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Radiocarbon studies of organic compound classes in plankton and sediment of the northeastern Pacific Ocean

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Abstract—Radiocarbon ($\Delta^{14}\text{C}$) and stable carbon isotopes ($\delta^{13}\text{C}$) were measured in total hydrolyzable amino acid (THAA), total carbohydrate (TCHO), total lipid, and acid-insoluble organic fractions that had been separated from phytoplankton, zooplankton, sediment floc, and sediment samples from an abyssal site in the northeastern Pacific Ocean. THAA, TCHO, and lipid fractions accounted for 91–99% of the total organic carbon (TOC) in phytoplankton and zooplankton, 57% of TOC in sediment floc, and 18–38% of TOC in sediment. Based on concentration profiles in sediment, first-order degradation rate constants below the bioturbation zone were calculated using a “multi-G” model considering both labile and refractory organic fractions. The calculated rate constants were in the order $\text{THAA} \approx \text{TCHO} > \text{TOC} \approx \text{TN} > \text{lipid}$, indicating the relative reactivities of these compound classes in the sediment during early diagenesis. Bioturbation affected the distributions of these compound classes in the top few centimeters of the sediment.

The $\Delta^{14}\text{C}$ values of all organic fractions decreased in the order plankton in surface water to sediment floc to sediments at 4100 m depth. Distinct differences in $\Delta^{14}\text{C}$ exist among THAA, TCHO, and lipid fractions in sediment floc and sediments. The lipid fraction exhibited lower $\Delta^{14}\text{C}$ signatures than THAA and TCHO fractions. Differential decomposition of organic matter and sorption and/or biological incorporation of ‘old’ DOC into sediment appear to be the major processes that likely control the observed $\Delta^{14}\text{C}$ signatures and abundances. $\delta^{13}\text{C}$ values of the organic compound classes in sediment are similar to their values in plankton indicating that organic matter input to sediment in the northeastern Pacific is mainly from marine sources. Also, distinct $\delta^{13}\text{C}$ signatures were found in each of the four organic fractions. Copyright © 1998 Elsevier Science Ltd

INTRODUCTION

Carbon isotopic ($\Delta^{14}\text{C}$, $\delta^{13}\text{C}$) analyses of organic matter provide a powerful tool for determining the sources and cycling of organic matter in the ocean (Williams and Linick, 1975; Druffel and Williams, 1992). Bomb ^{14}C , produced in the stratosphere during thermonuclear weapons testing in the late 1950s and early 1960s, has mixed into the oceans through air-sea gas exchange of CO_2 . Thus, all organic matter recently produced in the surface ocean by photosynthesis and subsequently ingested by organisms is tagged with bomb ^{14}C and is detected in subsurface organic carbon pools (Broecker et al., 1985; Druffel et al., 1992). Analyses of carbon isotopes in bulk samples can yield useful information regarding sources and transformation pathways. For example, Williams et al. (1992) used measurements of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ in the Santa Monica Basin, California, to show that terrestrial carbon accounted for 10% or less of the organic carbon in the sinking and suspended particulate organic matter (POM) and as high as 25% in the sediment. Bauer et al. (1992) and Druffel et al. (1992) found that DOC in the deep Pacific and Atlantic oceans has ^{14}C ages of several thousand years, and that this value in the deep Pacific is about 2000 yr ‘older’ than that in the deep Atlantic. They suggested that this difference in DOC age between the two oceans is largely

related to the deep-water circulation patterns and transit times between the oceans.

Organic matter in the ocean includes a variety of organic compounds, which reflect not only multiple origins but also multiple pathways of production and decomposition (Hedges, 1992; Wakeham and Lee, 1993). Thus, determination of $\Delta^{14}\text{C}$ and stable carbon isotope ($^{13}\text{C}/^{12}\text{C}$) ratios in the major organic compound classes and not just of bulk carbon is needed for a better understanding of the various sources of carbon to the oceans as well as the suite of diagenetic processes that likely take place there.

As part of a larger project to study organic carbon cycling at Station M (34°50'N, 123°00'W) in the North Pacific Ocean (Druffel et al., 1996; Bauer et al., 1998), we investigated $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ signatures of total hydrolyzable amino acid (THAA), total carbohydrate (TCHO), total lipid, and acid-insoluble fractions separated from phytoplankton, zooplankton, sediment floc, and sediment collected from this site. Hydrolyzable amino acids, carbohydrates, and lipids are major organic compound classes in marine organisms (Parsons et al., 1961; Cowey and Corner, 1966), POM, and sediments (Wakeham et al., 1984; Cowie and Hedges, 1984; Lee and Cronin, 1982; Henrichs et al., 1984). Their distributions and decomposition play an important role in organic carbon cycling in the ocean.

In conjunction with the $\Delta^{14}\text{C}$ measurements, depth profiles of TOC, TN, and THAA, TCHO and lipid fraction C in sediment were modeled using a two-component model. The degradation rate constants below the bioturbation zone were

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calculated. The distribution and decomposition processes of TOC, TN, and the organic fractions in the sediment of the deep Pacific Ocean are discussed. Major questions we address are: (1) What are the major organic carbon sources to sediments in the deep northeastern Pacific Ocean? (2) How is organic matter altered during transit in the water column and burial in the sediment?

2. METHODS

2.1. Study Site

Samples were collected from a single abyssal site (Station M, 34°50'N, 123°00'W) in the northeastern Pacific Ocean located 220 km west of Point Conception, California, USA. Water depth at Station M is 4100 m, and the sediment is mainly silty clay. The region is strongly affected by the southward-flowing California Current in the surface waters. There is strong interannual variability in primary production (Smith et al., 1988; Michaelsen et al., 1988). Maximum fluxes (10–25 mgC/m²d) of POM, measured at 3450 m depth, occur in late spring and early fall (Smith et al., 1994). Station M has been occupied several times each year since 1989 for a time series study of near-bottom pelagic carbon fluxes and their coupling with benthic processes (see Smith et al., 1994).

2.2. Sample Collection

All samples were collected on the Pulse 25 cruise aboard the R/V *Atlantis II* in late April 1995. Phytoplankton were collected using a 33 μ m net deployed at 0–1 m depth for 30 min. Samples were filtered by gentle vacuum filtration onto precombusted quartz-fiber filters (Whatman Ultrapure, QM-A, 43 mm diameter). Zooplankton were collected using a 335 μ m mesh, meter-net towed at 1 knot at 85 m depth for 30 min. Sediment was collected using plastic push cores (7 cm o.d. $\times$ 50 cm long) taken by one of the manipulator arms of the DSV *Alvin*. The top 2–4 mm loose, flocculent layer of sediment (sediment floc) was removed from the top of the core using a 25 mL plastic pipette. The sediment core was then sectioned at 0.5 cm intervals in the top 5 cm, and at 1–2 cm intervals down to 14 cm depth. All samples were stored in glass jars (acid-washed and baked at 550°C) and frozen at –20°C within 4 h after recovery of DSV *Alvin*.

2.3. Organic Extraction and Isolation

2.3.1. Lipid Extraction

Samples were removed from the freezer, subsampled, and oven-dried at 50°C overnight. For total lipid extraction, 0.1–0.2 g of the dried plankton or about 1g dried sediment was weighed into precombusted, 50 mL glass centrifuge tubes with Teflon-lined caps. A 2:1 v/v mixture of methylene chloride:methanol (both high purity, Burdick & Jackson Co.) was added to each tube, then ultrasonicated and centrifuged. The supernatant was removed and the extraction repeated four times for sediment and five times for phytoplankton and zooplankton samples until the supernatant was colorless. The combined solvent extracts from each sample were rotary evaporated to dryness in vacuo at 45°C. The sample was then transferred with methylene chloride into a precombusted quartz tube and dried with high purity N₂. The solid left in the centrifuge tube after lipid extraction was dried at room temperature for THAA and TCHO extractions.

2.3.2. THAA Extraction and Isolation

Isolation of the amino acid fraction from marine POM and sediments requires acid hydrolysis to break down the combined forms, such as proteins (or peptides), to the free amino acids (Whelan, 1977; Lee and Cronin, 1982; Henrichs et al., 1984). After lipid extraction, half of each dried sample was weighed directly into a 50 mL glass centrifuge tube and hydrolyzed with 6N HCl (Ultrax pure, J. T. Baker) under N₂ at 100°C in an oven for 19 h. After hydrolysis, samples were centrifuged and the supernatants transferred into 100 mL pear-shaped glass flasks.

The remaining solid was rinsed twice with Milli-Q water, centrifuged, and the supernatants combined with the acid hydrolysate. The hydrolysate was then dried by rotary evaporation in vacuo at 50–55°C and the remaining HCl removed with Milli-Q water and rotary evaporation; this process was repeated once.

The dried THAA fraction was dissolved in 2 mL of Milli-Q water and desalted using cation exchange column chromatography. The 20 mL cation exchange column was packed with AG 50 W-X8 resin (100–200 mesh, analytical grade, BioRad) that had been soaked in 6N, double-distilled HCl for at least one week and rinsed with Milli-Q water several times. Free amino acids were collected in a 1.5N NH₄OH eluate and dried by rotary evaporation. The dried sample was transferred with Milli-Q water to a precombusted quartz tube and dried again in a desiccator in vacuo for final combustion as described later. Selected samples were analyzed for individual amino acid concentrations as described later. After THAA elution, the column was cleaned by rinsing with 6 N HCl and Milli-Q water.

The solid left in the centrifuge tube after removal of the supernatant and rinses was defined as the acid-insoluble fraction. This solid material was transferred with 3–4 1-mL Milli-Q water washes into a precombusted quartz tube and dried in a desiccator in vacuo for later combustion.

2.3.3. TCHO Extraction and Isolation

The method used for extraction and isolation of total carbohydrates was based on the technique of Cowie and Hedges (1984). Half of the dried sample in the centrifuge tube after lipid extraction was hydrolyzed with H₂SO₄ (98% Ultrax pure, J. T. Baker) at 100°C for 3 h. After hydrolysis, finely-ground Ba(OH)₂ · 8H₂O, was added to neutralize the acid, and the resulting BaSO₄ was removed by centrifuging. The solution was then adjusted to a pH of 6–7 with 1.5 N NH₄OH. The hydrolysate containing free sugars was then desalted on a 20 mL mixed cation/anion column packed with mixed (1:1 v/v) cation AG 50W-X8 (100–200 mesh) and anion AG 1-X8 (100–200 mesh analytical grade, BioRad) resins. Both resins were cleaned as per above for the THAA extractions. The TCHO fraction collected by elution with Milli-Q water was rotary evaporated at 50°C to about 2 mL, then transferred into a precombusted quartz tube. After each sample, the column was cleaned by rinsing with 50 mL each of 1.5N NH₄OH, 6N HCl and Milli-Q water.

2.4. Sample Combustion and Isotope Measurements

Portions of the dried sediment, phytoplankton, and zooplankton were weighed directly into 13 mm precombusted quartz tubes for analyses of TOC ¹⁴C. The TOC and organic fractions were acidified in their combustion tubes with 1–2 mL 1% H₃PO₄ for >2 h in a refrigerator, and the pH was adjusted to ≤ 2 to remove carbonates and atmospheric CO₂ that sorbed into NH₄OH. After adding CuO (~100 mg) and Ag foil (~20 mg), all samples were dried in vacuo for 24 h and the tubes flame-sealed under vacuum. Samples were combusted at 850°C for 1 h according to standard techniques (Druffel et al., 1992), and the CO₂ was measured and split into subsamples for ¹³C and ¹⁴C analyses.

The CO₂ subsamples for ¹⁴C analyses were converted to graphite targets according to the method of Vogel et al. (1987). The ¹⁴C/¹³C ratio was measured using accelerator mass spectrometry (AMS) at the Lawrence Livermore National Laboratories (LLNL). Radiocarbon values are reported as $\Delta^{14}\text{C}$ (the per mil deviation from the 'standard' activity of nineteenth century wood) as defined by Stuiver and Polach (1977) for geochemical samples without known age. All $\Delta^{14}\text{C}$ values are corrected for blank CO₂ produced during the combustion and graphitization steps. CO₂ for ¹³C analyses was measured using a VG Micromass 602E isotope ratio mass spectrometer at the Woods Hole Oceanographic Institution with an overall uncertainty of $\pm 0.2\%$.

TOC and TN content of the samples was measured using a Carlo Erba 200 CHN analyzer. Samples for TOC analyses were first acidified with 1.5 N HCl for 24 h to remove inorganic carbon. The precision of duplicate analyses of samples was $\pm 8\%$ and $\pm 10\%$ of the mean for TOC and TN, respectively.

Table 1. Carbon recovery efficiency and effect of separation methods on $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measurements of standards after subsection to separation procedures.

Standard	mgC used	Blank (mgC)	C Recovery (%)	$\Delta^{14}\text{C}$ (‰)		$\delta^{13}\text{C}$ (‰)	
				Before	After	Before	After
Lipid-Cod Liver Oil	0.33–0.67	0.03	97 $\pm$ 5 (n=3)	38 $\pm$ 9	28 $\pm$ 6	–25.5	–25.3
Amino Acids	0.8–1.0	0.03	101 $\pm$ 3 (n=3)	–187 $\pm$ 7	–192 $\pm$ 8	–20.2	–20.2
D-Glucose	0.5–1.0	0.03	103 $\pm$ 4 (n=3)	145 $\pm$ 9	116 $\pm$ 10	–9.8	–9.9

2.5. THAA and TCHO Analysis

To determine if amino acids and sugars were the major organic compounds isolated in the THAA and TCHO fractions, selected samples were analyzed for individual amino acid and total sugar contents after hydrolysis and column isolation. Concentrations of amino acids were analyzed as fluorescent o-phthalaldehyde derivatives by high pressure liquid chromatography (Lindroth and Mopper, 1979; Lee, 1992). Identification of individual amino acids was determined by comparison with authentic standards. TCHO concentrations were measured spectrophotometrically using the MBTH assay of Burney and Sieburth (1977). UV absorption was measured using an HP 8453 UV-Spectrophotometer at a wavelength of 635 nm. Analytical precision was $\pm 10\%$.

2.5. Control Experiments

We tested the reliability and carbon yield efficiency of our methods using standards representing each organic compound class. A pure cod liver oil (SQUIBB), a liquid mixture of fifteen amino acids (Sigma) and D-glucose (Fisher) were tested separately using the procedures described above for each organic fraction to determine carbon yields and blanks of the methods on the carbon isotope measurements. The amount of each standard tested was in the same range as the samples (except for the lipid). Serial blank determinations (without standard) were also made for each organic fraction; the amount of CO_2 was measured for each blank. CO_2 combined to measure $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ for each fraction (approximately six blanks were needed in order to get enough CO_2 for AMS measurement). All glassware and tools used were acid-washed (10% HCl) and combusted at 550°C for >1h; quartz tubes were precombusted at 850°C for >2h not more than 2 days prior to use to avoid sorption of atmospheric CO_2 .

3. RESULTS

3.1. Control Experiments and Carbon Yield Efficiency

The results of our control experiments demonstrate that recovery of individual compounds is acceptable using the techniques described. Carbon yield efficiency determined for the three standards was 97 $\pm$ 5% (n = 3) for the cod liver oil, 101 $\pm$ 3% (n = 3) for the amino acids and 103 $\pm$ 4% (n = 3) for D-glucose (Table 1). $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values obtained for the standards before and after the treatment showed similar results (Table 1) indicating that, for 0.3–1.0 mg C samples, the extraction and isolation procedures did not bias the results significantly. Procedural blanks gave less than 0.06 mL CO_2 for each fraction which was <10% of sample CO_2 volume after combustion. $\Delta^{14}\text{C}$ values measured for the blanks were somewhat low, in the range of –447 to –778‰. For all the samples, CO_2 amounts, $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values were corrected for blank values by subtraction.

3.2. Organic Compound Class Distributions

Concentrations of TOC, TN, THAA, TCHO, total lipid, and acid-insoluble fractions separated from phytoplankton, zooplankton, sediment floc, and sediments are summarized in Table 2. Carbon yield was 99–100% as calculated from the sum of % C in each organic fraction separated from plankton (salt corrected dry weight). THAA, TCHO, and lipid fractions accounted for 24%, 48%, and 19% of the biomass carbon of phytoplankton and 46%, 14%, and 39% of the organic carbon in zooplankton, respectively. These results show somewhat protein-poor and lipid-rich material compared to previous values (Parsons et al., 1961). The C/N ratio (16.7) measured for phytoplankton collected at Station M is 2.5 times higher than the Redfield ratio (C/N = 6.6), consistent with phytoplankton growth under low nutrient conditions (Banse, 1977). As mentioned by Hunt (1995), the chemical composition of phytoplankton can vary greatly due to differences in species composition and nutrient availability. Phytoplankton grown in a nutrient-limited environments tend to contain higher lipid concentrations than those grown under more favorable conditions. We obtained samples at Station M during the season of highest primary production in April to May (Smith et al., 1988; Michaelsen et al., 1988), so that nutrients in surface waters were likely depleted. The C/N ratio (7.1) measured for zooplankton was in the same range (3–8) found in the north-central Pacific by Omori (1969).

Total organic carbon contents of sediment floc and sediments ranged from 1.1–1.5% dry weight (Table 2); TOC showed a relatively constant concentration to a depth of 6 cm, then decreased down to 13 cm (Fig. 1a). Total nitrogen values were 0.21% (2.1 mg N/g) in sediment floc and 0.15–0.22% (1.5–2.2 mg N/g) in sediment by dry weight and paralleled carbon content with depth (Fig. 1b). C/N molar ratios in sediment ranged between 7.8 and 8.6 (Fig. 1c). Carbon yield efficiency for analysis of sediment floc and sediment samples was 81–106% calculated as the sum of each fraction (Table 2). The relatively low (81–89%) C yield in sediments is due in part to the loss of sediment during sample transfer since some particles stuck to the centrifuge tube wall. In both sediment floc and sediment, total lipid concentration was lowest, accounting for only 2–3% of TOC. Carbon concentrations in THAA and TCHO fractions decreased in the surface 1 cm, remained relatively constant to about 5 cm, and then decreased again with depth (Fig. 1d,e). The lipid fraction, however, showed less decrease with depth and was more variable (Fig. 1f). Analysis of individual amino acids and total sugars indicated that amino acids and sugars were the dominant organic compounds present in the THAA and TCHO fractions, accounting for 97 $\pm$ 16%

Table 2. Concentrations of carbon in TOC, TN, THAA, TCHO, lipids and acid-insoluble fractions, and TN and C/N mole ratios separated from phytoplankton, zooplankton, sediment floc and sediments collected from Station M in the northeastern Pacific Ocean in 1993 and 1995.

Sample and Depth (cm)	TOC (wt%) ^a	TN (wt%) ^a	C/N (mole)	THAA Fraction		TCHO Fraction		Lipid Fraction		Acid-insoluble		Total C Yield (%)
				%C	μgC/gdw	%C	μgC/gdw	%C	μgC/gdw	%C	μgC/gdw	
Phytoplankton (1 m)	40	2.8	16.7	24	9.6×10^4	48	1.9×10^5	19	7.6×10^4	8	3.2×10^4	99
Zooplankton (85 m)	50	8.2	7.1	46	2.3×10^5	14	7.0×10^4	39	2.0×10^5	1	5.0×10^3	100
Sediment Floc	1.4	0.21	7.9	35	4910	19	2650	3	420	49	7250	106
Sediment												
0.2–0.5 ^c	1.4	0.20	8.2	18	2530	18	2520	2	280	49	6900	87
0.5–1.0 ^c	1.4	0.20	8.2	16	2300	14	1960	3	430	48	6750	81
1.0–1.5	1.4	0.21	7.8	— ^b	— ^b	9	1260	2	280	51	7150	
1.5–2.0	1.4	0.21	7.8									
2.0–2.5 ^c	1.4	0.20	8.7	16	2400	12	1850	3	450	57	8600	88
2.5–3.0	1.5	0.22	7.9									
3.0–3.5	1.5	0.20	8.7									
3.5–4.0	1.4	0.19	8.6	19	2660	— ^b	— ^b	3	420	60	8400	
4.0–4.5	1.4	0.19	8.6									
4.5–5.0 ^c	1.4	0.20	8.7	16	2400	13	1950	2	320	57	8550	88
5.0–6.0	1.4	0.19	8.6									
6.0–7.0	1.3	0.19	7.9	15	1950	5	650	3	390	63	8190	86
7.0–8.0	1.2	0.18	7.8	12	1500	5	590	3	320	68	8160	88
8.0–10	1.1	0.15	8.5	14	1540	3	330	3	310	69	7600	89
10–14	1.1	0.15	8.5	11	1210	5	550	2	220	67	7370	85

Note: ^a Weights were salt-corrected for the amount of seawater in each sample, assuming a salinity of 35.00‰.

^b Samples were lost during processing.

^c These samples were from a sediment core collected in July 1993 at Station M (Wang et al., 1996).

($n = 8$) and $94 \pm 12\%$ ($n = 7$), respectively, of the carbon in THAA and TCHO fractions. The composition of the hydrolyzable amino acids (data not shown) was similar to previously published values, with glycine being predominant (Whelan, 1977; Burdige and Martens, 1988).

In Fig. 2, we compare the relative abundances of THAA, TCHO, lipid, and acid-insoluble fractions separated from phytoplankton, zooplankton, sediment floc, and sediment with previously analyzed sinking POM and detrital aggregates collected at Station M (Wang et al., 1996). Detrital aggregates were the clumps of amorphous brown particulate matter with ellipsoid shapes (Smith et al., 1994) found on the surface of sediment (1–3 cm in diameter). The % carbon in TCHO and lipid fractions was highest in phytoplankton and zooplankton and lowest in sediment. THAA carbon abundance decreased from 24–46% in plankton to an average of 15% in the sediment. Sediment floc organic carbon had a higher THAA content (35%) than did sinking POM (27%) or detrital aggregates (20%). These relative contents are comparable to values reported recently by Colombo et al. (1996). They found that THAA, TCHO, and lipids accounted for 7–13%, 15–22%, and 1–5% of the organic carbon in sediments of the Laurentian Trough. Percent C in the TCHO fractions we determined here may be minimum values since some losses may occur due to hydrolytic destruction of sugars and incomplete hydrolysis as discussed by Cowie and Hedges (1984) and Walters and Hedges (1988).

Freshly deposited marine organic matter usually has C/N molar ratios of 6–8 (Redfield et al., 1963; Walsh et al., 1981), whereas terrestrial organic matter may have much higher C/N ratios (up to 100) (Ertel and Hedges, 1983). The C/N molar ratios (7.8–8.6) we measured for the sediment floc and sediments at Station M are slightly higher but comparable to values reported for marine organic matter.

3.3. Carbon Isotope Composition

Values of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measured for TOC and the four organic fractions are listed in Table 3 and shown in Figs. 3 and 4, respectively. $\Delta^{14}\text{C}$ values of TOC and THAA, TCHO, lipid, and acid-insoluble fractions separated from phytoplankton and zooplankton range from 45‰ to 81‰. This range of $\Delta^{14}\text{C}$ values clearly shows post-bomb ^{14}C signatures ($> -50\%$). In sediment floc and sediment, $\Delta^{14}\text{C}$ values of TOC and the four organic fractions are much lower, ranging from -94% to -723% . THAA and TCHO fractions in sediments have similar $\Delta^{14}\text{C}$ values (range -94% to -561%) that are higher overall than those for total lipid (-389% to -723%) and acid-insoluble fractions (-310% to -669%). Figures 3 and 4 also show previously reported values of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ for sinking POM collected by a sediment trap at 3450 m and detrital aggregates collected at the sediment surface of Station M (Wang et al., 1996). All values of $\Delta^{14}\text{C}$ decreased with depth from phytoplankton and zooplankton in the surface water to sinking POM, detrital aggregates, sediment floc, and then sediment (Fig. 3). The largest decrease of $\Delta^{14}\text{C}$ values occurred at the sediment-water interface, with this decrease being greater for lipid and acid-insoluble fractions than for THAA and TCHO fractions.

Within each fraction, $\delta^{13}\text{C}$ values of TOC and organic fractions separated from phytoplankton, zooplankton, sediment floc, and sediment all show similar values except for TCHO in detrital aggregate 2833–20 (Table 3). These relative constant values are illustrated in Fig. 4 as a function of depth. Values of $\delta^{13}\text{C}$ in phytoplankton are 1–4‰ higher than those of zooplankton. Among the four organic fractions, THAA and TCHO have higher $\delta^{13}\text{C}$ values (ranging from -16.3% to -22.0%) than those of the lipid (from -21.1% to -25.1%) and acid-insoluble fractions (from -19.6% to -24.1%). As expected,

Fig. 1. Concentration profiles of (a) TOC, (b) TN, (c) C/N ratios, (d) THAA, (e) TCHO, and (f) lipid fractions in sediment at Station M. The solid lines are the model best-fit curves for concentrations of TOC and TN (see text for explanation).

$\delta^{13}\text{C}$ values of TOC are intermediate, ranging from -18.3‰ to -22.9‰ .

4. DISCUSSION

4.1. Distribution of Organic Compound Classes in Plankton and Sediment

In their roles as structural components and in energy storage, amino acids, carbohydrates, and lipids are the major organic compound classes contained in marine organisms (Parsons et al., 1961; Cowey and Corner, 1966; Brown, 1991). Parsons et al. (1961) reported that protein, carbohydrate, and lipid accounted for 35–68%, 20–42% and 5–20%, respectively, of the organic carbon in eleven phytoplankton species common to the north Pacific harvested during the exponential phase of cultural

growth. In diatoms, protein was generally more abundant than carbohydrate and lipid fractions. The opposite was found in dinoflagellates, possibly owing to the abundance of carbohydrate material associated within cell walls in these organisms (Haug et al., 1973). Cowey and Corner (1966) found that most of the organic nitrogen in cultured phytoplankton species could be accounted for as hydrolyzable amino acids. Hunt (1995) found that carbohydrate concentrations ($\sim 60\%$) were much higher than proteins ($\sim 20\text{--}30\%$) in phytoplankton and diatoms while zooplankton contained much higher amounts of proteins ($\sim 60\%$) than that of carbohydrates ($\sim 20\%$).

For our samples, THAA carbon abundances in the phytoplankton was lower, and TCHO fraction C was slightly higher, than the ranges reported by Parsons et al. (1961) and comparable with the values reported by Hunt (1995). These differ-

Fig. 2. A comparison of abundances (as % of TOC) of THAA, TCHO, lipid, and acid-insoluble organic fractions separated from (a) phytoplankton, (b) zooplankton, (c) sinking POM (3450 m), (d) detrital aggregates (sediment surface), (e) sediment floc, and (f) sediment collected at Station M. Values for sinking POM and detrital aggregates are from Wang et al. (1996). The values for TOC are TOC% of dry weight of the samples.

ences may reflect temporal variations of the major chemical constituents among different species, different structure of the phytoplankton community, differences in collection net size, and different growing conditions between cultures and the natural environment. The compound class abundances we determined for the zooplankton are generally consistent with the values of Hunt (1995) and the results of Raymont et al. (1969) who found that protein was more abundant than lipid and carbohydrates in most zooplankton species they studied.

Total hydrolyzable amino acids, TCHO and lipids have been widely characterized in marine POM and sediments (e.g., Cowie and Hedges, 1984; Henrichs et al., 1984; Burdige and Martens, 1988; Wakeham and Canuel, 1988, 1988; Wakeham and Lee, 1993). During the transport of POM from open ocean surface water to sediment, extensive alteration and preferential decomposition of more labile compounds in the water column and at the sediment-water interface can result in significantly different chemical compositions for sedimentary organic matter than the material originally biosynthesized (Wakeham and Lee, 1993; Wakeham et al., 1997). As shown in Fig. 2, the decrease of carbon abundances we determined in THAA, TCHO, and lipid fractions and the increase of carbon abundances in the acid-insoluble fraction from plankton to sediments in our sam-

ples generally reflect such extensive alteration and decomposition during transport of POM from surface water to the sediment at Station M. In their study, Cowie and Hedges (1994) used % OC in amino acids and sugars as an indicator of organic matter alteration stages during diagenesis. They found that the % OC represented by these reactive biochemicals decreased rapidly during the early stage of organic degradation (in water column) to the later stages (in sediments). Our results are consistent with their findings showing that the % OC in THAA + TCHO decreased from phytoplankton (72%), to sediment floc (54%), to surface sediment (36%), to sediment (16%). These changes clearly indicate the alteration stages of the organic matter from water column to sediment at Station M.

Lipid carbon abundances decreased more rapidly with depth than either THAA or TCHO values. In contrast, carbon in the acid-insoluble fractions increased dramatically from plankton (1–8%) to sediment (48–69%). These changes in abundance of compound classes in different organic carbon pools reflect, in general, the selective alteration of organic matter during decomposition in the ocean. While plankton sinks as POM through the water column to the sediment surface, most labile organic material is degraded, and more refractory organic material is left to reach the sediment surface and be buried in the sediment (Lee and Wakeham, 1988). From the TOC concentration measured in phytoplankton (40%), zooplankton (50%) and surface sediment (1.4%), we estimate that about 3% $[(1.4/45) \times 100]$ of plankton biomass carbon reached the sediment surface and 97% was remineralized in the water column in late winter at Station M, consistent with results of other studies (Reimers et al., 1992; Smith et al., 1994; Cai et al., 1995). This is also supported at Station M by the $\delta^{14}\text{C}$ results for TOC and the organic fractions as described later.

Sediment floc contained a higher relative proportion of THAA than did the sinking POM (Fig. 2). THAA carbon enrichments at the sediment-water interface seem to be a common phenomenon and have been reported previously (Mayer, 1993 and references therein). Sediment floc consists of very loose and flocculent material. The limited number of studies performed on this layer suggest that the formation of sediment floc in the deep sea is closely related to water-column bloom events (Lampitt, 1985). Organic matter contained in sediment floc appears relatively labile and has mostly a phytoplankton origin (Christensen and Kannevorf, 1986; Rice et al., 1986; Wakeham and Lee, 1989).

In their studies of the relationship between deep carbon flux and benthic processes at Station M, Smith et al. (1994) observed large abundant detrital aggregates on the sediment surface following periods of high particulate organic flux to the deep ocean. By determining the macro- and microscopic compositions, Beaulieu and Smith (1997) reported that these detrital aggregates mainly contained radiolarians (radiolarian patches), diffuse floc, or zooplankton mucous webs (discrete aggregates). $\delta^{14}\text{C}$ values previously measured for TOC and THAA, TCHO, lipid, and acid-insoluble fractions separated from the detrital aggregates (radiolarian patch-type) fell between the values of sinking POM at 3450 m and surface sediment floc (at 4100 m depth; Wang et al., 1996). Wang et al. (1996) suggested that these detrital aggregates (radiolarian patches) were likely formed as a result of repackaging of sinking, suspended, and dissolved organic detritus in the deep

Table 3. Isotopic measurements of TOC and THAA, TCHO, Lipid and acid-insoluble fractions in samples collected from Station M in the northeastern Pacific Ocean from 1993 to 1995.

Sample and Depth	TOC			THAA Fraction			TCHO Fraction			Lipid Fraction			Acid-insoluble		
	UCID#	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	UCID#	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	UCID#	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	UCID#	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$	UCID#	$\Delta^{14}\text{C}$	$\delta^{13}\text{C}$
		(‰)			(‰)			(‰)			(‰)			(‰)	
Phytoplankton (1 m)	1281	59 ± 9	-18.3	1299	53 ± 12	-18.2	1308	79 ± 11	-16.6	1272	80 ± 10	-21.1	1290	51 ± 15	-19.6
Zooplankton (85 m)	1282	81 ± 7	-21.8	1300	45 ± 11	-18.9	1309	n.d. ^a	-17.5	1273	58 ± 8	-25.1	1291	n.d. ^a	-24.1
POM _{sink} (3450 m)															
cup # 11	888	21 ± 10	-21.2	677	56 ± 22	-18.4	712	22 ± 26	-18.0	665	25 ± 17	-23.6	684	-9 ± 13	-22.9
cup # 13	889	8 ± 12	-21.0	629	55 ± 16	-17.2	649	26 ± 41	-16.3	666	-27 ± 20	-22.7	685	-36 ± 12	22.9
Detrital aggregates (4100 m)															
2828-16	886	-197 ± 24	-22.6	633	-57 ± 37	-18.1		— ^b	— ^b	548	-263 ± 42	-24.4	643	-309 ± 20	-23.7
2833-20	887	-162 ± 16	-22.9	632	-52 ± 23	-18.6	970	-186 ± 39	-22.0	547	-170 ± 130	-24.6	642	-238 ± 12	-23.4
Sediment Floc (1)	1274	-242 ± 11	-21.5		— ^b	— ^b	1301	n.d. ^a	-18.8		— ^b	— ^b	1283	-366 ± 15	-23.6
(2) ^d	890	-255 ± 12	-21.8	683	-110 ± 25	-18.2	715	-107 ± 40	-16.4	671	-332 ± 48	-23.0	690	-364 ± 15	-22.8
Sediment (cm)															
0.2–0.5 ^c	891	-266 ± 11	-21.8	679	-114 ± 19	-18.5	650	-94 ± 37	-16.9	667	-404 ± 31	-23.4	686	-354 ± 9	-22.9
0.5–1.0 ^c	892	-253 ± 7	-21.8	680	-140 ± 18	-18.6	713	-149 ± 28	-17.8	668	-417 ± 31	-23.3	687	-355 ± 8	-23.0
1.0–1.5	1275	-242 ± 9	-21.6		— ^b	— ^b	1302	-161 ± 30	-17.8	1266	-389 ± 34	-23.5	1284	-336 ± 11	-23.4
2.0–2.5 ^c	893	-258 ± 7	-21.2	681	-122 ± 18	-18.6	714	-131 ± 26	-17.9	669	-436 ± 26	-24.0	688	-310 ± 8	-23.0
3.5–4.0	1276	-353 ± 8	-21.7	1294	-318 ± 20	-18.9		— ^b	— ^b	1267	-461 ± 29	-23.5	1285	-404 ± 9	-23.0
4.5–5.0 ^c	894	-317 ± 6	-21.3	682	-195 ± 18	-18.6	651	-149 ± 23	-18.3	670	-472 ± 26	-24.0	641	-454 ± 22	-23.1
6.0–7.0	1277	-372 ± 8	-21.6	1295	-283 ± 21	-18.1	1304	-295 ± 35	-17.5	1268	-511 ± 26	-23.5	1286	-432 ± 8	-23.0
7.0–8.0	1278	-444 ± 8	-21.6	1296	n.d. ^a	-18.3	1305	-367 ± 37	-17.4	1269	-594 ± 27	-23.6	1287	-495 ± 8	-22.9
8.0–10	1279	-571 ± 7	-21.7	1297	-464 ± 25	-18.5	1306	-457 ± 49	-16.3	1270	-654 ± 32	-23.0	1288	-585 ± 9	-22.8
10–14	1280	-630 ± 7	-21.6	1298	-561 ± 27	-19.0	1307	-559 ± 37	-17.7	1271	-723 ± 31	-22.9	1289	-669 ± 8	-22.7

Note: Values for both $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ are corrected for blanks. Errors for $\Delta^{14}\text{C}$ are calculated considering both sample processing blanks and AMS counting statistical errors.

^a Samples were either too small (<0.1 mg C) for $\Delta^{14}\text{C}$ measurements or did not give any ion current during AMS analysis.

^b Samples were lost or contaminated during processing.

^c These samples were from a sediment core collected in July 1993 at Station M (Wang et al. 1996).

^d These data are for the samples collected in September 1994 at Station M (Wang et al., 1996).

Fig. 3. $\Delta^{14}\text{C}$ profiles of (a) TOC and (b) THAA, (c) TCHO, (d) lipid, and (e) acid-insoluble organic fractions separated from plankton, sinking POM and detrital aggregates in the water column and in sediment floc and sediment at Station M. Values of $\Delta^{14}\text{C}$ for sinking POM and detrital aggregates are from Wang et al. (1996). Sinking POM was collected by a sediment trap deployed at 3450 m depth (650 m above bottom) for two 30 day periods from May to July 1993. Detrital aggregates were collected at the sediment surface during DSV *Alvin* dives in September 1994 (Smith et al., 1994).

Fig. 4. $\delta^{13}\text{C}$ profiles of (a) TOC and (b) THAA, (c) TCHO, (d) lipid, and (e) acid-insoluble organic fractions separated from plankton, sinking POM and detrital aggregates in the water column and in sediment floc and sediment at Station M. Values of $\delta^{13}\text{C}$ for sinking POM and detrital aggregates are from Wang et al. (1996).

water. A continuum may exist in the diagenetic state between the POM, detrital aggregates, and sediment floc in the deep northeastern Pacific Ocean. The relatively higher THAA abundance we found in the sediment floc could be partly from microbial biomass since benthic bacterial and macroorganism populations at the sediment-water interface are much greater than those in the overlying water column and the deeper sediment (Mayer, 1993). As biomass abundance was not determined in this study and since the $\delta^{13}\text{C}$ values of THAA in plankton, detrital aggregates, and sediment floc did not show significant differences, we are unable to distinguish between the sources of THAA-enriched carbon to the sediment floc.

4.2. Sources Affecting $\Delta^{14}\text{C}$ of POM and Sediment

As expected, $\Delta^{14}\text{C}$ of TOC and all organic fractions separated from plankton displayed post-bomb ^{14}C signatures, similar to the range of $\Delta^{14}\text{C}$ values (49–81‰) measured for dissolved inorganic carbon (DIC) in surface waters at Station M (Druffel et al., 1996; Massiello et al., 1998). In comparison with plankton, $\Delta^{14}\text{C}$ values of organic fractions in sediment floc and sediments were lower (Fig. 3). $\Delta^{14}\text{C}$ values for sinking POM collected at 3450 m were intermediate between plankton and sediment and ranged from 22‰ to 56‰ for THAA and TCHO fractions and –36‰ to 25‰ for lipid and acid-insoluble fractions (Wang et al., 1996). These post-bomb $\Delta^{14}\text{C}$ signatures in POM samples suggest that some fraction of the organic carbon produced in the surface water sinks quickly to the deep water at Station M.

The most dramatic change in $\Delta^{14}\text{C}$ values was observed between the sinking POM and the sediment floc (Fig. 3). As we discussed previously (Wang et al., 1996), several processes likely cause the low $\Delta^{14}\text{C}$ values of organic matter found at the sediment-water interface. First, bioturbation and sediment resuspension dilutes sediment surface $\Delta^{14}\text{C}$ values with ‘old’ carbon from deeper sediment. Second, rapid organic matter decomposition at the sediment-water interface will cause the loss of the most labile organic carbon; much of this carbon will be recently deposited and contain post-bomb $\Delta^{14}\text{C}$ signatures. Third, sorption and biological incorporation of ‘old’ DOC (average DOC $\Delta^{14}\text{C}$ = –549‰ at depths 1600–4050 m at Station M, Bauer et al., 1998) into POC in the deep water could also dilute surface $\Delta^{14}\text{C}$ signatures of POC. Finally, anapleurotic, dark reactions (Lehninger, 1970) by organisms in deep water using ‘old’ DIC (DIC $\Delta^{14}\text{C}$ = –246‰ at 3500 m at Station M, Masiello et al., 1997) to produce POC (Rau, 1991) is another possible source of old carbon to the TOC found at the sediment-water interface at Station M. The contribution of carbon in POC by these reactions is believed to be minor.

Lateral downslope transport of organic matter could also be a possible source of ‘old’ carbon to Station M. In sediment trap studies off the Oregon/California coast, Lyle et al. (1992) found that 20–40% of the TOC buried in the surface sediments at 2830 and 3664 m depths below the California Current was terrestrial, largely due to the high input of terrestrial organic matter from the Columbia River. Significant downslope input (50%) of refractory organic carbon from resuspended sediments was also found along the mid-slope of the Middle Atlantic Bight at 1000 m depth (Anderson et al., 1994). Based on $\Delta^{14}\text{C}$ and concentration measurements of suspended partic-

Fig. 5. A schematic model for the calculation of sorbed old DOC to sinking POM by $\Delta^{14}\text{C}$ balance, assuming organic matter sinking to deep water was produced in the surface with a $\Delta^{14}\text{C}$ value similar to that of plankton (+70‰). The average $\Delta^{14}\text{C}$ value of deep DOC at Station M (–533‰) is from Bauer et al. (1996).

ulate organic carbon (POC) collected in the deep water (50 m above bottom) at Station M, Druffel et al. (1998) calculated that only about 10% of the suspended POC could be derived from sediment resuspension and/or lateral transport of resuspended sediment from the continental shelf and slope. Minimal lateral transport of organic carbon is also supported by our $\delta^{13}\text{C}$ results and can not balance the observed $\Delta^{14}\text{C}$ decrease of suspended POC in the water column (124–160‰; Druffel et al., 1996). However, lateral bedload transport of sedimentary material cannot be excluded since we could not measure transient slumping events.

Sorption of ‘old’ DOC onto POM and sediment particles could be a major cause of low $\Delta^{14}\text{C}$ values observed in the deep northeastern Pacific Ocean (Druffel and Williams, 1990; Druffel et al., 1996). We can calculate the amount of DOC that would have to be sorbed onto sinking POM at Station M using the $\Delta^{14}\text{C}$ mass balance approach shown in Fig. 5. First, we assume that organic matter sinking to the deep water originates from POM produced in the surface water and has a $\Delta^{14}\text{C}$ value similar to that determined for planktonic carbon produced from surface DIC. Since average $\Delta^{14}\text{C}$ values of TOC decreased from 70‰ in surface plankton to 15‰ in sinking POM (at 3450 m; $n = 2$), a balance of the observed $\Delta^{14}\text{C}$ value [$(70\% \times .91) + (-549\% \times .09) = 15\%$] requires that 9% of TOC in sinking POM be ‘old’ DOC. A similar calculation indicates that a maximum of 35% of carbon in detrital aggregates (assuming no TOC from sediments was incorporated) is from ‘old’ DOC. This ‘old’ DOC could be sorbed onto particles (Hunter, 1980;

Fig. 6. Correlation plots of $\Delta^{14}\text{C}$ vs. $\delta^{13}\text{C}$ for THAA, TCHO, lipid, and acid-insoluble organic fractions separated from phytoplankton, zooplankton, sediment floc, and sediment collected at Station M.

Davis, 1982) or incorporated by bacteria onto sinking particles (Alldredge and Cohen, 1987; Cho and Azam, 1988; Lochte and Turley, 1988). The $\Delta^{14}\text{C}$ values of sediment floc and sediments are likely affected by sediment resuspension and bioturbation; thus, it is difficult to calculate the amount of 'old' carbon contributed from the DOC pool.

$\Delta^{14}\text{C}$ values indicate that sedimentary TOC contained both 'younger' (THAA and TCHO) and 'older' (lipid and acid-insoluble) organic components. The large differences between $\Delta^{14}\text{C}$ of lipid and THAA/TCHO fractions indicate varying degrees of selective alteration in different compound classes and reflect the differences in their decomposition pathways in the deep northeastern Pacific Ocean. Selective remineralization of labile lipids (e.g., fatty acids) over more refractory alkanes (e.g., long chain hydrocarbons) is seen in sediment trap POM and sediments (Wakeham et al., 1984; Wakeham and Canuel, 1988; Sun and Wakeham, 1994). The alkanes could thus have a lower $\Delta^{14}\text{C}$ value due to their longer residence time in the water column and/or their fossil origin; this could explain part of the large gradient of $\Delta^{14}\text{C}$ in lipids observed with depth. Alternatively, bacterial utilization of 'old' DOC in deep water and subsequent incorporation of that C into bacterial membrane lipids could also explain lower $\Delta^{14}\text{C}$ values observed for the lipid fraction in deep waters. Based on our isotope results, however, it is not possible to distinguish between these processes. Further determination of lipid concentrations and $\Delta^{14}\text{C}$ on the molecular level (Eglinton et al., 1996, 1997) in these samples may help to resolve these issues.

4.4. Remineralization of Organic Matter

The organic fractions in sediment floc and sediment can be separated into two groups on the basis of their $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ values (Fig. 6). Lipid and acid-insoluble fractions comprise one group that contains low ('old') $\Delta^{14}\text{C}$ and low $\delta^{13}\text{C}$ values

relative to the second group of THAA and TCHO fractions with higher ('younger') $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values. The $\delta^{13}\text{C}$ values of organic fractions in sediments are generally similar to their values in plankton. The depletion of $\delta^{13}\text{C}$ (−1 to −4‰) in zooplankton relative to phytoplankton at Station M (also shown in Fig. 4) is probably due to the higher lipid content of zooplankton and to compositional differences in lipid compounds between zooplankton and phytoplankton. The lower $\delta^{13}\text{C}$ values found in the lipid compared with the THAA and TCHO fractions are likely caused by isotopic fractionation during biosynthesis of these compounds (Fogel and Cifuentes, 1993). Earlier studies have shown that total lipid carbon is depleted in ^{13}C relative to amino acids and carbohydrates in marine plankton and bacteria (Degens et al., 1968; De Niro and Epstein, 1977; Monson and Hayes, 1982). In their studies of isotopic biogeochemistry of lipid biomarkers in the Black Sea, Wakeham et al. (1993) and Freeman et al. (1994) also found that hydrocarbons (part of the lipid fraction) were generally depleted in ^{13}C relative to bulk POC, suggesting that this depletion is preserved as material passes through the water column to the sediments. McNichol et al. (1991) previously suggested that selective remineralization of organic matter in marine sediment could result in fractionation of carbon isotopes. However, the $\delta^{13}\text{C}$ values we measured for TOC and each organic fraction in sediment are relatively constant with depth indicating that unlike $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$ was little affected by decomposition of organic matter.

The carbon content of THAA, TCHO, and lipid fractions decreases with depth in the sediment (Fig. 1) reflecting the degradation of these compound classes during early diagenesis. However, the sediment profiles shown in Fig. 1 reflect effects of the strong bioturbation in the surface 5 cm that has previously been observed at Station M (Reimers et al., 1992; Cai et al., 1995). It is interesting to note that $\Delta^{14}\text{C}$ values as shown in

Fig. 7. Plots of radiocarbon age distributions of TOC and organic fractions in sediment at Station M. The sedimentation rates were calculated from the slopes of the lines and summarized in Table 4.

Fig. 3 seem less affected by bioturbation. The reason for this difference is not clear. In these surface sediments, bioturbation is probably more important than sedimentation to downward mixing of organic carbon. This makes the calculation of degradation rate constants difficult from models of sediment profiles of TOC, TN, and the organic fractions. Therefore, here we calculate rate constants only for TOC, TN, and each organic fraction below the top 5 cm depth using the “multi-G” model of Berner (1980):

$$G_z = G_o e^{-kz/\omega} + G_u \quad (1)$$

where G_z is the total substrate concentration at depth z below 5 cm; G_o is the metabolizable substrate concentration at 5 cm; G_u is the refractory substrate concentration; and k is the first-order degradation rate constant (yr^{-1}) of metabolizable substrate. Assumptions involved in using the model are that the degradation rate is first-order with respect to metabolizable organic matter concentration, and the organic matter input to the sediments has been constant with time. We calculated values of the sedimentation rate, ω , at Station M using $\Delta^{14}\text{C}$ age distributions of TOC and each organic fraction in the core below 5 cm (Fig. 7). Although the $\Delta^{14}\text{C}$ ages among TOC and the four organic fractions were very different, they gave similar values of ω (Table 4). For our model calculation, we used the average calculated ω of 1.36 cm/kyr. This sedimentation rate is twenty times lower than the value (28.4 cm/kyr) calculated from ^{210}Pb profiles in these sediments at Station M (Cai et al., 1995). The sedimentation rate calculated from ^{210}Pb is likely to be much higher than actual values due to the short half-life of ^{210}Pb (22 yr).

By fitting the data to Eqn. 1, we obtained k values of 0.0005 yr^{-1} for both TOC and TN; and 0.0014 yr^{-1} , 0.0012 yr^{-1} , and 0.0004 yr^{-1} for THAA, TCHO, and lipid fractions, respec-

tively. These rate constants for TOC and TN are much lower than those reported for most coastal marine sediments (e. g., 0.02–11 yr^{-1} , see Henrichs, 1993 and references within), and comparable with the values for TOC reported for the central equatorial Pacific (0.0003–0.01 yr^{-1} , Grundmanis and Murray, 1982) and higher than the value for northeastern Pacific red clay sediments (0.000083 yr^{-1} , Murray and Kuivila, 1990) where organic carbon contents were much lower than in Station M sediments. Rate constants calculated for Station M are for decomposition of material below 5 cm and are thus for material that presumably is already substantially degraded. Rate constants for the organic fractions in Station M sediment are also lower than values reported for THAA, TCHO, and lipid in some coastal and shallow marine sediments (e. g., 0.02–1.4 yr^{-1} , Henrichs and Farrington, 1987; Burdige and Martens, 1988; Haugen and Lichtentaler, 1991; Sun and Wakeham, 1994; Colombo et al., 1996), also suggesting that compounds in the organic fractions in Station M sediments below 5 cm are more refractory. The relative biological reactivity of organic carbon in each fraction as determined by the order of degrada-

Table 4. Calculated sedimentation rates for TOC and each organic fraction from their radiocarbon age distributions with depth in sediments (see Table 3) at Station M. See text for details.

Component	Sedimentation rate (cm/1000 yr)	Linear Coefficient (r^2)
TOC	1.28	0.95
THAA	1.41	0.99
TCHO	1.37	0.99
Lipid	1.29	0.97
Acid-insoluble	1.45	0.91
Average	1.36	

tion rate constants was THAA $\approx$ TCHO $>$ TOC $>$ lipid; this is in good agreement with the order of average $\Delta^{14}\text{C}$ values in the sediment (THAA: -275‰ $\approx$ TCHO: -262‰ $>$ TOC: -371‰ $>$ lipid: -506‰).

Profiles of TOC and individual organic fractions and the model calculations also indicate that a significant amount of THAA and TCHO, and most of the lipid in the surface sediment were not decomposed deeper in the sediment. This preservation may be due to adsorption processes which may play a major role in preservation of organic matter in marine sediment or to decreasing oxygen in the sediment (Mayer, 1993; Hedges and Keil, 1995; Keil et al., 1994). A recent study by Keil et al. (1994) indicated that sorption of organic matter to mineral surfaces in marine sediments could stabilize the component molecules, slowing remineralization rates by up to 5 orders of magnitude. Adsorption may also play an important role in the preservation of THAA, TCHO, and lipid fractions in sediment at Station M. Constant distributions of THAA, TCHO, and lipid fraction carbon and their decreased $\Delta^{14}\text{C}$ ages below 5 cm in the sediment suggest that these preserved organic fractions are refractory and are degraded only slowly, if at all, over time.

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