)	0.03 (1.5)
16:0	1.37 (18.5)	1.54 (20.9)	1.51 (19.5)	1.33 (21.0)	1.20 (20.7)	0.88 (32.4)	0.89 (39.2)
16:1(n-7)	0.59 (8.0)	0.67 (9.1)	0.55 (7.0)	0.55 (8.8)	0.43 (7.5)	0.14 (5.3)	0.11 (4.8)
16:2(n-3)	–	0.02 (0.3)	0.02 (0.3)	–	–	–	–
16:3(n-3)	0.02 (0.3)	0.02 (0.2)	0.02 (0.3)	–	–	–	–
16:4(n-1)	0.03 (0.4)	0.04 (0.5)	0.04 (0.5)	0.03 (0.4)	0.0 2 (0.4)	0.03 (1.2)	0.01 (0.4)
17:0	0.08 (1.1)	0.09 (1.2)	0.10 (1.3)	0.07 (1.2)	0.06 (1.0)	0.04 (1.5)	0.05 (2.1)
18:0	0.48 (6.5)	0.44 (5.9)	0.48 (6.1)	0.43 (6.8)	0.44 (7.6)	0.41 (15.1)	0.60 (26.4)
18:1(n-9)	0.29 (3.9)	0.30 (4.1)	0.29 (3.7)	0.20 (3.1)	0.16 (2.7)	0.12 (4.3)	0.10 (4.4)
18:1(n-7)	0.18 (2.4)	0.21 (2.9)	0.18 (2.3)	0.16 (2.6)	0.16 (2.7)	0.10 (3.6)	0.04 (1.7)
18:2(n-6)	0.23 (3.1)	0.20 (2.7)	0.21 (2.7)	0.14 (2.3)	0.15 (2.6)	0.03 (1.2)	0.03 (1.5)
18:3(n-3)	0.32 (4.3)	0.23 (3.2)	0.23 (2.9)	0.16 (2.6)	0.14 (2.5)	0.03 (1.2)	0.01 (0.6)
18:4(n-3)	0.78 (10.6)	0.61 (8.3)	0.66 (8.5)	0.49 (7.7)	0.41 (7.1)	0.15 (5.6)	0.02 (1.0)
18:5(n-3)	0.76 (10.3)	0.54 (7.3)	0.63 (8.1)	0.46 (7.2)	0.45 (7.8)	0.23 (8.3)	0.06 (2.5)
20:0	–	0.02 (0.3)	0.02 (0.3)	–	–	–	–
20:4(n-6)	–	0.01 (0.1)	0.01 (0.1)	–	–	–	–
22:5(n-3)	0.69 (9.3)	1.02 (13.8)	1.28 (16.4)	1.03 (16.3)	0.98 (17.0)	0.23 (8.3)	0.05 (2.4)
22:6(n-3)	0.79 (10.8)	0.60 (8.1)	0.78 (10.0)	0.63 (9.9)	0.60 (10.4)	0.30 (10.9)	0.10 (4.4)
Total	7.38	7.4	7.77	6.32	5.78	2.72	2.26
SFA	2.70 (36.6)	2.92 (39.4)	2.89 (37.2)	2.48 (39.1)	2.28 (39.4)	1.54 (56.8)	1.72 (78.4)
SFA/Chl *a*	4	4.5	4.2	3.9	4.5	7.5	16
MUFA	1.06 (14.4)	1.19 (16.1)	1.01 (13.0)	0.91 (14.5)	0.75 (13.0)	0.36 (13.2)	0.25 (10.8)
MUFA/Chl *a*	1.6	1.8	1.5	1.4	1.5	1.8	2.4
PUFA	3.82 (49.0)	3.29 (44.5)	3.87 (49.8)	2.93 (46.4)	2.75 (47.6)	0.82 (30.0)	0.29 (12.8)
PUFA/Chl *a*	5.4	5.1	5.7	4.7	5.4	4.9	2.7*

Table III. As Table I, but at Station B

	0 m	10 m	20 m	55 m	90 m	135 m	165 m
14:0	0.23 (6.4)	0.34 (6.4)	0.37 (6.5)	0.46 (9.9)	0.30 (7.8)	0.27 (6.4)	0.16 (4.7)
iso 15:0	–	–	0.01 (0.2)	0.04 (0.9)	0.03 (0.7)	0.04 (0.9)	0.02 (0.6)
anteiso 15:0	0.02 (0.6)	–	0.02 (0.4)	0.02 (0.5)	0.01 (0.3)	0.02 (0.5)	0.01 (0.3)
15:0	–	–	0.05 (0.9)	0.05 (1.1)	0.04 (1.0)	0.05 (1.2)	0.04 (1.1)
16:0	1.11 (30.9)	2.00 (37.7)	2.08 (37.2)	1.65 (35.5)	1.30 (33.3)	1.14 (27.1)	1.00 (30.2)
16:1(n-7)	0.06 (1.8)	0.15 (2.9)	0.21 (3.8)	0.38 (8.1)	0.16 (4.1)	0.25 (5.9)	0.09 (2.6)
16:2(n-3)	0.01 (0.3)	0.06 (1.2)	0.01 (0.2)	0.03 (0.6)	0.04 (1.0)	0.02 (0.4)	0.01 (0.3)
16:3(n-3)	–	–	0.01 (0.2)	–	0.01 (0.2)	0.01 (0.3)	0.01 (0.3)
16:4(n-1)	0.01 (0.3)	–	0.02 (0.4)	–	0.15 (3.9)	0.24 (5.8)	0.04 (1.3)
17:0	0.05 (1.5)	–	0.06 (1.2)	0.05 (1.1)	0.04 (1.1)	0.05 (1.2)	0.04 (1.3)
18:0	1.74 (48.6)	2.27 (42.8)	2.16 (38.6)	1.36 (29.3)	1.32 (33.9)	1.57 (37.2)	1.55 (46.9)
18:1(n-9)	0.12 (3.3)	0.15 (2.8)	0.23 (4.1)	0.17 (3.7)	0.16 (4.2)	0.12 (2.9)	0.14 (4.3)
18:1(n-7)	0.10 (2.9)	0.07 (1.2)	0.08 (1.4)	0.10 (2.1)	0.06 (1.5)	0.09 (2.1)	0.03 (0.8)
18:2(n-6)	0.02 (0.7)	0.06 (1.1)	0.10 (1.7)	0.06 (1.4)	0.05 (1.2)	0.04 (1.0)	0.02 (0.6)
18:3(n-3)	–	0.01 (0.2)	0.02 (0.3)	0.01 (0.2)	0.01 (0.3)	0.02 (0.4)	0.01 (0.2)
18:4(n-3)	0.05 (1.3)	0.03 (0.6)	0.07 (1.3)	0.03 (0.7)	0.03 (0.8)	0.02 (0.5)	0.03 (1.0)
18:5(n-3)	0.03 (0.8)	0.03 (0.5)	0.04 (0.8)	0.02 (0.4)	0.03 (0.8)	0.05 (1.2)	0.02 (0.7)
20:0	–	–	–	0.04 (0.8)	0.04 (1.1)	0.05 (1.1)	0.04 (1.1)
20:4(n-6)	–	–	–	–	–	0.02 (0.5)	–
22:5(n-3)	0.01 (0.3)	0.03 (0.6)	0.03 (0.6)	0.05 (1.1)	0.04 (0.9)	0.06 (1.5)	0.02 (0.6)
22:6(n-3)	0.02 (0.5)	0.11 (2.1)	0.02 (0.3)	0.12 (2.6)	0.07 (1.8)	0.08 (2.0)	0.04 (1.2)
Total	3.58	5.31	5.59	4.64	3.89	4.22	3.31
SFA	3.15 (88.0)	4.62 (86.9)	4.76 (85.1)	3.67 (79.0)	3.19 (75.6)	3.19 (75.6)	2.86 (86.2)
SFA/Chl *a*	66	87	87	66	37	13	21
MUFA	0.29 (9.0)	0.37 (6.9)	0.52 (9.2)	0.65 (13.9)	0.46 (10.9)	0.46 (10.9)	0.25 (7.6)
MUFA/Chl *a*	5.8	7	9.5	12	4.6	1.9	1.9
PUFA	0.15 (4.0)	0.33 (6.2)	0.32 (5.7)	0.33 (7.1)	0.57 (13.6)	0.57 (13.6)	0.20 (6.2)
PUFA/Chl *a*	3.1	6.2	5.8	5.7	5.2	2.3	1.4

found at the subtropical station, showing a maximum contribution at the subsurface chlorophyll maximum layers (90 and 135 m).

The ratio of PUFA to Chl *a* at Station B varied from 1.4 to 5.8 through the euphotic zone, being almost comparable with the subarctic area.

Fatty acid production rates

Tables IV and V summarize the fatty acid production rates in the subarctic area. The production rate of total fatty acids ranged from 1.71 at the surface to 0.35 mg C m^{-3} day^{-1} at 50 m depth at Station A. The major SFA product was 16:0, accounting for 22% at the surface. This contribution showed a definite decrease with depth to ~10% at 50 m depth. The second important SFA was 14:0, ranging from 4.6 to 7.4%. Although 18:0 was the one of the major acids in particulate matter in the subarctic area (Tables I and II), its contribution to photosynthetic products was quite small, accounting for only 0.2–1.6% of the photosynthetically produced fatty acids. SFA totally accounted for 15–28% of the total fatty acids in the photosynthetic products at Station A. An almost comparable contribution of SFA was

Table IV. Production rates of fatty acids at Station A (μg C m^{-3} day^{-1}). The percent to total fatty acid production rate is shown in parentheses

	0 m	20 m	30 m	50 m
14:0	88 (5.1)	67 (7.1)	46 (7.4)	16 (4.6)
iso 15:0	–	–	–	–
anteiso 15:0	–	–	–	–
15:0	–	–	–	–
16:0	368 (21.5)	184 (19.4)	102 (16.5)	34 (9.9)
16:1(n-7)	108 (6.3)	47 (5.0)	33 (5.3)	9 (2.6)
16:2(n-3)	–	–	–	–
16:3(n-3)	–	–	–	–
16:4(n-1)	–	–	–	–
17:0	–	–	–	–
18:0	27 (1.6)	8 (0.8)	1 (0.2)	2 (0.6)
18:1(n-9)	109 (6.4)	26 (2.7)	15 (2.4)	9 (2.6)
18:1(n-7)	29 (1.7)	20 (2.1)	9 (1.4)	7 (2.0)
18:2(n-6)	53 (3.1)	–	35 (5.7)	14 (4.1)
18:3(n-3)	99 (5.8)	42 (4.4)	36 (5.8)	14 (4.1)
18:4(n-3)	217 (12.7)	191 (20.1)	103 (16.7)	44 (12.8)
18:5(n-3)	162 (9.5)	77 (8.1)	100 (16.2)	56 (16.2)
20:0	–	–	–	–
20:4(n-6)	–	–	–	–
22:5(n-3)	178 (10.4)	120 (12.7)	66 (10.7)	71 (20.6)
22:6(n-3)	274 (16.0)	166 (17.5)	72 (11.7)	69 (20.0)
Total	1712	948	618	345
SFA	483 (28.2)	259 (27.3)	149 (24.1)	52 (15.1)
MUFA	246 (14.4)	93 (9.8)	57 (9.2)	25 (7.2)
PUFA	983 (57.4)	596 (62.9)	412 (66.7)	268 (77.7)

observed after 20 days, but it was less pronounced at Station A′ than at Station A.

MUFA totally accounted for 7.2–14% and 7.9–14% of the total fatty acid at Stations A and A′, respectively, and 16:1(n-7) was the main component of MUFA. The high contribution of PUFA observed in particulate matter in the subarctic region was again found in the photosynthetic products. The contribution of PUFA was >50% throughout the surface to 50 m depth (55 m at Station A′). The main PUFA components were 18:4(n-3), 18:5(n-3), 20:5(n-3) and 22:6(n-3).

Fatty acid compositions of photosynthetic products were quite simple at Station B (Table VI). The main fatty acids were 16:0 and 14:0, each accounting for 36–50% and 22–30% of total acids, respectively. In contrast to the highest contribution of 18:0 to particulate matter, its contribution ranged only from 5.9 to 13% in the photosynthetic products. The lower contribution of 18:0 to photosynthetic products than particulate matter was the same as observed in the subarctic region. MUFA such as 16:1(n-7) and 18:1(n-9) totally accounted for 22–35% of total acids. It is noted here that the production rates of PUFA could not be estimated at this station, although some PUFA were present in the particulate matter (totally 4.0–14%; Table III), due to the limitation of their low concentrations mentioned in Method.

Total fatty acids accounted for 12–20% and 14–18% of total primary

Table V. As Table IV, but at Station A′

	0 m	10 m	20 m	30 m	55 m
14:0	110 (4.2)	91 (4.5)	90 (8.4)	34 (6.2)	13 (4.7)
iso 15:0	–	–	–	–	–
anteiso 15:0	–	–	–	–	–
15:0	–	–	–	–	–
16:0	482 (18.3)	316 (15.7)	92 (8.6)	42 (7.7)	22 (7.9)
16:1(n-7)	160 (6.1)	114 (5.6)	62 (5.8)	29 (5.3)	8 (2.9)
16:2(n-3)	–	–	–	–	–
16:3(n-3)	–	–	–	–	–
16:4(n-1)	–	–	–	–	–
17:0	–	–	–	–	–
18:0	39 (1.5)	30 (1.5)	19 (1.8)	13 (2.4)	9 (3.2)
18:1(n-9)	168 (6.4)	110 (5.4)	34 (3.2)	18 (3.3)	8 (2.9)
18:1(n-7)	42 (1.6)	36 (1.8)	18 (1.7)	8 (1.5)	6 (2.2)
18:2(n-6)	91 (3.5)	78 (3.9)	32 (3.0)	16 (3.0)	17 (6.1)
18:3(n-3)	152 (5.8)	127 (6.3)	43 (4.1)	20 (3.6)	16 (5.8)
18:4(n-3)	338 (12.8)	276 (13.7)	152 (14.2)	84 (15.4)	52 (18.7)
18:5(n-3)	324 (12.3)	242 (12.0)	161 (15.1)	92 (16.8)	43 (15.5)
20:0	–	–	–	–	–
20:4(n-6)	–	–	–	–	–
22:5(n-3)	293 (11.1)	249 (12.3)	163 (15.3)	92 (16.8)	43 (15.5)
22:6(n-3)	435 (16.5)	348 (17.2)	201 (18.8)	98 (18.0)	41 (14.7)
Total	2634	2017	1067	546	278
SFA	631 (24.0)	437 (21.7)	201 (18.8)	89 (16.3)	44 (15.8)
MUFA	370 (14.0)	260 (12.9)	114 (10.7)	55 (10.1)	22 (7.9)
PUFA	1633 (62.0)	1320 (65.4)	752 (70.5)	402 (73.6)	212 (76.3)

production rates at Stations A and A′, respectively. There was a lower fatty acid contribution (6.5–9.9%) in the subtropical region.

Discussion

Relationship of the fatty acid composition of particulate matter and photosynthetic products

'Particulate matter' collected onto a glass fiber filter contains not only phytoplankton, but also other microorganisms such as zooplankton and some portion of bacteria, and non-living particles. Fatty acid composition determined for lipid materials from particulate matter, thus, provides 'mixed' information originating from phytoplankton and non-phytoplankton lipids. The analyses of ^{13}C-enriched samples by GC/MS make it possible to determine the fatty acid composition of photosynthetic products of phytoplankton and one can thus compare both the compositions in photosynthetic products and in particulate matter.

Figure 3 compares the contribution of each fatty acid in lipid materials of photosynthetic products and particulate matter of samples at the depths at which the rates of primary production were maximal (0 m at Stations A and A′, and 10 m at Station B). A positive correlation between the contributions to particulate matter and to photosynthetic products confirms their gross similarity.

Table VI. As Table IV, but at Station B. The production rates for PUFA were not estimated due to their low concentration (see the text)

	0 m	10 m	20 m	30 m	55 m
14:0	31 (22.7)	86 (28.2)	73 (22.1)	78 (29.5)	21 (26.3)
iso 15:0	–	–	–	–	–
anteiso 15:0	–	–	–	–	–
15:0	–	–	–	–	–
16:0	68 (49.9)	129 (42.3)	140 (42.4)	95 (36.0)	38 (47.5)
16:1(n-7)	10 (7.6)	26 (8.5)	13 (3.9)	22 (8.3)	3 (3.8)
16:2(n-3)	–	–	–	–	–
16:3(n-3)	–	–	–	–	–
16:4(n-1)	–	–	–	–	–
17:0	–	–	–	–	–
18:0	8 (5.9)	19 (6.2)	35 (10.6)	28 (10.6)	10 (12.5)
18:1(n-9)	19 (14.0)	45 (14.8)	69 (20.9)	41 (15.5)	8 (10.0)
18:1(n-7)	–	–	–	–	–
18:2(n-6)	–	–	–	–	–
18:3(n-3)	–	–	–	–	–
18:4(n-3)	–	–	–	–	–
18:5(n-3)	–	–	–	–	–
20:0	–	–	–	–	–
20:4(n-6)	–	–	–	–	–
22:5(n-3)	–	–	–	–	–
22:6(n-3)	–	–	–	–	–
Total	136	305	330	264	80
SFA	107 (78.4)	234 (76.7)	248 (75.2)	173 (65.5)	59 (73.8)
MUFA	29 (21.6)	71 (23.3)	82 (24.8)	91 (34.5)	21 (26.2)
PUFA	–	–	–	–	–

However, some fatty acids showed a marked difference in their contributions to photosynthetic products and particulate matter. PUFA generally had a higher contribution to photosynthetic products than to particulate matter, whereas SFA, especially 18:0, were less prominent in the photosynthetic products. This relationship can reflect variability in the contribution of the phytoplankton fraction to lipids in particulate matter.

Relative constancy of PUFA/Chl *a* through the euphotic zone in the subarctic region (Tables I and II) indicates that PUFA primarily exist as phytoplanktonic constituents. No increase in PUFA/Chl *a* ratio in the layer with the lower Chl *a* concentration in turn suggests that only a small amount of PUFA are present in non-phytoplanktonic lipids and thus their contribution is higher to photosynthetic products than to particulate matter.

Microorganisms such as zooplankton and some portion of bacteria, which are collected onto filter paper, along with non-living particles, are possible constituents of marine particles other than phytoplankton. Although the contribution of PUFA [20:5(n-3) and 22:6(n-3) especially] to zooplanktonic lipids is reported to be substantial (Lee *et al*., 1971; Harvey *et al*., 1987), the higher contribution of PUFA in the photosynthetically produced lipids than lipids in particulate matter (Figure 3) strongly suggests that zooplanktonic lipids are not main components of PUFA in particulate lipids. Further, judging from the low

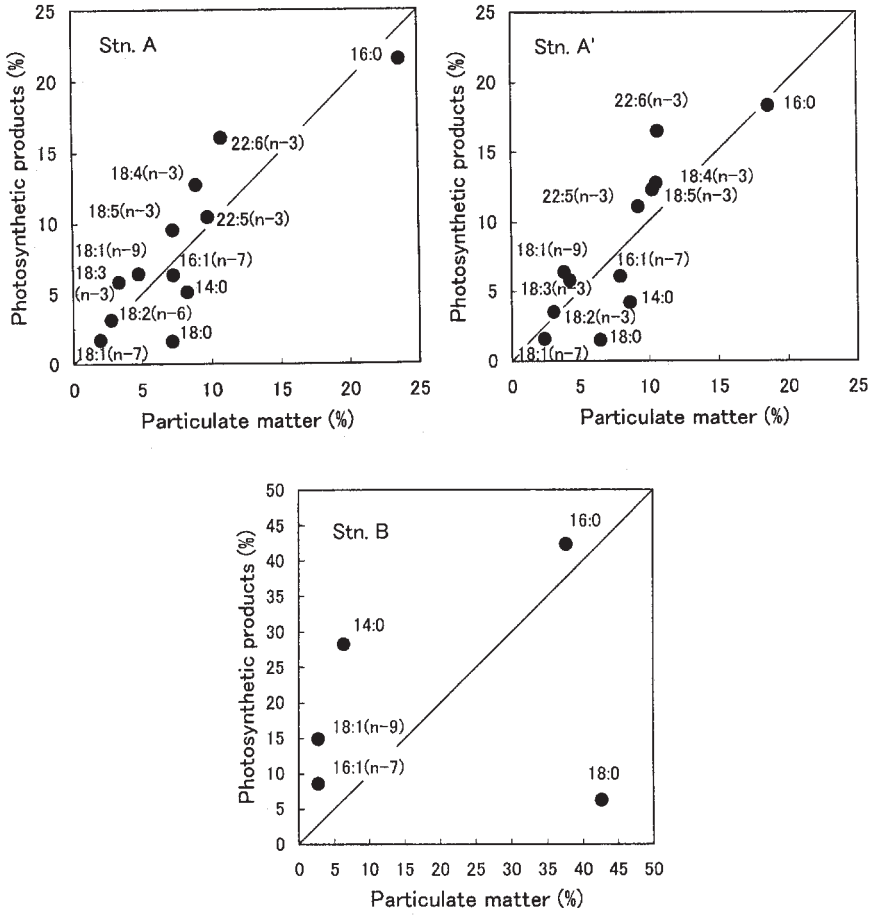

Fig. 3. Ratio of each fatty acid to total fatty acid in particulate matter and photosynthetic products. Fatty acids, which are determined as the constituents both in particulate matter and photosynthetic products, are compared. The contributions obtained from the depth with maximum primary production rate are shown (0 m for Stations A and A′, and 10 m for Station B). The solid line indicates the 1:1 relationship.

contribution of branched chain fatty acids such as iso 15:0 and anteiso 15:0, that have been regarded as specific for bacteria (Joint and Morris, 1982; Wakeham and Lee, 1993), it is unlikely that bacteria significantly affect the fatty acid composition of particulate lipids. Non-living particles are thus likely components with little PUFA.

The possible low PUFA content of non-living particles is very likely due to the susceptibility of PUFA to degradation compare with SFA and MUFA, as has been observed in various biogeochemical processes. Harvey *et al.* (1987) compared the fatty acid compositions of fecal pellets of the marine copepod, *Calanus helgolandicus*, and its food, *Scrippsiella trochoidea* (dinoflagellate). They found that only a minor component of PUFA in food was present in fecal pellets,

indicating a high absorption efficiency of dietary PUFA by the animals. Moreover, it has widely been observed that PUFA disappear more rapidly than SFA or MUFA in suspended particles, sinking particles in the water column and sediments (De Baar *et al*., 1983; Meyers and Ishiwatari, 1993; Wakeham and Lee, 1993; Fileman *et al*., 1998). These findings strongly suggest that only a small amount of PUFA survives as a constituent in lipids of non-living particles in natural environments and, thus, refractory compounds mainly constitute the lipid of non-living particles.

The relationship between photosynthetic products and particulate matter suggests that the phytoplanktonic contribution of 18:0 can be quite low despite this acid being one of the major components of lipid in particulate matter in both stations and as has been repeatedly observed (Morris, 1984; Wakeham and Lee, 1993). This is been supported by numerous analyses of the fatty acid composition of cultured phytoplankton lipids (Wood, 1974; Cobelas and Lechado, 1989; Kayama *et al*., 1989; Napolitano, 1998). In almost all cultured phytoplankton, this acid usually accounts for <2% of the total fatty acid (comparable with its contribution in photosynthetic products in the subarctic region found here). The result in the enclosure experiment in which the concentration of 18:0 in the lipid of particulate matter remained constant through a *Skeletonema costatum* bloom in contrast to the increase in total fatty acid concentration by 10 times (Kattner and Brockmann, 1990), also suggests that the major portion of 18:0 in the lipid of particulate matter may be constituted by non-phytoplankton lipid.

Microorganisms other than phytoplankton, such as zooplankton (Lee *et al*., 1971; Bottino, 1974; Miller *et al*., 1998) and bacteria (Johns *et al*., 1977; Volkman *et al*., 1980), which are one of the possible constituents of particulate matter, have little of this acid. Thus, it is likely that 18:0 exists as a component of lipid of non-living particles.

The possible refractory nature of lipid containing 18:0 is a likely reason why the contribution of this acid increased from a few percent in the lipids of living particles to a few tenths of a percent in those of non-living particles. Although limited knowledge has been available concerning the stability of 18:0 in the biogeochemical cycle, Harvey *et al*. (1987) obtained the result from the feeding experiment that the contribution of 18:0 increased from 6.3% in the food (*S.trochoidea*) to 12.3–18.8% in the fecal pellets of the copepod *C.helgolandicus*, due to the selective degradation of other major fatty acids such as 16:0, 14:0, 22:6, 18:1(n-9), 18:5(n-3) and 18:4(n-3). However, during the sinking process of particles in marine environments, the estimated half-depths of 18:0 which correspond to the depth range over which 50% has been lost were almost comparable with other major SFA (14:0 and 16:0), although the values of PUFA were much smaller (De Baar *et al*., 1983). Thus, the preferential resistivity of the lipid containing 18:0 in the biogeochemical cycle has not been fully established so far.

On the other hand, Tanoue and Handa (1980) suggested that adsorption of dissolved lipids onto particulate affected the fatty acid composition of particulate lipids. In the case of 18:0, especially, they indicated that adsorption was the important factor in the production of lipids containing 18:0 in the particulate phase from

the fact that the concentration of 18:0 in particulate matter was higher at increasing water depth (Tanoue and Handa, 1980) and that 18:0 is one of the most important acids of the dissolved lipids (Kattner *et al*., 1983). Qualitative and quantitative analysis of particulate and dissolved lipids, including lipid class composition (Parrish, 1988; Arts *et al*., 1997), can yield significant information on the origin and lability of lipids containing 18:0 in the particulate matter.

Differences in fatty acid compositions between subarctic and subtropical Pacific

Fatty acid compositions of both particulate matter and photosynthetic products showed a marked difference in the subarctic and subtropical Pacific. Particulate matter in the subarctic Pacific had a rich composition including many species of PUFA. In the subtropical Pacific, on the other hand, a rather simple spectrum dominated by SFA was observed, although some PUFA were present in the particulate mater (totally 4.0–14%; Table III). However, the concentrations of fatty acid groups specific to the concentration of Chl *a* clearly show that PUFA/Chl *a* are comparable between subtropical (1.4–6.2) and subarctic (2.7–5.7) Pacific, in contrast to the fact that the concentrations per water volume were very different in upper layers of the euphotic zone between both stations. Volkman *et al*. (1989) determined the PUFA/Chl *a* of 10 species of cultured phytoplankton and reported that the ratio varied within a relatively small range (0.26–3.2). Although this ratio may be variable depending on the physiological condition of phytoplankton in addition to the interspecies variation, the bulk correspondence of PUFA/Chl *a* among Stations A, A′ and B and cultured phytoplankton suggests that PUFA contents in phytoplankton lipids are not conspicuously different between subarctic and subtropical stations, regardless of the fatty acid composition of the particulate matter.

This possibility would be inconsistent with the fatty acid composition of photosynthetic products obtained in the present study, showing that the photosynthetic products of the phytoplankton population in subtropical Pacific contain no PUFA (Table VI). However, this was mainly due to the fact that the ^{13}C atom% of PUFA in the subtropical Pacific was impossible to estimate by GC/MS because of low concentration. In the present study, 8 l of sample was used for the analysis of ^{13}C atom% of fatty acid. Thus, it was likely that PUFA were measured as the constituents of photosynthetic products, when the sample volume had been increased.

Concerning the fatty acid composition of lipids in particulate matter in the surface layer of the North Central Pacific Gyre (25°N, 155°W), Wakeham and Lee (1989) reported that PUFA were one of the major components (up to a few tenths of a percent). Their result is not comparable with the results of the present study obtained at Station B (25°N, 165°E). This incomparability is probably due to the difference in the contribution of phytoplankton lipids to particulate lipids between two stations. The reported primary productivity (Laws *et al*., 1987; Marra and Heinemann, 1987; Wakeham and Lee, 1993) and phytoplankton biomass (Marra and Heinemann, 1987) around their station were considerably higher than

those at Station B in the present study. The fatty acid composition of particulate lipids reported by Wakeham and Lee (1989), thus, was not modified considerably from the composition of phytoplankton lipids by the presence of non-living lipids with the lesser amount. At Station B in the present study, on the other hand, the 'blurring' effect of lipids in non-living particles is probably so serious that the fatty acid composition of phytoplankton lipids was not easily estimated. The extremely high SFA/Chl *a* in particulate matter at Station B found in the present study (13–87 in the euphotic zone and 37–87 except the Chl *a* maxima layers; Table III) compared with cultured phytoplankton (0.40–3.16; Volkman *et al*., 1989) supports the serious 'blurring' effect of SFA in non-living lipids at Station B.

These considerations strongly suggest that the difference in the fatty acid composition between subarctic and subtropical Pacific found in the present study is mainly caused by the difference in the degree of the 'blurring' effect between two stations. Further, it is possible that the geographical differences in fatty acid composition observed so far reflect the variation of the contribution of phytoplankton lipids to particulate lipids. Tanoue and Handa (1982) reported the fatty acid composition of lipids in particulate matter from various oceanic regions (7°N–64°S). They found that the PUFA content was higher in the southern area of the Antarctic convergence, which was characterized by low water temperature and high nutrient concentration, than the northern area from the Antarctic convergence. This regional distribution of the PUFA contribution in particulate lipids seemingly concerns the regional distribution of environmental factors such as water temperature and nutrient concentration which reportedly affect the fatty acid composition of phytoplankton (Pugh, 1971; Sato *et al*., 1979; Okuyama *et al*., 1992; Thompson *et al*., 1992). However, the low water temperature and high nutrient concentration found in the euphotic zone in the higher latitude are usually accompanied by the higher phytoplankton biomass and imply the higher contribution of phytoplankton lipids to particulate lipids. On the contrary, low phytoplankton biomass is usually found in high water temperature and the low nutrient concentration conditions in the stratified water. The low phytoplankton biomass likely results in the higher 'blurring' effect of non-living lipids on the fatty acid composition of particulate lipids as expected at Station B in this study. Although the environmental factors such as water temperature and nutrient concentration, as well as time and regional variability of phytoplankton species composition, can affect the fatty acid composition of phytoplankton lipid in natural environments, which is not fully discussed in this study due to the impossibility of determining PUFA production rates in the subtropical area, the results obtained indicate that the contribution of phytoplankton lipids in the particulate lipids is the important factor controlling the gross fatty acid composition of the lipids in the particulate matter.

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