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Seasonal variability of particulate organic radiocarbon in the northeast Pacific Ocean

Ellen R. M. Druffel,¹ James E. Bauer,² Peter M. Williams,³ Sheila Griffin,¹ and David Wolgast³

Abstract. We present Δ^{14} C measurements of particulate organic carbon (POC) collected on four cruises at our time series site (station M) in the northeast Pacific Ocean. We observe a large gradient with depth in the suspended POC Δ^{14} C values (124–160‰). These profiles display lower Δ^{14} C values (by 20–30‰) in samples between 2500 m and the bottom during June 1992 and July 1993 than those during February and October 1992. Values of Δ^{14} C in sinking POC from deep-moored sediment trap collections suggest a semiannual trend that displays lower overall Δ^{14} C in material collected during periods of high flux. A limited number of Δ^{14} C measurements of small swimmers picked from the trap 650 m above bottom are similar to surface Δ^{14} C measurements of dissolved inorganic carbon (DIC) and suspended POC, indicating a surface carbon source. Overall, we postulate that the major process causing lower Δ^{14} C values of deep suspended and sinking POC is sorption (or biological incorporation) of "old" DOC onto particulate matter. There appears to be a higher ratio of DOC sorbed to sinking particulate matter at times of high flux (late spring and early fall) that can be thought of as a "stripping out" of DOC from the water column. The DIC Δ^{14} C display a small seasonal variation in the surface waters and is not the sole source of the observed seasonality in the POC Δ^{14} C signals.

Introduction

A major reason the oceanic carbon cycle is an important study area is its connection, via gas exchange, with the atmospheric greenhouse gas CO_2 . The residence time of ${}^{14}CO_2$ in the atmosphere with respect to exchange with the oceans is about 10 years, relatively rapid compared to the e-folding time for fossil fuel CO₂ [Broecker et al., 1960; Druffel and Linick, 1978]. Following its diffusion across the air-sea interface, CO₂ is hydrated and mixed into the upper layer of the water column as dissolved inorganic carbon (DIC). The DIC is fixed by photosynthesis in the euphotic zone to particulate organic carbon (POC), and a portion of the POC falls through the water column (POC_{sink}). A large portion of this POC_{sink} is remineralized by marine organisms including bacteria or otherwise transformed into smaller particles that remain suspended (POC_{susp}) in the water column for variable periods of time. These two particle fractions act as a short circuit between the surface and deep ocean carbon pools. This short circuit connection is the subject of this paper.

One of the major questions we address is, How fast does POC that is produced in the surface waters of the ocean transit the water column en route to the deep sea, and how is it altered during its transit? Stable carbon isotope ratios of foraminiferal tests falling into a deep trap in the North Atlantic have been shown to be reliable recorders of near-surface properties 1

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Paper number 96JC01850. 0148-0227/96/96JC-01850\$09.00 month prior to their arrival in the trap [Deuser, 1986]. Thorium isotope results were used to show that the turnover time of suspended matter in the deep tropical Pacific was of the order of 5 to 10 years [Bacon and Anderson, 1982]. This is irrespective of the fact that reaction times are short (a few months), indicating that the surfaces of suspended particles in the deep sea are close to equilibrium, at least with respect to the exchange of metals.

Measurements of bomb-produced ¹⁴C in POC_{susp} in the North Pacific [*Druffel and Williams*, 1990] and North Atlantic [*Druffel et al.*, 1992] during the late 1980s revealed large gradients of Δ^{14} C with depth (Figure 1). The bomb radiocarbon signal of DIC reached a maximum in the temperate surface oceans in the early 1970s [*Druffel and Linick*, 1978; *Druffel*, 1987]. Thus one would not expect a gradient with depth in POC_{susp} Δ^{14} C values in the late 1980s, assuming that POC turns over quickly (≤ 10 years) and vertical fluxes, originating from the surface water, dominate the POC input to the deep ocean. However, it appeared that old carbon was transported to the deep sea via POC_{susp} (and to a lesser extent via POC_{sink}) transiting through the water column.

The impetus for this study was to evaluate, on a seasonal basis, the role of POC in the transport of old carbon to the deep sea. While previous measurements of Δ^{14} C in POC_{susp} and POC_{sink} from the oligotrophic North Pacific and North Atlantic Oceans [*Druffel and Williams*, 1990; *Druffel et al.*, 1992] were made during single cruises, they revealed no information about the seasonal variability of Δ^{14} C. Hence we chose to examine an area of the ocean where surface primary productivity and near-bottom fluxes of POC_{sink} varied severalfold on a seasonal basis. This provided an opportunity to study a natural system in which these factors regulated time- and depth-dependent changes in Δ^{14} C of POC.

This study was part of a larger project that included the study of carbon isotopes $({}^{14}C, {}^{13}C)$ and concentrations of dis-

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Figure 1. Comparison of the Δ^{14} C measurements for DOC_{UV} and POC_{susp} from the North Atlantic (32°N, 64°W) in June–July 1989 and the north central Pacific (31°N, 159°W) in June–July 1987 [after *Druffel et al.*, 1992].

solved organic carbon (DOC) in the same set of water samples collected for the DIC Δ^{14} C analyses discussed here. Suspended and sinking POC samples were also collected during the same cruises. Results of the DOC and DIC concentrations and $\Delta^{14}C$ measurements are published elsewhere (J. Bauer et al., Interand intra-annual variability in isotopic (14C and 13C) signatures of dissolved organic carbon in the eastern North Pacific Ocean. submitted to Journal of Geophysical Research, 1995, hereinafter referred to as BDWWG; E. R. M. Druffel and C. Masiello, manuscript in preparation, 1996). It is important to remember that the difference between POC and DOC is based purely on a size-dependent, operational definition. DOC is the organic carbon that passes a $1-\mu m$ filter, and POC is that which is collected by it. It may be appropriate to think of DOC and POC as being similar in a number of respects [Vernonclark et al., 1995], such as their chemical, physical, and isotopic properties. One example of where this may be true is for small POC $(1-10 \ \mu m)$ and large DOC (10,000 daltons to 1 μm).

It is also important to note here that the carbon isotopic signatures reported here for POC and DOC samples are of bulk analyses that represent averages of the individual molecular components of each sample. Thus generalizations based on the bulk average isotopic values are all that can be quantified now, until new techniques designed to date individual organic compounds are widely applied to geochemical samples [cf. Eglinton et al., 1996].

Sampling Site

Our area of study was a single site (station M, $34^{\circ}50'$ N, $123^{\circ}00'$ W, depth ~4100 m) located 220 km west of Point Conception, California, in the northeast Pacific Ocean. Sediments are composed of red clay, and the seafloor has low relief. The southward flowing California Current exerts a dominant influence on the sea surface in this region, and there are spring plumes of chlorophyll [*Michaelsen et al.*, 1988; *Smith et al.*, 1988] [*Peláez and McGowan*, 1986] that vary on an interannual basis.

Two maxima per year are usually observed in the flux of particulate organic material to the deep sea at station M, the primary one in late spring and the secondary one in early fall [*Smith et al.*, 1994]. The flux values at 600 m above bottom (mab) range from a low of 1–3 mg C m⁻² d⁻¹ in winter and early spring to a high of 10–25 mg C m⁻² d⁻¹ during and

immediately after the major late spring bloom [Smith et al., 1994]. Fluxes during late spring of 1992 were lower than normal (5–7 mg m⁻² d⁻¹) and are attributed to the El Niño–Southern Oscillation (ENSO) event that peaked during this year (K. L. Smith, personal communication, 1995).

We report data from samples collected during four cruises to station M: Pulse 11 (February 19 to March 2, 1992), Pulse 12 (June 19 to July 1, 1992), Pulse 15 (October 15–27, 1992), and Pulse 17 (July 14–23, 1993). These cruises were part of a separate program that emphasized the study of the coupling between near-bottom pelagic POC fluxes and benthic processes [*Smith et al.*, 1994].

Methods

Suspended POC was collected using in situ Yentsch pumps [Druffel et al., 1992; Williams et al., 1980] deployed for 2–8 hours at 8–10 depths during February, June, and October 1992 and July 1993. During each deployment, 600-2500 L of seawater were filtered through $0.8-\mu$ m pore diameter, precombusted (550°C) quartz fiber filters (Whatman ultrapure QM-A, 145 mm diameter). The filters were then frozen at -20° C in glass jars in the dark.

Sediment traps were used to collect sinking POC at 650, 600, 100, and 50 mab. The traps were Teflon-coated fiberglass cones (120 cm long, 57 cm diameter) with a mouth opening of 0.25 m² [Bruland et al., 1981]. Collections were taken for 10–30 days at each depth, with mercuric chloride used in all trap deployments as a poison. There were numerous breaks in the sampling sequences owing to inadequate availability of material. The reader is referred to a separate publication for further details of the sediment trap program for samples collected at 50 and 600 mab [Smith et al., 1994]. Sinking POC was concentrated by gentle vacuum filtration of approximately 0.7 L trap liquid onto precombusted, quartz fiber filters (45 mm diameter, 0.8 μ m pore diameter).

The filters containing the suspended POC were acidified to pH < 2 with 1% H_3PO_4 for 24 hours to remove the carbonates, dried under vacuum, and combusted at 850°C for 1 hour in double quartz tubes with CuO and silver according to standard techniques [*Druffel et al.*, 1992]. Aliquots of the sinking POC samples were acidified with 1% H_3PO_4 and dried at 50°C before combustion as above.

Seawater DIC samples were filtered through a precombusted (550°C), 147-mm-diameter, glass fiber filter (Gelman type A/E glass) from 12-L or 30-L Go-Flo sampling bottles. The sample (0.5 L) was poisoned with 100 μ L of saturated HgCl₂ solution, sealed, and stored at room temperature. DIC was extracted from 0.25-L subsamples after acidification with concentrated H₃PO₄ according to standard techniques [*McNichol et al.*, 1994].

The CO₂ from POC and DIC was converted to graphite targets [*Vogel et al.*, 1987] either at Lawrence Livermore National Laboratory (LLNL) or at the University of California, Irvine (UCI), and ¹⁴C was measured using accelerator mass spectrometry (AMS) at the Center for AMS Research at LLNL. A few of the samples were converted to graphite and analyzed for ¹⁴C at the National Ocean Sciences AMS Facility at the Woods Hole Oceanographic Institution (WHOI). Radiocarbon measurements are reported as Δ^{14} C (per mil) [*Stuiver and Polach*, 1977]. Total errors (laboratory plus statistical) for the individual AMS Δ^{14} C measurements range in general from ±5 to ±9‰. Δ^{14} C values are corrected for blank

20,545

 CO_2 added during combustion (POC) and acidification (DIC) as well as that added during the production of graphite. Combustion blanks were larger and comprised 0.2% to 8.0% of the sample CO_2 volumes; they had an average $\Delta^{14}C$ value of $-800 \pm 50\%$ for double-tube combustions. Stable carbon isotope results ($\delta^{13}C$) for samples in this study were performed on splits of CO_2 from the double-tube combustion step (POC) or the acidification step (DIC). The $\delta^{13}C$ measurements were made on the VG Micromass 602E isotope ratio mass spectrometer and had an overall error of $\pm 0.10\%$.

Results

DIC

Knowledge of the Δ^{14} C signature of DIC in surface seawater is important for interpreting the Δ^{14} C of POC, because during photosynthesis the phytoplankton draw from the DIC pool to produce organic matter. Theoretically, the Δ^{14} C of organic matter produced during photosynthesis should equal that in the DIC of the surrounding surface seawater [*Williams and Linick*, 1975]. Results of Δ^{14} C of DIC measurements made in samples from four cruises are shown in Figures 2a and 2b. These data and that from several other cruises to station M are described fully in a separate publication (E. R. M. Druffel and C. Masiello, manuscript in preparation, 1996).

The Δ^{14} C results were highest in surface waters, and ranged from 72‰ (June 1992) to 58‰ (July 1993) at 25 m depth. The lowest Δ^{14} C values were found between 1600 m and 3500 m and ranged from -233‰ to -247‰. Intercruise comparisons of Δ^{14} C values measured at a given depth showed the most variability above 800 m (54‰ range observed at 450 m, N =



Figure 2. Δ^{14} C of DIC samples collected using Go-Flo bottles at depths of (a) 0-5000 m and (b) 0-1000 m during four cruises from February 1992 to June 1993. Only three analyses are available from Pulse 11 (February 1992), since most of the samples were lost during processing.



Figure 3. Comparison of the Δ^{14} C measurements for POC_{susp} at station M during four time periods in 1992 and 1993 at depths of (a) 0-4050 m and (b) 0-1000 m. Points are February 1992 (open squares), June 1992 (open triangles), October 1992 (solid circles), and July 1993 (solid triangles). Averages of duplicate Δ^{14} C values are plotted.

3); at 4060 m depth, the range (21% range, N = 4) was less than half that at 450 m. Δ^{14} C measurements for samples from depths between 800 and 3500 m varied by no more than the 2σ error (~14%). It is interesting to note that the two lowest DIC Δ^{14} C results at 50 mab (4060 m depth) were from late spring to early summer (June 1992 and July 1993).

In surface waters (25–85 m), Δ^{14} C values for DIC were available from three time periods, June and October 1992 and July 1993 (Figure 2b). Values were high during October 1992 at both 25 m (68‰) and 85 m (76‰) and somewhat lower at the three shallowest surface depths during July 1993 (64‰ at 7 m, 58‰ at 25 m, and 55‰ at 85 m). There was a gradient of 30‰ between 25 and 85 m in the June 1992 data ($\Delta^{14}C_{25m}$ minus $\Delta^{14}C_{85m} = 72\% - 42\%$). Upwelling normally occurs at this site during the summer, causing ¹⁴C-depleted subsurface waters to invade the surface water, accounting for the low values during June 1993. However, the ENSO conditions during 1992 inhibited upwelling during this time, resulting in a stratified water column with a high DIC Δ^{14} C value in the warm near-surface waters. From these limited data the seasonal variability of the surface (≤ 25 m) DIC Δ^{14} C signature appeared to have been at least 14‰ (E. R. M. Druffel and C. Masiello, manuscript in preparation, 1996).

Suspended POC

The suspended POC (POC_{susp}) Δ^{14} C profiles for the four sampling periods (Figure 3 and Table 1) decreased markedly

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1200 449 N6472 33 ± 7 -21.05 1600 419 N6073 -14 ± 6 -20.53 2500 336 4901 -10 ± 6 -21.46 3500 338 5606 -40 ± 7 -21.20 4060 418 N6071 -97 ± 6 -20.46	2.99
1600419N6073 -14 ± 6 -20.53 25003364901 -10 ± 6 -21.46 35003385606 -40 ± 7 -21.20 4060418N6071 -97 ± 6 -20.46	2.38
25003364901 -10 ± 6 -21.46 35003385606 -40 ± 7 -21.20 4060418N6071 -97 ± 6 -20.46	3.19
3500 338 5606 -40 ± 7 -21.20 4060 418 $N6071$ -97 ± 6 -20.46	1.81
4060 418 $N6071$ $-97 + 6$ -20.46	1.63
	5.63
Pulse 15 (October 1992)	
25 427 N6078 59 ± 7 -21.89	78.40
85 421 N6453 40 ± 7 -22.77	26.20
450 420 N6074 $36 \pm 7 - 20.22$	7.24
700 423 N6076 35 ± 10	5.40
900 428 N6077 41 \pm 7 -20.59	5.48
1200 429 N6066 12 ± 7	5.07
1600 426 N6075 8 ± 7 -20.60	4.40
2500 424 N6069 8 ± 6 -20.97	4.55
3500 425 N6068 2 ± 7 -20.67	2.50
4060 422 $N6072$ -65 ± 7 -21.46	4.00
Pulse 17 (July 1003)	
25 540	38.33
$85 510 17432 68 \pm 5 -20.02$	24.02
450 539 $59 + 6$ -21.36	4.45
700 452 N6475 19 + 7 -20 39	4.08
1600 451 $N6474$ $13 + 8 - 20.23$	3.04
2500 481 15739 $-22 + 7$ -2130	1 86
3510 444 N6467 $-17 + 6$ -20.84	1 24
4060 482 15242 -95 ± 7 -21.10	2.48

Table 1. Measurements of Δ^{14} C and δ^{13} C for Suspended Particulate Organic Carbon During Four Cruises to Station M in the Northeast Pacific

 Δ^{14} C is reported as per mil according to convention [*Stuiver and Polach*, 1977], and δ^{13} C are the per mil deviation from PDB 1 standard. Also listed are the AMS target numbers (CAMS for LLNL and OSG for WHOI NOSAMS samples), and UCID CO₂ gas numbers associated with each POC_{susp} sample. The reported concentrations of POC_{susp} are calculated using the manometric measure of CO₂ obtained from the double-tube combustion of a single quartz filter (see text) and the measured volume of seawater filtered through each quartz filter. Two filters were run for Pulse 11 2500 m (UCID 286, 287), and the two Δ^{14} C values (7 ± 9, -4 ± 6‰) were within 2 σ error. Splits of the CO₂ run for Pulse 11 25 m and 85 m (UCID 280 and 281) were analyzed at WHOI (OSG) and LLNL (CAMS) and the Δ^{14} C values were within 2.5 σ error.

with depth. We found no relationship between the volume of seawater filtered and the Δ^{14} C of the POC_{susp}, eliminating the possibility that DOC was being adsorbed onto filters in a cumulative fashion. Values ranged from +58 to 82% at 25 m depth, and -64 to -97% at 50 mab (~4060 m depth). This reflected depth gradients ($\Delta^{14}C_{25m}$ minus $\Delta^{14}C_{50mab}$) in the water column during February, June and October 1992 and July 1993 of 130%, 155%, 124% and ~177%, respectively. The depth gradients were significantly larger (by 25–53%) for June 1992 and July 1993 than for the other two sampling periods. Below 1600 m depth, the $\Delta^{14}C$ values for POC_{susp} from the June 1992 and July 1993 profiles were consistently lower (20–30%) than those for February or October 1992.

Also, Δ^{14} C values from 85 m samples were 20–30‰ higher for the June 1992 and July 1993 than for February and October 1992 (Figure 3b). This was in contrast to the DIC Δ^{14} C data, where June 1992 and July 1993 values at 85 m were lower (by 25–35‰) than that from October 1992.

All of the Δ^{14} C POC_{susp} profiles exhibited lower values at 50 mab than the trends higher in the water column would have predicted. These lower values indicated that old POC from bottom sediments had been resuspended into the water column.

The subsurface values of POC_{susp} concentrations from the four cruises varied by a factor of 3 in the water column on a temporal basis (Figure 4, plotted on a log scale, and Table 1).



Figure 4. Comparison of POC_{susp} concentrations (in micrograms per liter) at station M during four time periods in 1992 and 1993. Note the log scale used for the x axis. POC_{susp} concentration values have an error of approximately $\pm 10\%$. Points are the same as for Figure 3.

Concentrations of POC_{susp} were lowest throughout the water column (at all but 25 m depth) during the month of February 1992 and were highest during October 1992. At the surface (25 m), POC_{susp} concentrations were lower during June 1992 and July 1993 (38.7 and 33.3 μ g C L⁻¹) than either February or October 1992 (74.5 and 78.4 μ g C L⁻¹). All profiles showed an increase at the depth nearest the seafloor (50 mab or ~4050 m depth) and indicated, along with low Δ^{14} C values, resuspension of POC from bottom sediments. This agreed with transmissometer data that showed a significant decrease in light transmission below 200 mab at this site [*Smith et al.*, 1994]. It also agreed with higher suspended mass values at 50 and 100 mab during the June 1992 and November 1993 cruises to station M [*Sherrell*, 1994; also R. Sherrell, manuscript in preparation, 1996].

Whereas the June 1992 and July 1993 profiles below 1600 m depth displayed the lowest Δ^{14} C values, the corresponding POC_{susp} concentrations were intermediate between those in February and October 1992. Nonetheless, the POC_{susp} concentrations increased during 1992, from the lowest values in February to the highest values in October. Despite the fact that February and October 1992 displayed extremes in POC_{susp} concentrations, their Δ^{14} C profiles were virtually identical. There was also no direct correlation between the POC concentration profiles and the DOC concentration profiles obtained during these cruises at station M (BDWWG).

The δ^{13} C values for POC_{susp} ranged from a low of -23.8%in the chlorophyll maximum (85 m) during June 1992 to a high



Figure 5. Comparison of the δ^{13} C measurements for POC_{susp} at station M during four time periods in 1992 and 1993. Points are the same as for Figure 3.



Figure 6. (a) Δ^{14} C of POC_{smk} collected in sediment traps deployed at station M at four depths (650, 600, 100, and 50 mab; see legend). All samples were collected over a 30-day period, with the exception of the 50-mab samples (10-day period). For comparison, Δ^{14} C of POC_{susp} samples collected during three time periods at 50 and 650 mab are plotted as pluses. (b) Flux rate (milligrams per square meter per day) versus Δ^{14} C of POC_{sink} for samples collected in sediment traps from four depths in the deep sea (650, 600, 100, and 50 mab; see legend). The least squares fit of the values from the 650and 600-mab traps is indicated by a solid line (r = 0.59, N =11, correlation significant to the 90% level), and that from the 100- and 50-mab traps is indicated by a dashed line (r =0.538, N = 15, correlation significant to the 95% level).

of -20.0% at the same depth in July 1993 (Figure 5). General trends were similar in the four δ^{13} C profiles: (1) low values in surface samples (25–85 m, except 85 m in July 1993), and (2) values in the middepth region had a larger range (~1.4‰) than those deeper in the water column. There was also a progression toward higher values with time from February 1992 to July 1993 between the depths of 700 and 1600 m. The highest δ^{13} C values were observed in October 1992 and July 1993, when higher flux rates of POC_{sink} to the deep sea were observed (K. L. Smith, personal communication, 1995). In contrast, the lowest δ^{13} C values and the smallest amount of variability of δ^{13} C with depth were observed in the profile for February 1992, the period of lowest flux.

Sinking POC

The Δ^{14} C measurements of sinking POC (POC_{sink}) for the 1.5-year time period between February 1991 and June 1992 are shown in Figure 6a. Results are presented for samples that were available from four sampling heights above the seafloor: 650, 600, 100, and 50 mab. Also shown in Figure 6a for comparison are the Δ^{14} C values obtained for POC_{susp} from 650 and 50 mab during three sampling times in 1992. The sample from 650 mab in April 1992 had been contaminated with tracer

Table 2. Measurements of Δ^{14} C and δ^{13} C and Associated Errors for Sinking Particulate Organic Carbon Collected From March 1991 to June 1992 at Station M in the Northeast Pacific

Number			Dette	T		0	\$130
UCID	CAMS	days	(Midpoint)	Cup Number	$M_{\text{sink}} \Delta^{\text{suc}}$	Δ^{14} C, ‰	8≃C, %0
			65	50 mab			
400	8457	30	Nov. 12, 1991	1020, A	22 ± 7		-21.73
405	8480	30	Dec. 12, 1991	1020, B	20 ± 7		-21.87
408	8482	30	March 11, 1992	1118, 1A	89 ± 9		-22.07
412	8506	30	March 11, 1992	1118, 1		60 ± 10	-21.05
411	8507	30	April 10, 1992	1118, 2B	*		-22.68
413	8466	30	April 10, 1992	1118, 2		27 ± 8	-20.63
409	8483	30	May 10, 1992	1118, 3C	63 ± 9		-21.94
414	8508	30	May 10, 1992	1118, 3		76 ± 7	-19.10
410	8505	30	June 9, 1992	1118, 4D	22 ± 7		-22.00
415	8525	30	June 9, 1992	1118, 4		71 ± 8	-19.96
			60	00 mab			
377	8412	10	June 20, 1991	621, #12	38 ± 6		-21.05
383	8418	30	July 10, 1991	728, 1A#1	57 ± 10		-21.72
384	8419	30	July 10, 1991	728, 1A#2	39 ± 7		-21.95
385	8422	30	July 10, 1991	728, 1A#3	40 ± 7		-21.93
403	8524	30	Nov. 12, 1991	1020, A	22 ± 7		-21.68
396	8523	30	Dec. 12, 1991	1020, B	45 ± 8		-21.39
397	8429	30	Jan. 11, 1992	1020, C	76 ± 7		
398	8455	30	Feb. 10, 1992	1020, D	99 ± 8		-21.94
			10	00 mab			
381	8416	30	March 12, 1991	621, 1	34 ± 8		-21.83
382	8417	30	April 11, 1991	621, 2	99 ± 7		-21.60
380	8415	30	June 10, 1991	621, 4	50 ± 7		-20.70
389	8424	30	July 10, 1991	725, 1A	34 ± 6		-21.31
388	8421	30	Aug. 9, 1991	725, 2B	121 ± 12		-21.75
386	8420	30	Sept. 8, 1991	725, 3C	110 ± 8		
387	8423	30	Oct. 8, 1991	725, 4D	154 ± 7		-22.94
395	8428	30	Nov. 12, 1991	1014, 1A	5 ± 7		-21.80
406	8481	30	Dec. 12, 1991	1014, B	-21 ± 8		-21.73
399	8456	30	Jan. 11, 1992	1014, C	41 ± 9		-21.78
401	8479	30	Feb. 10, 1992	1014, 4D	98 ± 9		-21.69
			5	0 mab			
379	8414	10	June 10, 1991	621, #11	50 ± 9		-20.90
378	8413	10	June 20, 1991	621, #12	38 ± 7		-20.81
390	8426	10	June 30, 1991	725, #1	54 ± 7		-21.34
391	8425	10	July 10, 1991	725, #2	87 ± 7		-21.87

CAMS and UCID numbers are as described in Table 1 caption. Also listed are the trap collection duration, midpoint date for each collection, and cruise event and cup number. Three filter pads from a single cup deployment (600 mab, event 728, 1A) were run for Δ^{14} C, and the three values were within 2σ error. The Δ^{14} C and δ^{13} C measurements of organisms (swimmers) picked out of the four trap cups recovered from 650 mab during the Pulse 12 cruise (June 1992) are also listed; dates of these collections are February 25 to March 26, March 26 to April 25, April 25 to May 25, and May 25 to June 24, 1992. The last cup (1118, 4) did not sequence shut before being retrieved through the water column during recovery; thus some POC and organisms could have been from depths shallower than 650 mab.

*A sample from the 650-mab trap whose Δ^{14} C value was 360‰, which indicated contamination with tracer levels of ¹⁴C.

levels of ¹⁴C, and the Δ^{14} C value was not included in Figure 6a or Table 2. Because of numerous breaks in the isotope records from each depth, it is difficult to make unequivocal statements regarding trends in these data. However, several observations are noteworthy.

First, the Δ^{14} C of POC_{sink} varied from a high value of 154‰ in October 1991 to a low value of -21‰ in December 1991; both of these extreme values were from samples in the 100mab trap. The POC_{sink} Δ^{14} C values from trap material collected in June 1991 from 600 mab (38 ± 6‰) and 100 mab (50 ± 7‰) were within 2σ error of the DIC Δ^{14} C value available for 25 m depth in June 1991, 49 ± 10‰ (P. M. Williams, unpublished data, 1991). The Δ^{14} C value of POC_{sink} from 100 mab in February 1992 (98 \pm 9‰) was within 2 σ of one of the surface (25 m) POC_{susp} Δ^{14} C values found during February 1992 (81 \pm 12‰). There were no other surface Δ^{14} C values of DIC or POC taken from February 91 to June 1992 for comparison with the POC_{sink} values. The three Δ^{14} C values from the 100-mab trap from August, September, and October 1991 (110–154‰) seemed high in comparison with the highest DIC Δ^{14} C value obtained for surface waters at station M taken over a 4-year period. Though we do not think that these three POC_{sink} Δ^{14} C analyses were contaminated with tracer ¹⁴C, this possibility could not be ruled out.

Second, there appeared to be two minima in $POC_{sink} \Delta^{14}C$ in 1991 and one in the middle of 1992. These periods coincided

with maxima in deep sinking POC flux rates of greater than 5 mg C m⁻² d⁻¹ as measured at this site during May to June 1991 (30-day average flux rates at 50 mab of 9.6-17.2 mg C m⁻² d⁻¹), October to mid-January 1992 (30-day average flux rates of $13.9-6.4 \text{ mg C m}^{-2} \text{ d}^{-1}$), and May to June 1992 [Smith et al., 1994; K. L. Smith, personal communication, 1995]. When the flux of organic carbon in these deep traps was plotted versus the Δ^{14} C values of the POC_{sunk} (Figure 6b) there was an apparent inverse correlation. The data representing the 650and 600-mab traps were less scattered and had lower average Δ^{14} C values than those from the deeper traps. This apparent correlation between high flux and low Δ^{14} C was initially counterintuitive. We would have expected a higher Δ^{14} C signature associated with the periods of high POC flux, indicative of a greater portion of surface-derived material arriving in the deep sea. Instead, we saw the opposite trend. This relationship between low Δ^{14} C of POC_{sink} and high POC_{sink} flux rates are likely the result of increased communication between the sinking and suspended forms of POC (see discussion).

Third, the Δ^{14} C values of the four POC_{sink} samples from 10-day deployments of the 50-mab trap during mid-1991 were not significantly different from those of the two 30-day samples collected at the same time in the 100-mab trap. This indicated that the relative amounts of surface-derived organic carbon (high Δ^{14} C) and resuspended organic carbon (low Δ^{14} C) present at the two near-bottom depths were similar during this time.

Fourth, POC_{sink} Δ^{14} C values from samples collected from 650 mab in March and June 1992 were 85‰ and 62‰ greater than the POC_{susp} Δ^{14} C values collected from 600 mab during February and June 1992 (Figure 6a). A similar observation was also reported from the north central Pacific (NCP) site (31°N, 159°W) in 1987 [*Druffel et al.*, 1992], where POC_{sink} Δ^{14} C values were 86‰ and 81‰ higher than POC_{susp} Δ^{14} C from 600 and 1600 mab, respectively. This trend seemed logical, as POC_{sink} fell at a much faster rate than POC_{susp} and contained a greater proportion of labile organic compounds [*Lee and Wakeham*, 1988]. Presumably, these labile compounds reflected mostly a surface-derived source of carbon, high in ¹⁴C.

The Δ^{14} C measurements of groups of small organisms (swimmers) picked from the 650-mab trap material were available for the four time periods March, April, May and June 1992 (Table 2). The organisms in all four traps were a mixture of two or three pteropods (*Clio scheelei* predominantly, 2-4



Figure 7. The δ^{13} C of POC collected in sediment traps deployed at station M at four depths: 650, 600, 100, and 50 mab. All samples were collected over a 30-day period, with the exception of the 50-mab samples, which were collected over 10-day periods. For comparison, δ^{13} C of POC_{susp} samples collected during three time periods at 50 and 650 mab are plotted as pluses.



Figure 8. A comparison of the Δ^{14} C measurements for POC_{susp} at station M (this work) and the north central Pacific (NCP) [*Druffel et al.*, 1992] during 1992 to 1993 and 1987, respectively.

mm in length) and amphipods, and one copepod each in the March and June traps. Three of the four Δ^{14} C values were as high as surface DIC Δ^{14} C values (72‰ at 25 m, 42‰ at 85 m) and POC_{susp} Δ^{14} C values (58‰ at 25 m, 73‰ at 85 m) measured in samples from this site in June 1992. This agreement indicated that the carbon source to these organisms was mostly surface-derived POC. The April trap contained an amphipod that had about 100 small juveniles in its pouch. The reason for the low Δ^{14} C value (27‰) of this sample may be the result of a relatively large amount of POC_{susp} assimilated from depth (with low Δ^{14} C values) during the amphipod's gestation of its young.

The δ^{13} C signatures of the POC_{sink} are shown in Figure 7. All but five values fall within the range -21.0 to -22.1%. The three high outliers occur in the 100-mab and 50-mab traps during May–June 1991, a period of very high flux. The lowest value (100 mab, October 1991) is -22.9%; the accompanying Δ^{14} C value for this sample is the highest value obtained for any POC_{sink} sample. There is no simple correlation between the δ^{13} C and Δ^{14} C values for the POC_{sink} samples. Overall, POC_{sink} δ^{13} C values are lower by 0.4-0.7% than the two POC_{susp} δ^{13} C values available for samples collected from 600 mab at the same time (Pulse 11 and 12, see Table 1 and Figure 7).

Discussion

$POC_{susp} \Delta^{14}C$ Gradient With Depth: Comparison With North Central Pacific Data

We observed a large gradient of $POC_{susp} \Delta^{14}C$ values (80-160‰) between surface and deep ocean (3500 m) from our four cruises. A similar gradient (100-130%) was observed in NCP samples collected during a single cruise in June-July 1987 (see Figure 8), where values were +150% in the surface and 20-50% in the deep ocean [Druffel and Williams, 1990]. Higher surface values were obtained in the NCP because the samples were collected 5 years earlier when the bomb ¹⁴C signal was higher overall in the temperate surface ocean [Druffel, 1987]. In addition, unlike the NCP, station M is located in the California Current, where upwelling brings low- Δ^{14} C waters from below the mixed layer up to the surface. Aside from the consistent offset of 80% between the two sites (excluding the 50-mab samples at station M), the NCP and station M POC_{susp} Δ^{14} C records are similar in shape (Figure 8).

The DOC Δ^{14} C data published separately from the NCP [Druffel and Williams, 1990] and station M (BDWWG) reveal a similar pattern. There is a consistent 40% offset between the DOC Δ^{14} C profiles from the NCP site and the average station M values, with the NCP profile having higher values. The offset toward lower values for both the POC_{susp} and DOC Δ^{14} C at station M is likely due to the lowering of bomb Δ^{14} C in the surface since the late 1970s [Druffel and Williams, 1991] and the upwelling of low Δ^{14} C carbon to the surface. The smaller offset observed between the DOC Δ^{14} C profiles (40%) at NCP and station M than between the POC Δ^{14} C profiles (80%) is, in part, a function of the different turnover times for POC_{susp} and DOC in the water column. POC_{susp} is recycled on a much faster timescale with the labile organic matter remineralized relatively quickly as compared with the refractory nature of most of the DOC.

POC-DOC Association

The real mystery of these isotope data lies in the very existence of the POC_{susp} (and to a lesser extent the POC_{sink}) Δ^{14} C gradient with depth. As was discussed in the introduction, a gradient should not be present if (1) the carbon source for deep POC_{susp} is strictly from the surface waters and (2) POCsusp transits the water column on relatively short timescales (weeks to 10 years).

Indeed, the $\Delta^{14}C$ measurement of POC_{susp} reported here do not support these assumptions but instead suggest another possibility. Could the Δ^{14} C gradient with depth reflect a general aging of POC_{susp} with depth in the oceans? In order to obtain an average deep $POC_{susp} \Delta^{14}C$ value of 8‰ (average of 1600 and 2500 m values in February and October 92), we calculate that 36% of this deep carbon pool still has its prebomb Δ^{14} C value of -70% [Berger et al., 1966] and 64% has been replaced with postbomb POC_{susp} from the surface ocean (52‰, average of 25 and 85 m Δ^{14} C POC_{susp} measurements, February and October 92). This result would suggest that the turnover time of POC_{susp} in the deep ocean is several decades, instead of the value of 5-10 years obtained from Th isotope studies [Bacon and Anderson, 1982]. What does not fit this analysis is the seasonal change in the concentration of POC_{susp} at middepth, which shows that 70% of the POC_{susp} is removed in less than half a year (from October 1992 to February 93) (Figure 4 and E. R. M. Druffel, unpublished data from Pulse 16, February 1993). This agrees with Sherrell [1994; also manuscript in preparation, 1996], who finds that suspended mass concentration from 400 to 3600 m decreased by approximately a factor of 2 between June 1991 and February 1992 at station M. It is not known where this POC_{susp} goes each year, though it may be stripped out of the water column by midwater grazers who produce marine snow and fecal pellets (POC_{sunk}) that fall to the deep ocean. This POC_{sink}/POC_{susp} association mechanism may cause the POC_{sink} to have low $\Delta^{14}C$ signature during high flux periods. We cannot address the mechanism of this change in isotopic signature, but we can speak to the source of the low- Δ^{14} C carbon.

Another scenario deals with the fact that organic particles (POC) are suspended in a soup of relatively concentrated dissolved organic matter (DOC), and sorption of DOC by POC_{susp} or any particle is likely. Studies of the characteristic surface charge exhibited by solids in seawater have shown that dissolved organic matter quickly and irreversibly sorbs to particles [*Hunter and Liss*, 1982; *Neihof and Loeb*, 1973]. In the upper 25 m at station M, DOC concentrations ranged from 63

to 74 μ M (BDWWG), a factor of 10–25 times higher than our POC_{susp} concentrations (3–6 μ M). In the deep water column at station M, DOC (37–41 μ M) is a factor of 90–400 times higher than POC_{susp} (0.1–0.4 μ M). Mechanisms for the incorporation of DOC into the POC pool may include (1) abiotic incorporation by physical sorption of DOC on/into the particle, (2) biotic incorporation of DOC by heterotrophic bacteria associated with the particles, and (3) anapleurotic reactions in the deep ocean that incorporate old, deep DIC into the POC pool [*Rau et al.*, 1986].

Estimates can be made of the amount of "old," sorbed DOC needed to decrease the Δ^{14} C of the "modern" POC_{susp} to the observed average deepwater values for the four profiles. Assuming that DOC Δ^{14} C is $-450\%_{o}$ at 450 m and $-550\%_{o}$ below 700 m (BDWWG) we calculate that 7% of the POC_{susp} at 450 m and 12% of the POC_{susp} at 3500 m would need to consist of DOC to obtain the observed average POC_{susp} Δ^{14} C values. This constitutes about 1% or less of the water column DOC inventory; hence, it would not be associated with a detectable seasonal depletion in the concentration of DOC due to the proposed "stripping out" of DOC and subsequent incorporation with POC_{susp}. At the same time, some POC is likely converted to DOC via dissolution or degradation (BDWWG) and contributes to the labile fraction of DOC in the water column.

The similarity of the Δ^{14} C POC_{susp} profiles for February and October 1992 (Figure 3a), despite the factor-of-3 difference in POC_{susp} concentration between these two time periods (Figure 4), points to similar relative amounts of old DOC sorbed to young POC during both seasons. The incorporation of DOC onto suspended particulate matter is a plausible mechanism to explain the gradient of Δ^{14} C in POC_{susp} observed during the seasons that were studied at our northeastern Pacific site.

Changes in DOC concentrations were observed at station M by BDWWG. They observed that at all subsurface depths (except the oxygen minimum at 700 m), DOC concentrations were lowest (by 5–7 μM) during periods of highest flux (>10 mg C $m^{-2} d^{-1}$, June 1991 and July 1993). Consequently, DOC concentrations were highest during the extended low-flux ENSO period of 1992. Low POC_{sink} Δ^{14} C values found during periods of high flux (Figures 6a and 6b) appear to occur concomitantly with low DOC concentrations in the deep sea. These data indicate that DOC may be stripped out of the water column during periods of high POC flux, and sorbed onto particles. The δ^{13} C values of POC_{sink} support this hypothesis, as the δ^{13} C is highest (and closer to DOC δ^{13} C values) during the high-flux period of June 1991. However, sorption of DOC onto particles could not account for the seasonal changes observed in DOC concentrations. If we assumed that a flux rate of 20 mg C m⁻² d^{-1} in the deep sea (1000-4000 m) was the only loss of DOC, it would take 25 years to reduce the DOC concentration from 43 to 38 μM . Obviously, the POC_{sink} flux rate is too slow to account for the observed seasonal change in DOC concentration, just as the sorption of DOC onto POC_{susp} accounts for less than 1% of the available DOC. Instead, heterotrophic utilization of labile DOC that arrives seasonally to the deep sea is the likely cause of the observed seasonal DOC concentration changes.

The POC_{susp} Δ^{14} C data shows a small seasonal change of Δ^{14} C (20–30‰ in June 1992 and July 1993) superimposed on a large depth gradient. POC_{susp} appears to be influenced less by changes in flux rates than the quickly falling, and much larger-sized POC_{sink} particles. Surprisingly, the concentration

of POC_{susp} below 700 m varies by a factor of 3 from February to October 1992 (Figure 4). Given the relatively small seasonal variability of POC_{susp} Δ^{14} C values compared with the large depth gradient, the amount of DOC associated with POC_{susp} (and particulate matter in general) appears to vary directly with the POC_{susp} concentration. That is, the amount of DOC sorbed to POC_{susp} during October 1992 would have to be approximately 3 times greater than that sorbed during February 1992. This suggests a physicochemical control of the association between the DOC and POC_{susp} (or particulate matter), a process that would depend on the surface area that is available for sorption. The overall higher δ^{13} C values observed for POC_{susp} than for POC_{susp} pool, which agrees with the lower Δ^{14} C

Lateral Transport of POC Locally or From the Continental Slope to Station M

values observed in POC_{susp}.

Smith et al. [1994] observed an increase in particle fluxes at 50 mab over those at 600 mab during the summers of 1990 and 1991 at station M. They assert that lateral advection of particulate material is likely at this site during summer because of its proximity to the continental shelf and slope and the Monterey deep-sea fan. The $\Delta^{14}C$ data display seasonal changes in two ways: (1) the seasonal variability of $POC_{sink} \Delta^{14}C$ is higher in the deeper (100 mab) trap material (Figures 6a and 6b), and (2) the overall Δ^{14} C values of POC_{susp} in the 50-mab samples are lower for all of the profiles (Figure 3a). We estimate the Δ^{14} C signature of the organic carbon transported from the surface sediments to 50 mab for each POC_{susp} profile, assuming that the baseline concentration of POC_{susp} is equal to that at 600 mab. For example, during February 1992, if 68% (1.42 $\mu g \ L^{-1}/2.08 \ \mu g \ L^{-1})$ of the POC $_{susp}$ at 50 mab had a $\Delta^{14}C$ value of 4‰ (the average value at 650 mab), then the remainder of POC_{susp} (32%) at 50 mab would have had a Δ^{14} C of -208% in order to balance the observed POC_{susp} Δ^{14} C of -64% at 50 mab (see Table 1). In this way, the Δ^{14} C of the organic carbon resuspended from bottom sediments to 50 mab during June 1992, October 1992, and June 1993 would have been -120%, -177%, and -173%, respectively. These values are similar to that $(-232 \pm 20\%)$ measured for surface sedimentary organic carbon at station M [Bauer et al., 1995; BDWWG] and supports our hypothesis that most of the extra POC_{susp} found at 50 mab is resuspended sediment.

We observed 20% lower Δ^{14} C values for most deep POC_{susp} samples during June 1992 and July 1993 than for other months of the year (February and October 1992), despite similar or lower values in the surface waters (Figure 3b). The lower $POC_{susp} \Delta^{14}C$ values may be due to lateral advection of low Δ^{14} C sedimentary organic carbon that had been resuspended locally or resuspended and transported from the continental slope to the abyssal plain via eddies. The presence of an anticyclonic eddy was reported off the coast of northern California during June-July 1988 by Washburn et al. [1993]. They observed a turbidity layer between 200 and 260 m depth and concluded that it was the result of advection of resuspended sediments from the continental shelf into the deep ocean. They estimated the cross-shelf sediment mass flux is of the order of 10^{6} kg sediment/d⁻¹ and is a dominant feature during summer, when other transport processes are weak.

For comparison, we estimate the amount of advected carbon that would have had to be added to the POC_{susp} pool at station M during June 1992 and July 1993 to lower the $\Delta^{14}C$ profiles.

The average offset below 700 m of POC_{susp} Δ^{14} C during the two early summer periods from that of February and October 1992 is 20 \pm 5‰. If we assume that the Δ^{14} C of the advected POC from the shelf is equal to the surface SOC at station M (-232‰) [Bauer et al., 1995], then about 10% of the POC_{susp} in early summer would need to have been derived from resuspended SOC to account for the 20% lowering of Δ^{14} C. This contribution of 10% to deep POC_{susp} concentration during early summer (10% = 0.2-0.4 μ g L⁻¹; see Figure 4) is small compared with the seasonal range of POC_{susp} concentration and would not necessarily have been detected in the concentration data (Figure 4). However, our data do not allow us to distinguish between local resuspension and lateral transport of resuspended sediment from the continental shelf and slope. In any case, it seems unlikely that resuspended sediment from any location could be the cause of a Δ^{14} C decrease for so large a portion of the water column. It is more likely that increased sorption of DOC is responsible for the 20% lowering of POC_{susp} Δ^{14} C in the middepth and deep water pools in early summer.

ENSO Effect on POC Δ^{14} C

April through August 1992 was a period of lower than normal flux to the deep sea at station M [*Smith et al.*, 1994]. This period coincided with the ENSO event that was observed worldwide from 1991 to 1993. This site experienced unseasonably warm sea surface temperatures and unusually low flux during 1992 (K. L. Smith, personal communication, 1995). Despite the presence of ENSO during 1992 at this site, the Δ^{14} C of POC_{susp} was similar for the two profiles during June 1992 and July 1993. This points to factors other than ENSO as the cause for low POC_{susp} Δ^{14} C during early summer, the most likely factor being additional sorption (via stripping out of the water column) of DOC by POC during June–July.

Future Studies

The time series of carbon isotope results presented here in deep sinking POC and suspended POC, as well as DOC and DIC, are continuing at station M. We are also pursuing isotope studies of detrital aggregates that have been observed on the seafloor at this site during and subsequent to periods of high flux [*Smith et al.*, 1994]. If the seawater-sediment boundary is the likely remineralization site for most of the POC falling to the deep sea, then isotope studies of the detrital aggregates and sediment slurry will help reveal the turnover time of this fraction of the actively cycling carbon pool.

Conclusions

The large gradient of POC_{susp} Δ^{14} C observed with depth can be explained by the incorporation of "old" DOC, in an amount equal to 7–12% of the standing stock of POC_{susp}. The lowest POC_{susp} Δ^{14} C values were observed in the water column during June 1992 and July 1993, and are likely the result of additional sorption (via "stripping out" of the water column) of DOC by POC_{susp} and particulate matter in general during high-flux periods. Laterally derived POC resuspended from the continental slope and shelf sediment with subsequent transport to the deep ocean site could also contribute to these lower Δ^{14} C values, though it seems an unlikely mechanism for causing a consistent lowering of Δ^{14} C in POC_{susp} over such a large depth range of the water column. Sinking POC has higher average Δ^{14} C values than POC_{susp}, indicating the faster transit time of this fraction of POC from the surface to the deep sea. POC_{sink} has low Δ^{14} C values during periods of high flux, indicating that old DOC may be stripped out of the water column, directly or indirectly (by exchange between POC_{sink} and older POC_{susp}). The seasonal variability of DIC Δ^{14} C is too small to account for the observed temporal changes in deep POC_{susp} or POC_{sink} Δ^{14} C. Instead, sorption of DOC by POC, and particulate matter in general, during periods of high flux appears to dominate the POC Δ^{14} C signal at this site.

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