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Temporal variability in dissolved organic carbon and radiocarbon in the eastern North Pacific Ocean

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Abstract. The factors regulating the steady state inventories and residence times of dissolved organic carbon (DOC) in the deep ocean are not well established. Previous studies of DOC have been limited to single time-point profiles that provide general information on the potential role of vertical advective-diffusive processes in controlling DOC distributions and mean apparent ages. We present results from a 2-year time series station in the eastern North Pacific (station M) where short-term (months) changes in inventories and $\Delta^{14}C$ signatures of DOC as measured in deep profiles were examined in conjunction with changes in particulate organic carbon (POC) pools. Significant long-term (i.e., months to years) changes in both DOC concentrations and $\Delta^{14}C$ values were observed. These changes were especially evident at mesopelagic ($\sim$450 and 700 m) depths, close to the oxygen minimum. Both within the mixed layer and at mesopelagic depths, positive relationships were found between DOC $\Delta^{14}C$ values and concentrations of station M, primarily reflecting diminishing vertical inputs of "recent" DOC throughout the main thermocline. At abyssal depths ($\geq$1600 m), however, $\Delta^{14}C$ was inversely correlated with DOC concentration. The $\Delta^{14}C$ signature of the less abundant suspended and sinking POC pools has been observed to fluctuate over seasonal timescales at station M, presumably due in part to sorption of DOC to POC [*Druffel et al.*, 1996]. However, the $\Delta^{14}C$ values and concentrations of the correspondingly much larger DOC pool do not appear to be related to seasonal changes in either sinking POC fluxes or suspended POC abundances. Significantly elevated concentrations of DOC were observed at station M when compared with a previously occupied site in the north central Pacific (NCP) in all regions of the water column except mesopelagic depths, where concentrations were lower. The corresponding $\Delta^{14}C$ values of DOC at all depths at station M were lower than in the NCP. We speculate that dissimilarities in the size and $\Delta^{14}C$ signature of the DOC pools at seasonally productive station M and the oligotrophic NCP result from differences in DOC sources and sinks between the two regions, as well as from the magnitude of interaction between DOC and POC at these sites.

1. Introduction

Dissolved organic carbon (DOC) in seawater represents one of the largest pools of exchangeable organic matter at the earth's surface. The total size of the oceanic DOC reservoir has been estimated at 0.6–1.0 $\times$ 10^{18} g C [*Williams and Druffel*, 1987; *Hedges*, 1992] and far exceeds all other forms of marine organic carbon, both living and dead. As a result of its relatively low concentration in seawater ($\sim$40 μM in deep waters and up to $\sim$100 μM in surface waters) and its apparent relationship to the generation of particulate organic matter by primary and secondary production [*Williams and Yentsch*, 1976; *Eppley et al.*, 1981; *Lancelot*, 1983; *Moller-Jensen*, 1983; *Baines and Pace*, 1991], the DOC pool is potentially influenced by both biological and physicochemical processes on a variety of spatial and temporal scales. Furthermore, the relatively narrow range of open ocean DOC concentrations reported indicates that the processes leading to the production and consumption of labile DOC are tightly coupled. In spite of these general relationships, little is known of the specific mechanisms leading to the formation and persistence of the long-lived (^{14}C age of 4000–6000 years [*Williams and Druffel*, 1987; *Bauer et al.*, 1992a; *Druffel et al.*, 1992], apparently refractory marine DOC [*Rakestraw*, 1947; *Barber*, 1968] that dominates the mesopelagic and abyssopelagic reservoirs.

The majority of oceanic DOC is derived presumably from nonliving forms of particulate organic carbon (POC). The diffusion of soluble organic matter from rapidly sinking fecal pellets [*Jumars et al.*, 1989] and other particles has been hypothesized as one mechanism for the release of labile components from nonliving particulate organic matter [*Ittekkot et al.*, 1984]. *Smith et al.* [1992] observed that POC dissolution to DOC was responsible for up to 10–15% of the total organic carbon flux to the deep ($\sim$4100 m) ocean at 50–600 m above the seafloor at station M off the coast of central California. These estimates of DOC flux from POC solubilization are conservative given the likelihood that the POC at such great depths has been extensively solubilized and/or degraded. Other means by which nonliving POC may be converted to soluble

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DOC are through the hydrolytic effects of bacterial exoenzymes on small particulate or colloidal forms of POC [Somville and Billen, 1983; Somville, 1984; Hoppe et al., 1993] and the fragmentation of POC to small particulate or colloidal organic matter (usually included in bulk dissolved organic matter measurements) as a result of shear effects [Honeyman and Santschi, 1989].

The final sinks for old, ^{14}C-depleted DOC in seawater are similarly unresolved. While microheterotrophic utilization of DOC is responsible for the remineralization of specific components of bulk DOC [Azam et al., 1994; Hansell et al., 1995; Rich et al., 1996], the identifiable, presumably labile constituents (e.g., amino acids, carbohydrates, lipids, and nucleic acids) generally constitute a small percentage of the total DOC [Williams and Druffel, 1988; Williams, 1992; Druffel et al., 1992], and their turnover is therefore not representative of the turnover for the bulk pool. In fact, much of the DOC produced in the photic zone appears to become resistant to microbial degradation over relatively short timescales [e.g., Keil and Kirchman, 1994] and may be exported to the deep ocean during seasonal weakening or breakdown of the thermocline [Toggweiler, 1989; Bacastow and Maier-Reimer, 1991; Carlson et al., 1994; Ducklow et al., 1995]. Mechanisms for the formation of refractory DOC include photochemical modification [Keiber et al., 1989; Mopper et al., 1991] and sorption of DOC to either inorganic or organic particles [Keil et al., 1994]. Both hydrophobic and charged (e.g., with carboxylic or phenolic functional groups) components of DOC may be associated with other nonpolar substances already dissolved in seawater or with small particles or colloids [Neihof and Loeb, 1974; Hunter, 1980; Hunter and Liss, 1982]. Previous findings of older-than-expected POC in open ocean profiles [Druffel and Williams, 1990; Druffel et al., 1992] may support the idea that old DOC can be removed from solution through sorption to particles.

The Δ^{14}C values of DOC in the open ocean have been observed to range from ~ −150 to −230‰ in surface waters of the oligotrophic Atlantic and Pacific Oceans, to ~ −400‰ (~4000 ^{14}C years B.P.) and −525‰ (~6000 ^{14}C years B.P.) in the deep North Atlantic and North Pacific, respectively [Williams and Druffel, 1987; Bauer et al., 1992a; Druffel et al., 1992]. This ~2000 year age difference is believed to be a result of both DOC aging during deep water mass transport and bomb ^{14}C present in the deep north Atlantic [Bauer et al., 1992a; Druffel et al., 1992]. Furthermore, the seemingly "old" apparent ages observed even in surface waters (~1200-2000 ^{14}C years B.P.) can be explained by admixtures of DOC from deep waters (the so-called old, refractory background material) with surface-derived DOC that contains bomb ^{14}C [Druffel et al., 1992]. To date, however, little information is available on the temporal or spatial variability of DOC concentrations and Δ^{14}C values due to inputs of recently produced DOC and/or the selective removal of different DOC components.

The uniformity of deep ocean DOC concentrations and Δ^{14}C values measured previously from single profiles [Williams and Druffel, 1987; Bauer et al., 1992a] has been taken as an indication of the steady state and relative invariance in these parameters over large time and space scales. The present study was undertaken in an effort to evaluate the temporal variability in DOC concentrations and radiocarbon signatures as indicators of seasonal and longer-term sources and sinks of DOC to the deep ocean. A single time series station, having a typical maximum in upwelling-associated surface productivity and pelagic POC flux in early to midsummer [Smith et al., 1992, 1994]

was occupied periodically for 2 years. This study was designed to examine (1) if DOC concentrations and radiocarbon signatures in the deep ocean are temporally variant and related to the concentrations and fluxes of sinking and/or suspended POM, and (2) how DOC concentrations and radiocarbon signatures in the eastern margin of the North Pacific compare with those in the central North Pacific gyre [Williams and Druffel, 1987]. To help evaluate these relationships, the concentrations, fluxes, and ^{14}C natural abundances of both suspended and sinking POC were also measured during this 2-year period; results of this aspect of the study are presented separately [Druffel et al., 1996]. During the course of this study, both normal and El Niño–Southern Oscillation (ENSO) conditions were encountered, further allowing us to compare DOC concentrations and radiocarbon signatures during periods of typical and atypical meteorological and organic matter flux conditions.

2. Materials and Methods

2.1. Study Site

The area chosen for this study has been occupied every 3–4 months since 1987 by Smith et al. [1992b, 1994] for studies of deep ocean POC flux, benthic respiration and other parameters related to food sources and sinks in the benthic boundary layer. Station "M" is located at 34°50'N, 123°00'W, at the base of the Monterey Deep Sea Fan, and average water depth is approximately 4100 m (Figure 1).

Wind-driven upwelling occurs in late spring and summer along the California coast, and much of the biomass produced from this coastal upwelling is carried offshore in the form of discrete plumes or jets of chlorophyll [Smith et al., 1988; Michaelson et al., 1988]. Independent long-term studies in this region [Hayward et al., 1994 and references therein] indicate a range in primary production values during 1991 and 1993 (i.e., non–El Niño) years of approximately 570–5560 mg C m^{-2} d^{-1} near station M and inshore. During the 1992 El Niño, primary production ranged from 390 to 1559 mg C m^{-2} d^{-1} [Lynn et al., 1995, and references therein]. This production drives a seasonally varying vertical flux to the deep ocean at station M, with a primary peak occurring in early to mid summer and a secondary peak in the late fall [Smith et al., 1994].

Station M was occupied on six separate occasions from July 1991 to July 1993 (Table 1). The flux rate of POC at 50 m above bottom (mab) at this site ranges from less than ~2 mg C m^{-2} d^{-1} during nonupwelling periods to greater than 20 mg C m^{-2} d^{-1} during the summer [Smith et al., 1994] (Table 1). During the 1992 ENSO event, near-bottom POC flux rates were significantly lower than those measured during the summers of 1991 and 1993. As shown by Baldwin et al. [1998], climatic perturbations such as the 1992-1993 ENSO event caused significant interannual deviations from the normal seasonal pattern and greatly reduced the maximum POC flux typically observed in summer (Table 1). Thus station M waters and sediments experienced a protracted period of low POC flux, in contrast to the two annual maxima in flux rates normally observed at this site [Smith et al., 1994; Baldwin et al., 1998].

2.2. Sampling Methods

All sampling preparations and sample processing procedures were conducted using organic- and isotopic-contamination-free protocols [Druffel et al., 1992]. Seawater samples were
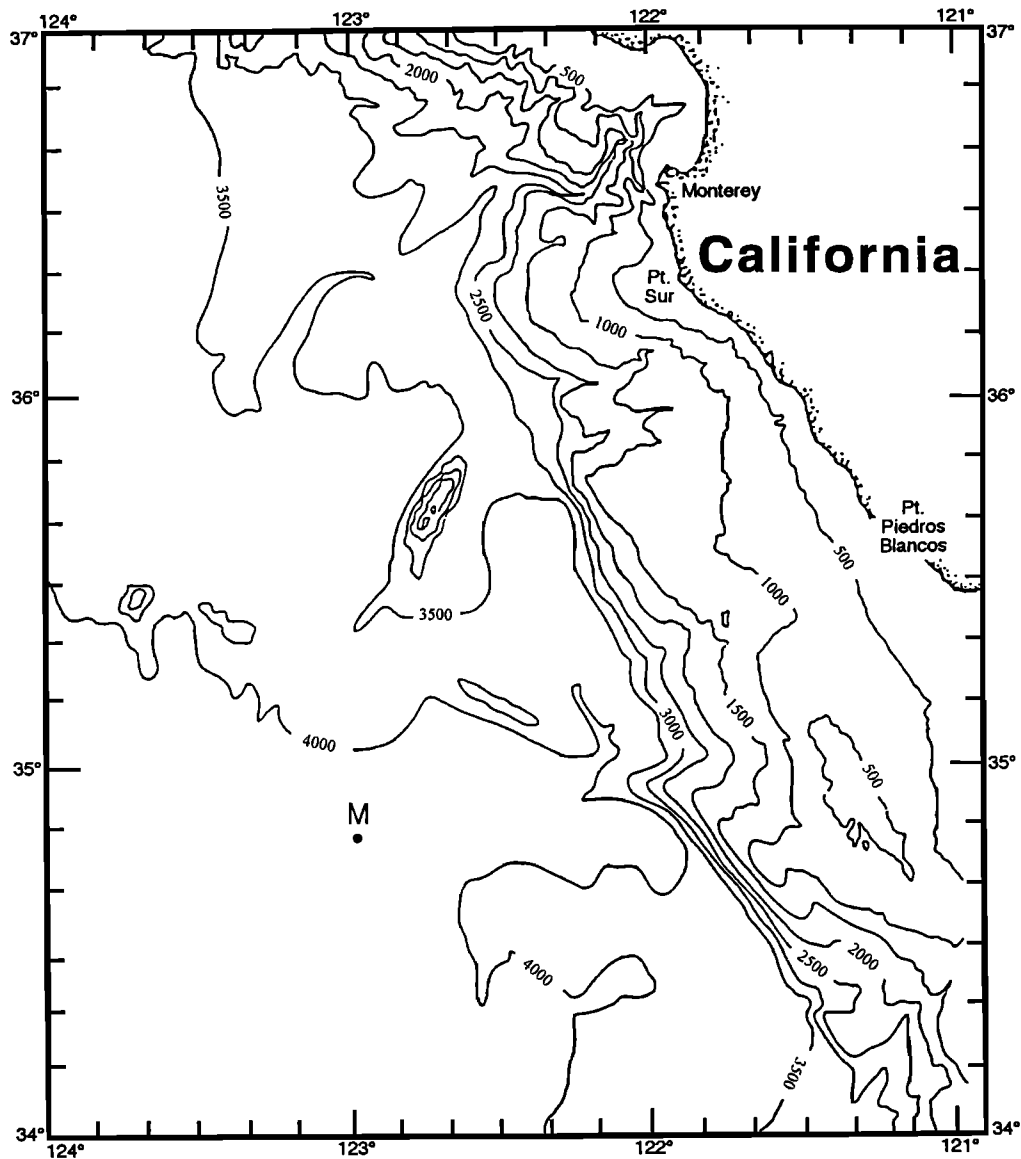
Figure 1. Location and regional bathymetry of the study site, station M.

collected on a standard hydrowire using 12- or 30-L Go-Flo bottles that were cleaned with methanol, 10% HCl, and double-distilled water and air-dried in the laboratory prior to use. Go-Flos were allowed to "soak" and rinse at the depth of

Table 1. Station M Near-Bottom Sinking POC Flux Rates

Pulse Cruise	Flux Period	Maximum POC Flux,* mg C m^{-2} d^{-1}
7	June 1991	21
11	Jan.–Feb. 1992	≤5
12	May–June 1992	≤5
15	Sept.–Oct. 1992	2
16	Jan.–Feb. 1993	≤5
17	June–July 1993	18

Rates reported are estimated maximal rates recorded in 50-mab (meters above bottom) sediment trap in the month prior to water column sampling.

*Values derived from *Smith et al.* [1994] and from K. Smith (personal communication, 1996).

sample collection for ~30 min prior to tripping. Bottles were kept closed and covered in the ship's lab at all times in order to reduce contamination from atmospheric and other sources.

Seawater for both total DOC concentrations and Δ^{14}C measurements was gravity filtered directly from the sampling bottles through a precombusted (525°C) 147-mm-diameter GF/C (1-μm nominal pore size) glass fiber filter. Samples were collected in precombusted 1-L glass bottles with Teflon-lined caps for measurements of Δ^{14}C in DOC (DOC-Δ^{14}C). All samples were stored at -20°C in the dark until analysis. The sample collection, processing, and storage protocol used here was found not to contribute any measurable blank carbon to the samples. As part of the larger study at station M, concentrations and Δ^{14}C signatures of suspended and sinking POC were determined concurrently with DOC concentrations and Δ^{14}C, and sampling details and results are presented by *Druffel et al.* [1996]. In addition to DOC, samples were also collected at the same times and from the same sampling bottles for dissolved inorganic carbon (DIC) concentrations and Δ^{14}C signatures,

Table 2. Values of $\Delta^{14}C$ in DOC Extracted by Ultraviolet Oxidation (UV) and Continuous Injection High-Temperature Catalytic Oxidation (HTCO)

Depth, m	Pulse 7		Pulse 11	
	UV	HTCO*	UV	HTCO*
25			-287 ± 5	-267
30	-302 ± 6	-284		
85			-299 ± 6	-285
700	-526 ± 6	-570	-498 ± 5	-481

Data are from depths where samples were extracted using both techniques.

*All continuous injection HTCO samples were corrected by appropriate system blank carbon convents and $\Delta^{14}C$ values of blanks. Total carbon yields from continuous injection HTCO analyses were too small (usually <100 μg C) to allow splitting of samples for $\delta^{13}C$ analyses. Therefore $\Delta^{14}C$ values were calculated using assumed $\delta^{13}C$ values of $-21\%o$. The large average error ($\pm 1\sigma$) of $\sim \pm 40\%o$ for the HTCO $\Delta^{14}C$ values is a result of the propagation of the error following blank correction, which could comprise up to 20% of the uncorrected sample size in some cases.

total CO_2, and alkalinity [*Duffel et al.*, 1996; *Masiello et al.*, 1998]; free and combined amino acids and carbohydrates [*Schultz*, 1995] and salinity and oxygen.

2.3. Short-Term Collections for DOC and $\Delta^{14}C$ of Surface Waters

During the occupation of station M in October 1992 (Pulse 15 cruise), seawater samples were collected from 85-m depth at 1- to 2-day intervals in order to document short-term fluctuations of DOC concentrations and $\Delta^{14}C$ in surface waters. This depth was selected because (1) it exhibited significant variability in DOC concentrations and $\Delta^{14}C$ between early cruises and (2) it was located at or near the chlorophyll maximum [*Bianchi et al.*, 1998]. It was not possible to perform these collections on all days or at the same time on each day. Samples were collected and stored as was described above. In addition to DOC and $\Delta^{14}C$, dissolved oxygen concentrations were also monitored.

2.4. Analytical Methods

Concentrations of DOC were measured by high energy ultraviolet (UV) irradiation of seawater samples. The UV determinations of DOC concentration were conducted as a routine part of the measurement of ^{14}C natural abundance of DOC. The DOC was oxidized by a modification of the method described by *Williams and Druffel* [1987] and *Druffel et al.* [1992]. Seawater samples (650 mL) were initially acidified to pH 2–2.5 with 85% H_3PO_4 and sparged free of inorganic carbon for 45 min with ultrahigh-purity nitrogen or oxygen. All steps of this procedure were carried out following the transfer of the thawed sample from the sample bottle to an optically clear quartz vessel designed to interface directly to a vacuum extraction line. The quartz vessel containing the sparged seawater sample was irradiated at the focal point of a 2400-W, medium-pressure mercury arc UV lamp equipped with reflector assembly (Canrad-Hanovia Co., Newark, N. J.) for 120 min. Following irradiation, the CO_2 evolved from the oxidation of DOC was purged from the quartz vessel using ultrahigh-purity nitrogen, transferred to the vacuum extraction line through a KIO_3 trap to remove Cl_2 gas, cryogenically purified, and quantified using an absolute pressure gauge (MKS Corporation). The

sample was then split, with $\sim 90\%$ of the volume being used for subsequent $\Delta^{14}C$ analysis and $\sim 10\%$ for $\delta^{13}C$, and flame sealed into 6-mm Pyrex tubes.

The CO_2 for $\Delta^{14}C$ measurements was converted to graphite targets in an atmosphere of H_2 over Co catalyst [*Vogel et al.*, 1987] and analyzed at the Center for Accelerator Mass Spectrometry at Lawrence Livermore National Laboratory. Typical $\Delta^{14}C$ measurement errors for sample sizes in the range analyzed (~ 250–600 μg C) were ± 4–$6\%o$. All reported $\Delta^{14}C$ values were corrected for fractionation using the appropriate $\delta^{13}C$ value of each sample [*Stuiver and Pollach*, 1977], which was measured using either a VG Micromass 602E or a Finnegan Delta S isotope ratio mass spectrometer having analytical precisions of better than $\pm 0.1\%o$. Irradiations of replicate seawater samples collected from the same cruise and depth were within approximately ± 1 μM C (i.e., $\pm 1\sigma$) of each other with respect to DOC concentrations calculated from CO_2 yields. Hence the UV method has a higher precision and sensitivity than the high-temperature catalytic oxidation (HTCO) methods ($\pm 1\sigma = \sim 3$ μM C) in common use. The $\Delta^{14}C$ values of these replicate samples had a precision that was within the $\Delta^{14}C$ measurement error of 3–$6\%o$. The total blank for the UV oxidation procedure (including sample handling and sparging) was determined by reprocessing and reirradiating both seawater and double distilled water samples that had been previously processed and the DOC removed by UV oxidation. The total processing blank was found to be <1 μmol CO_2.

On two of the early cruises (Pulse 7 and 11) to station M, we compared the $\Delta^{14}C$ of DOC extracted by UV oxidation to that extracted by continuous injection high-temperature catalytic oxidation (CI-HTCO) for selected samples (Table 2). Previous comparisons of UV and CI-HTCO results [*Bauer et al.*, 1992a] indicated that the two methods yielded similar $\Delta^{14}C$ values for DOC in the north central Pacific and Atlantic Oceans. Details of the CI-HTCO procedure are described by *Bauer et al.* [1992a, b] and *Druffel et al.* [1992]. The $\Delta^{14}C$ values of DOC as determined by the two methods were in good agreement for both shallow (25–85 m) and intermediate (~ 700 m) waters. Although CI-HTCO showed slightly elevated $\Delta^{14}C$ values in four out of five cases, these values agreed to within $\pm 2\sigma$ with the UV-derived values, and thus we conclude that $\Delta^{14}C$ values were not influenced significantly by the specific method used for oxidizing DOC. This confirms previous findings [*Bauer et al.*, 1992a; *Druffel et al.*, 1992] that the two methods yield comparable results and that differences in specific methodological oxidation reactions do not yield $\Delta^{14}C$ artifacts. Because of the simplicity and low experimental blank of the UV oxidation method compared to the CI-HTCO method for $\Delta^{14}C$ determinations, the UV method was used for all subsequent DOC extractions.

3. Results

3.1. Seasonal DOC Concentrations in the Eastern North Pacific

All data from samples collected for water column profiles in this study are tabulated and presented in Table 3. Concentrations of DOC as determined by UV photooxidation as a function of depth for all cruises are shown in Figures 2a and 2b. Similar to other open ocean DOC profiles, DOC concentrations at station M were highest in shallow euphotic waters and decreased to near-constant levels below ~ 700-m sampling

Table 3. Hydrographic and Carbon Isotopic Information From All Samples Collected on Pulse Cruises From July 1991 to July 1993

Depth, m	LJA	Temperature, °C	Salinity	O_2, mL L^{-1}	DOC, μM	$\Delta^{14}C$, ‰	σ	$\delta^{13}C$, ‰
			Pulse 7 (July 2–12, 1991)					
25	140				62	−302	6	−20.5
85				4.91				
450	139			4.50	42	−491	5	−21.7
722	138			0.39	39	−526	5	−20.6
1642	136			1.72	33	−540	6	−21.7
1619	183*				35	−558	6	−21.0
2556	151			2.44	36	−554	5	−21.4
3582	134			2.98	38	−558	6	
3966	137				34	−536	5	−20.9
4100*	193				36	−525	4	−21.1
			Pulse 11 (February 19 to March 2, 1992)					
20	130	13.633	32.831	6.29	70	−287	5	
83	129	10.744	33.031	5.72	59	−299	6	
449	135	5.840	34.164	0.87	44	−469	5	−20.5
710	132	4.765	34.350	0.33	39	−498	5	
1649	131	2.565	34.563	1.23	39	−564	5	−20.6
2572	128	1.756	34.650	2.23	41	−510	5	
3459	134	1.570	34.671	2.94	40	−559	5	−20.5
3832	141	1.511	34.668	3.29	38	−549	5	−20.3
4100*	194				41	−549	6	
			Pulse 12 (June 19 to July 1, 1992)					
25	192		32.991	5.96	72	−238	8	−21.2
85	191		33.083	5.44	61	−286	6	
456	184	6.000	34.053	0.77	41	−436	4	−21.2
767	189	4.781	34.290	0.42	38	−505	4	−20.8
1206	186	3.315	34.496		38	−536	5	
1595	185	2.558	34.561	1.22	38	−562	5	−21.2
2560	188	1.735	34.460	2.41	39	−573	5	−22.3
3470	187	1.568	34.660	2.88	39	−562	4	−21.0
4050	190				39	−542	3	−21.7
4063	182	1.503	34.681	3.16	39	−549	5	−21.0
			Pulse 15 (October 15–27, 1992)					
24	164	17.232	33.134	5.95	72	−250	5	−22.3
85	168	11.492	33.197	4.91	55	−312	5	−21.3
453	199	6.641	34.115	1.08	45	−428	5	−21.0
700	202				40	−483	5	
716	196	5.006	34.285	0.30	41	−474	4	−20.5
1619	201	2.639	34.518	1.17	38	−546	4	−21.4
2530	197	1.794	34.628	2.29	38	−546	4	−21.1
3515	200	1.559	34.667	3.21	37	−536	4	−21.1
4096	198	1.495	34.644	3.31	38	−550	4	−22.0
			Pulse 16 (February 17–26, 1992)					
25	207			6.06	67	−244	5	−20.9
85								
471	205	5.370		0.71	44	−443	4	−20.9
794	206	4.355		0.24	38	−485	4	−21.4
1606	203	2.574		3.36	38	−546	4	−21.0
2703	195	1.770		2.29	37	−546	4	
3766	204	1.558		3.10	37	−540	3	−21.2
4050				3.10				
			Pulse 17 (July 14–22, 1993)					
25	234		31.045	6.28	74	−257	5	−22.4
85			31.260	4.68				
450	236	6.596	34.153	0.80	43	−430	3	−21.4
711		5.210	32.688	0.17				
1451	233	2.967	34.554	0.63	36	−540	3	−21.5
2379	232	1.752	34.278	1.67	37	−539	3	−21.6
3542	231	1.524	34.763	2.39	37	−543	3	−21.5
4050		1.404	34.501	2.54				

Abbreviations are LJA, La Jolla Radiocarbon Laboratory sample number; DOC, dissolved organic carbon. Values missing from a given category were not measured for that cruise.
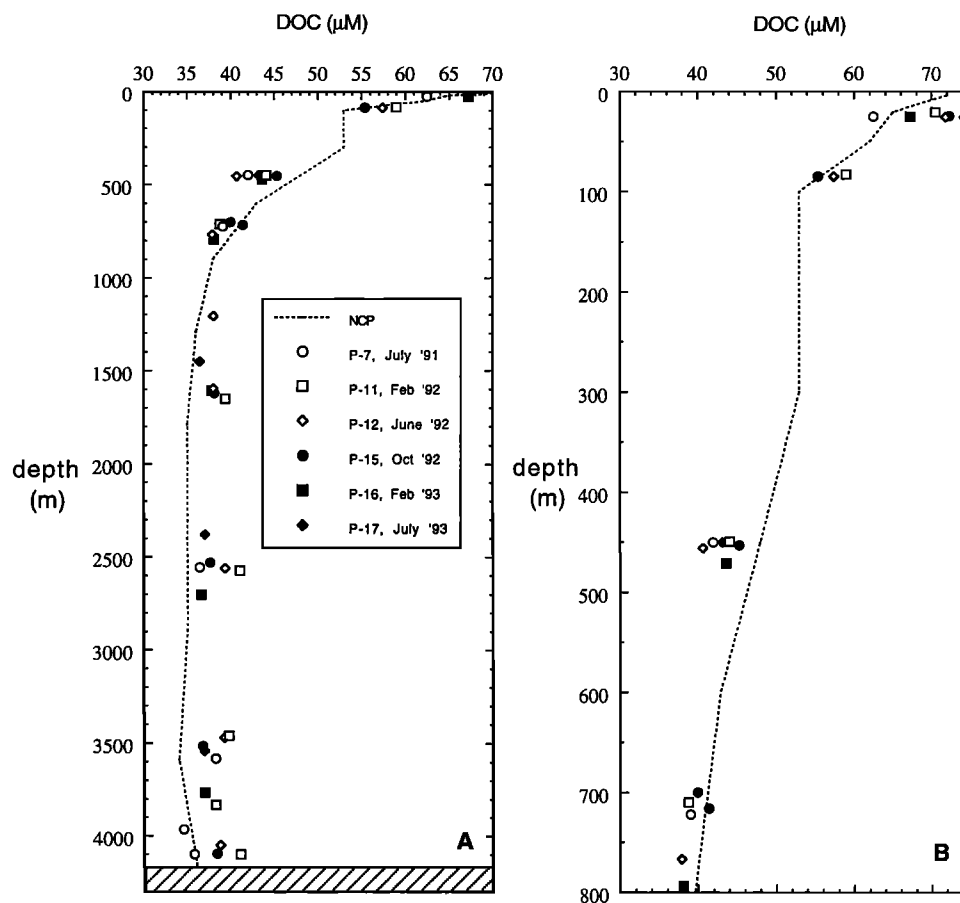*Samples collected from free-vehicle lander ~1 m above seafloor.

Figure 2. Profiles of DOC at station M as determined by UV photooxidation for Pulse cruises 7–17 for (a) the entire water column and (b) 0–800 m. The dashed line represents DOC concentrations determined for a station from the north central Pacific (NCP, 31°00′N, 159°00′W [*Williams and Druffel*, 1987; *Druffel et al.*, 1992]) for comparison.

depth. The greatest variability in DOC concentrations was seen in the shallowest waters sampled at 25 m (Figure 2b). At this depth, concentrations ranged from a low of 63 μM in July 1991 to a high of 74 μM in July 1993. These differences in surface DOC concentrations correspond to the two highest sinking POC flux periods of the entire study (Table 1). The higher variability observed in station M surface waters may also in part be a result of greater "patchiness" in general there (see below and Figure 4). At ~1600-m depth, a slightly greater range (6 μM) in subsurface DOC concentration was observed compared to all other depths sampled (average range = 4 ± 1 μM). Profiles of DOC concentration did not exhibit consistent season-to-season differences, but concentrations in July 1991, the period of highest sinking POC flux, were among the lowest observed throughout the entire water column (Figure 2a). In addition, there was no obvious relationship between the concentrations of DOC and suspended POC [*Druffel et al.*, 1996] in the water column.

Several significant differences in DOC concentrations were noted between station M and a previously occupied site in the north Central Pacific (station NCP; 31°00′N, 159°00′W [*Williams and Druffel*, 1987; *Druffel et al.*, 1992)]. At depths greater than ~1000 m, DOC concentrations at station M exceeded those from the same depths in north central Pacific (NCP) waters by 2–5 μM in all cases (Figures 2a and 2b). This was also true at the shallowest depth sampled in the present study

(Figure 2b). However, at ~450- and 700-m depths, concentrations were consistently lower at station M than in the NCP (Figure 2b). These differences in DOC concentrations are likely related to variability in the relative strengths of DOC sources and sinks in various parts of the water column at these two sites (see Section 4).

3.2. Temporal Variations in $\Delta^{14}C$ Signatures of DOC in the Eastern North Pacific

Similar to DOC concentrations, the $\Delta^{14}C$ values of DOC exhibited relatively little temporal variability (Figures 3a and 3b), in spite of sinking POC fluxes to the deep ocean at station M that varied by nearly an order of magnitude between cruises and seasons (Table 1). During the six cruises, shallow surface waters exhibited a moderate amount of temporal variability in $\Delta^{14}C$-DOC, and variability was also seen in intermediate waters (Figures 3a and 3b) and at ~2500 m (Figure 3a) (although the value of 2572 m for Pulse 11 appears to be anomalously high). At 25-m depth the range of $\Delta^{14}C$ values over all cruises was 59‰, while at ~450 m and ~700 m the ranges were 63‰ and 52‰, respectively. Three duplicate measurements of the $\Delta^{14}C$ of DOC are reported for deep (≳700 m) samples collected from similar depths (within ~15–20 m of each other) during three cruises (Pulse 7, 12, and 15 (Table 3)). Two of these duplicate analyses were within ±2σ of the measurement error for $\Delta^{14}C$ (7 and 9‰ for Pulse 12 and 15, respectively),
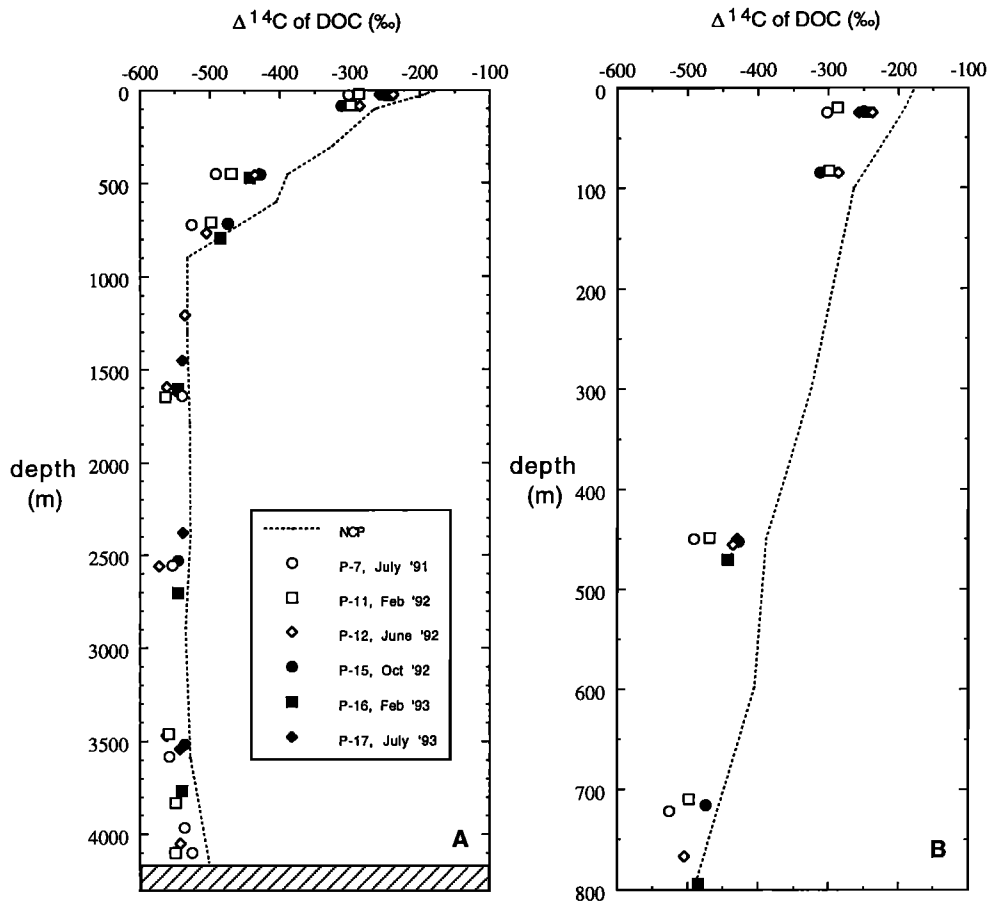
Figure 3. Profiles of $\Delta^{14}C$ of DOC at station M as determined by UV photooxidation for Pulse cruises 7–17 for (a) the entire water column and (b) 0–800 m. The dashed line represents $\Delta^{14}C$ of DOC determined for a station from the north central Pacific (NCP, 31°00'N, 159°00'W [Williams and Druffel, 1987; Druffel et al., 1992]) for comparison.

and one pair was within $\pm 3\sigma$ of the measurement error (16‰ for Pulse 7).

At depths shallower than ~700 m, $\Delta^{14}C$ values at a given depth were lowest during the period of highest sinking POC flux (Pulse 7, July 1991) (Figure 3b), but this apparent relationship was not observed during the other high flux time (Pulse 17, July 1993) or at greater depths (Figure 3a). In contrast, values of $\Delta^{14}C$ were highest during the period of lowest sinking POC flux (Pulse 15, October 1992) at intermediate depths. The average $\Delta^{14}C$ value for all samples taken at ~1600 m and deeper was $-549 \pm 10‰$ ($n = 21$, excluding the 2572-m value from Pulse 11). The standard deviation of this average $\Delta^{14}C$ value ($\sigma = \pm 10‰$) is only about twice the average error of the individual $\Delta^{14}C$ measurements.

Samples collected by a free-vehicle benthic lander during Pulse 7 and 11 (sampling bottle located ~1 m above the seafloor, ~4100-m depth [Smith et al., 1994]) had DOC concentrations and $\Delta^{14}C$ values that were at times slightly (but in all cases nonsignificantly) elevated relative to the rest of the water column below ~1600-m depth (Table 3, Figures 2a and 3a). This indicates that near-bottom processes such as sediment resuspension in the benthic nepheloid layer (which has been noted previously at station M [Smith et al., 1994; Druffel et al., 1996]) do not exert a major or consistent influence on the DOC close to the seafloor. Also, in agreement with previous observations [Bauer et al., 1995], the elevated DOC concentrations

and ^{14}C enrichments in sediment pore waters in this same area are not reflected in elevated amounts and $\Delta^{14}C$ values of DOC in the deep water column, thus constraining sediments and pore waters as a source of DOC to this region of the deep ocean.

We also compare the profiles of $\Delta^{14}C$ of DOC from the eastern North Pacific to a profile obtained previously in the NCP in 1987 [Williams and Druffel, 1987; Druffel et al., 1992] (Figures 3a and 3b). With the exception of the one anomalously high $\Delta^{14}C$ value at 2572 m (Pulse 11, February–March 1992), all of the $\Delta^{14}C$ values at station M are depleted in ^{14}C relative to the NCP profile taken in June–July 1987. The average surface (20–25 m) to deep ocean (≥ 900 m) gradient in $\Delta^{14}C$ of the DOC was greater at the NCP site (336‰) than at station M (289‰). This is primarily a result of the much larger average $\Delta^{14}C$ difference between the surface waters (69‰) than between the deep waters (23‰) of the two sites.

The $\delta^{13}C$ values of DOC at station M for all sampling periods (Figure 4; Table 3) ranged from $-22.4‰$ to $-20.3‰$. The average $\delta^{13}C$ for all samples and depths was $-21.2 \pm 0.6‰$ ($n = 37$) and was not significantly different from a profile previously measured in the NCP [Williams and Druffel, 1987]. No consistent seasonal or longer patterns of $\delta^{13}C$ emerged. The ranges in the $\delta^{13}C$ values were greatest in surface and near-bottom samples, suggesting a greater variability in the $\delta^{13}C$ of sources of DOC to these two regions of the water
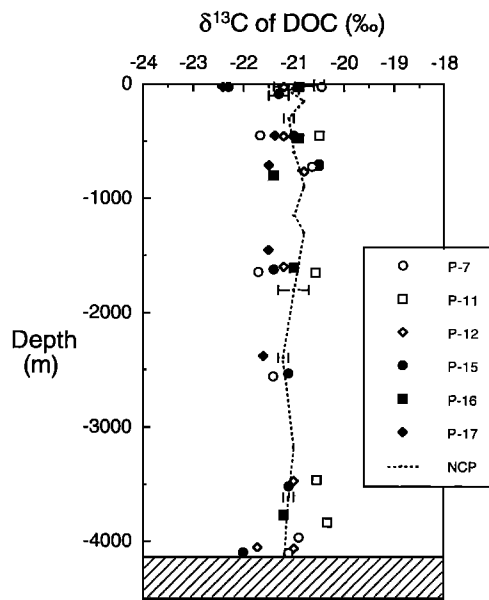
Figure 4. Profile of $\delta^{13}C$ of DOC at station M as determined by UV photooxidation for Pulse cruises 7–17.

column. There were also no apparent relationships between $\delta^{13}C$-DOC and depth (Table 3) or between $\delta^{13}C$ DOC and either DOC concentration or $\Delta^{14}C$-DOC. There were, however, differences in the level of variability of $\Delta^{14}C$ as a function of $\delta^{13}C$ in different depths zones of the water column at station M (see Section 4).

3.3. Short-Term Changes in DOC and $\Delta^{14}C$ of DOC

Significant daily changes in DOC concentrations, $\Delta^{14}C$ and oxygen (Figure 5) were observed at 85-m depth at station M during October 1992 (Pulse 15 cruise). DOC concentrations appeared to generally decrease over the course of the cruise (Figure 5a) and ranged from 45 to 58 μM (coefficient of variation c_v = 8.5%). The $\Delta^{14}C$ values of DOC at 85-m depth were relatively invariant (i.e., within ±2σ of the measurement errors) compared with concentrations and ranged from −329 to −308‰ (c_v = 2.2%) (Figure 5b). Thus $\Delta^{14}C$ of DOC in station M surface waters was proportionally less variable than total DOC concentrations. Oxygen also generally decreased with time, with notable and significant increases on October 21 and 25 and a minimum on October 24. No obvious all-inclusive relationships between $\Delta^{14}C$-DOC, DOC concentration, or oxygen (Figure 5c) were observed in these samples. However, it should be noted that the lowest $\Delta^{14}C$ value of DOC occurred on the same date (October 21) as the maximum in oxygen concentration. Conversely, the maximum $\Delta^{14}C$ of DOC occurred at the same time (October 24) as the minimum oxygen concentration. These observations suggest a possible inverse relationship between the apparent radiocarbon age of DOC and oxygen. In addition, the level of variability of "patchiness" in DOC and $\Delta^{14}C$-DOC in station M surface waters is indicated and constrained by these daily measurements.

4. Discussion

4.1. Influence of POC Flux on DOC and $\Delta^{14}C$-DOC

The major source of DOC to the deep ocean ultimately derives from soluble or solubilized forms of organic matter

produced in the surface ocean by living organisms. However, the geochemical and microbial transformations leading to the formation of the large residual DOC pool observed in the oceans are not well understood. Therefore an interpretation of the ^{14}C signature of the bulk DOC pool is complicated because the signature integrates the influence of numerous factors relating to DOC sources and sinks, and the isotopic signatures of DOC added to and removed from the standing pool.

At station M, seasonal profiles of DOC (Figures 2a and 2b) and $\Delta^{14}C$ of DOC (Figures 3a and 3b) reveal subtle changes that result from both inputs and losses of DOC to and from the water column and possibly from natural "patchiness" between sampling periods. The greatest temporal variability in both the concentration and $\Delta^{14}C$ of DOC was observed in the water column above ~700 m (the oxygen minimum), where seasonal effects of photosynthetic carbon fixation, remineralization, solubilization and flux are also greatest. The changes in both concentration and $\Delta^{14}C$ of DOC were not those predicted on the basis of the sinking POC flux rates to the deep ocean (i.e., that greater POC flux would introduce greater amounts of ^{14}C-enriched DOC to the deep ocean). In fact, no significant change in water column dissolved O_2 (Table 3) was found in spite of periodic differences in sinking POC flux of up to an order of magnitude (Table 1). As was observed in the daily patterns of DOC concentration and $\Delta^{14}C$ in October 1992 (Figures 5a and 5b), large fluctuations in concentration are not always accompanied by concomitantly large changes in $\Delta^{14}C$. Therefore, in addition to its production from living and nonliving POC, a variety of biological and physicochemical mechanisms may control the persistence of DOC through remineralization [*Kirchman et al.*, 1991; *Cherier et al.*, 1996], structural transformation [*Keiber et al.*, 1989; *Keil and Kirchman*, 1994] and hydrophobic adsorption [*Keil et al.*, 1994].

The period of highest sinking POC flux (July 1991, Pulse 7) resulted in some of the lowest DOC concentrations and $\Delta^{14}C$ values of the entire study (Figures 2 and 3). If simple dissolution or enzymatic hydrolysis of POM to DOM were the dominant mechanisms controlling inputs of DOC to the deep ocean, we would expect to see both concentrations and $\Delta^{14}C$ values increase during such periods. Therefore alternate explanations are needed to explain the observed fluctuations in DOC concentration (~8 μM) and $\Delta^{14}C$ (~70‰) in the deep ($\gtrsim 700$ m) ocean at station M. One possibility is that during periods of upwelling, ^{14}C-depleted DIC, derived from deeper upwelled water, is fixed into living POM, which is conveyed into other pools including the DOC. However, fluctuations in ^{14}C-DIC values between upwelling and nonupwelling periods at station M were small ($< \sim 20‰$ [*Druffel et al.*, 1996]) and are unlikely to account for a major part of the variations in the ^{14}C-DOC pool. A second possibility is that there exists a true causal relationship between sinking POC flux and the amount of ^{14}C-enriched DOC in the deep ocean. In support of this, *Druffel et al.* [1996] also observed that the $\Delta^{14}C$ values of suspended POC (POC_{susp}) decreased in the summers of 1992 and 1993, a period when sinking POC (POC_{sink}) flux rates are typically greatest on an annual basis. Likewise, they also reported that the $\Delta^{14}C$ values of POC_{sink} decreased at station M in June and October 1991 (both elevated flux periods [*Smith et al.*, 1992]) and in June 1992. In this scenario, POC would be required to physically remove ^{14}C-enriched DOC from the water column. As calculated by *Druffel et al.* [1996], the amount of DOC having an average $\Delta^{14}C$ (−550‰) needed to account for the observed ^{14}C depletion in POC is exceedingly small
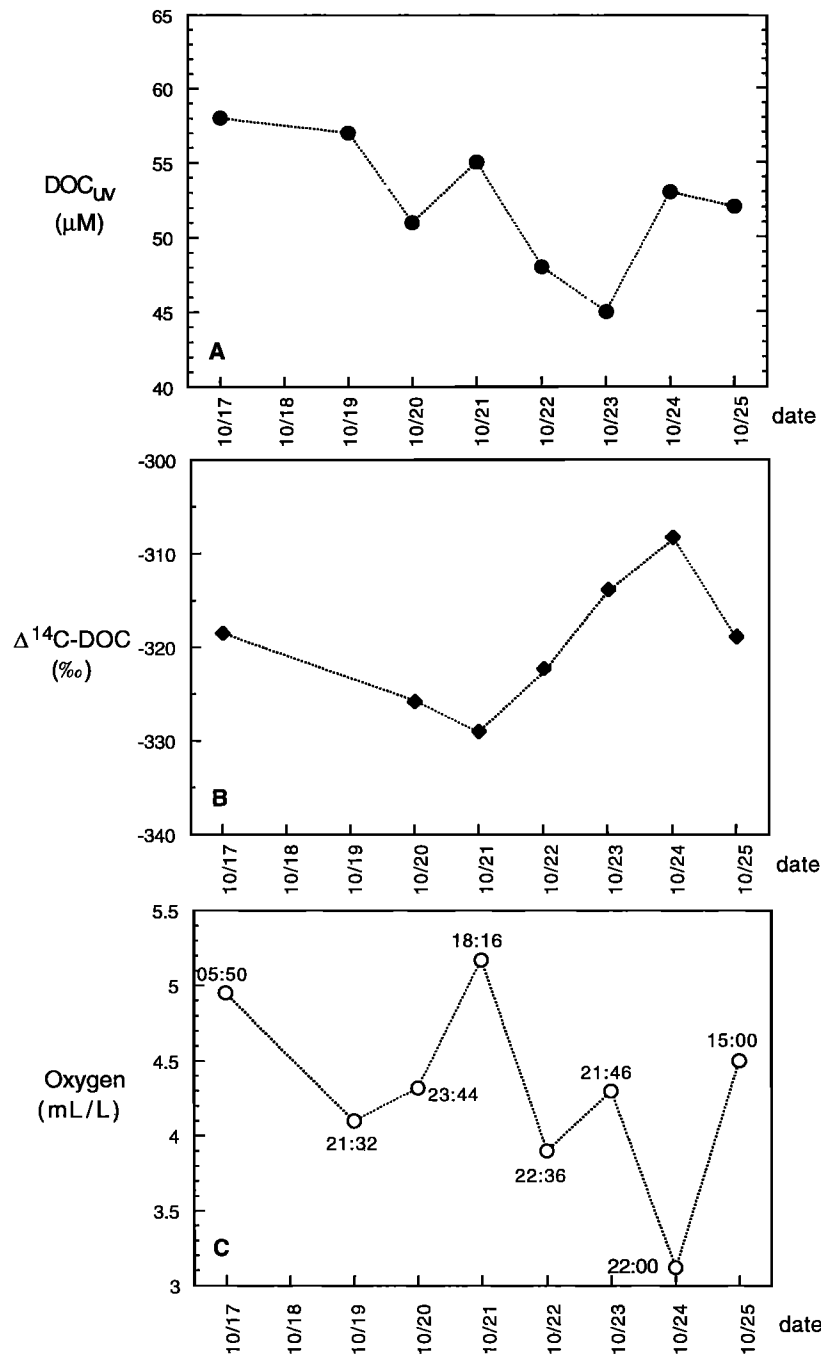
Figure 5. (a) Daily values of DOC concentration, (b) $\Delta^{14}C$ of DOC and (c) oxygen at 85 m depth during Pulse 15 cruise to station M. Month and day in 1992 are indicated on the x axis, and the time of day that each sample was collected is indicated next to the oxygen data points. Measurement errors ($\pm 1\sigma$) were 1 μM for DOC and 5‰ for $\Delta^{14}C$.

($\geq 1\%$ of the DOC pool). However, if a ^{14}C-enriched (i.e., relative to the average deep $\Delta^{14}C$-DOC value of $-550‰$) component of the DOC is removed or released via sorption to or desorption from POC, the amount of DOC removed by this mechanism could be adequate to account for a substantial part of the variations in both DOC concentration and $\Delta^{14}C$ in deep waters at station M. We calculate by mass balance that only ~ 6–12% of DOC with $\Delta^{14}C$ of $-250‰$ (typical surface ocean value at station M) to $\sim +70‰$ (typical surface ocean $\Delta^{14}C$-DIC and net plankton value at station M [*Druffel et al.*, 1996;

Masiello et al., 1997], respectively, would need to be sorbed to or desorbed from particles to account for the observed ranges in DOC concentration (~ 8 μM) and $\Delta^{14}C$ ($\sim 70‰$).

If the magnitude of the POC flux at least in part controls deep ocean DOC values and ^{14}C signatures, we would expect to observe a similar response of the DOC for similar POC flux rates. In July 1993 (Pulse 17) the flux of POC to the deep ocean nearly equaled that measured during July 1991 (Pulse 7), with lower fluxes generally observed between these two periods (Table 1). Figure 6a illustrates that average concentrations of
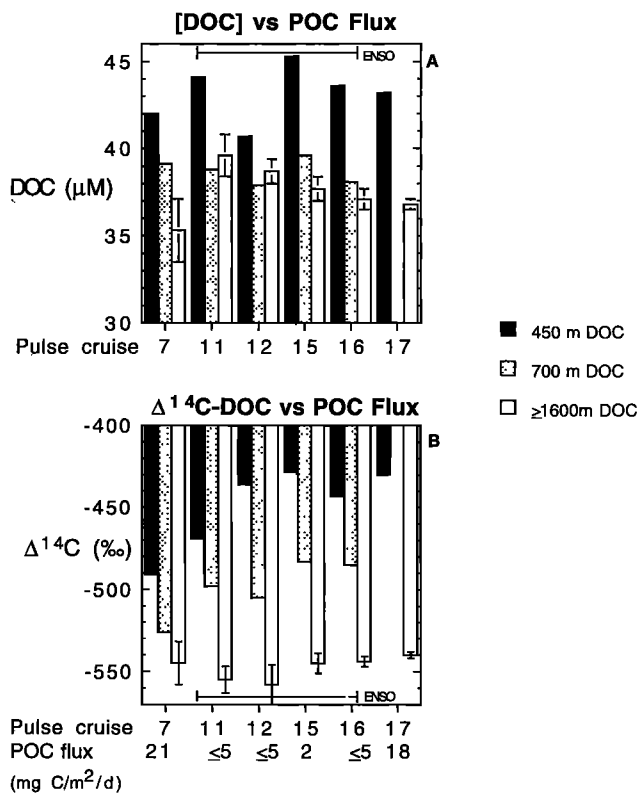
[DOC] vs POC Flux

DOC (μM)

45 · 40 · 35 · 30

Pulse cruise 7 11 12 15 16 17

■ 450 m DOC
▨ 700 m DOC
☐ ≥1600m DOC

Δ¹⁴C-DOC vs POC Flux

$\Delta^{14}C$ (‰)

-400 · -450 · -500 · -550

Pulse cruise 7 11 12 15 16 17
POC flux   21 ≤5 ≤5 2 ≤5 18
(mg C/m²/d)

Figure 6. (a) Time-dependent changes in DOC concentrations and (b) $\Delta^{14}C$ of DOC for non-mixed-layer depth zones as a function of deep POC flux rates [*Smith et al.*, 1994; K. Smith, personal communication, 1996). Data for ~450- and ~700-m depths were plotted separately due to the large gradient that exists in DOC concentration and $\Delta^{14}C$ between these two depths. Depths ≳1600 m were averaged because of the relative uniformity in the profiles. Errors (±1σ) for DOC concentrations (Figure 6a) from ~450 and ~700 m were ±1 μM (from UV oxidations) and are not plotted; errors shown for ≳1600 m are for the average of all deep samples during a given sampling time. Similarly, average measurement errors for $\Delta^{14}C$ values for ~450 and ~700 m were ±5‰, while the errors presented for ≳1600 m are for the average of all deep samples during a given sampling period. The errors associated with these ≳1600 m concentrations indicate that DOC concentrations and $\Delta^{14}C$ values became less variable in the deep ocean at station M with each succeeding sampling period. The 700-m sample from Pulse 17 was lost. Horizontal bars indicate cruises affected by the 1992–1993 El Niño–Southern Oscillation event.

DOC at depths ≳1600 m were lowest during the two highest flux periods (Pulse 7 and 17) and greater during the extended low flux period. Another notable trend was for samples from ≳1600-m depth, in which an initial increase in DOC during Pulse 11 was followed by a long-term decrease (Figure 6a). One possible explanation for this is that during periods of low particle flux (i.e., Pulse 11–16), less DOC becomes sorbed to POC_{sink} and POC_{susp} in the deep ocean. The increasing particle fluxes generated at the termination of the 1992 ENSO event (Pulse 17) may have caused the buildup of deep ocean DOC to be "stripped out" of the deep water column and returned concentrations to previous levels by the time of Pulse 17. On two occasions (Pulse 11 and 12), average deep ocean (≳~1600 m) concentrations equaled or exceeded (though not significantly) those at ~700 m (Figure 6a), a pattern that has

not been observed in previous studies. In the 450-m zone, DOC concentrations had maximum and minimum concentrations during ENSO, while DOC variability was lowest in the 700-m zone. The DOC concentrations of the different depth zones did not covary (Figure 6a).

In contrast to DOC concentrations, $\Delta^{14}C$ values for DOC in each depth zone (Figure 6B) increased significantly at ~450 and 700 m over the time course of the study, the beginning of which was coincident with the onset of the 1992 ENSO event and the corresponding lower fluxes of POC_{sink}. A similar trend was not observed for waters ≳1600 m. These data indicate that (1) input and removal mechanisms of ¹⁴C-enriched or depleted DOC varied throughout the water column, (2) mesopelagic (~450 and 700 m) waters experienced significant 40–60‰ increases in the $\Delta^{14}C$ of DOC at both depths (Figure 6b); and (3) increases in $\Delta^{14}C$ were not correlated with changes in DOC concentrations at these two depths (Figure 6a). This last observation suggests that some process(es) other than (or in addition to) simple input of a younger DOC fraction were influencing the mesopelagic increase in $\Delta^{14}C$-DOC. The significant depletion in oxygen at ~450 and 700 m depths (Table 3) also suggests that organic matter respiration may be less efficient (i.e., oxygen limited) in this part of the water column.

An alternate hypothesis for the relationship between DOC, $\Delta^{14}C$-DOC, and POC flux is that the rate of change in DOC concentration and $\Delta^{14}C$ is related to flux. In this regard, the rise in DOC concentrations below 1600 m after June 1991 may be evidence for extensive POC solubilization following (in contrast to during) the high-flux period. Similarly, the decline in deep DOC concentrations after February 1992 (Pulse 11) may be related to the buildup of suspended POC and may be evidence for the conversion of DOC (or its sorption) to suspended POC during a relatively quiescent period between high-flux events. If true, this conjecture could be shown unequivocally by performing a longer or more frequently sampled time series to further elucidate these trends.

4.2. Relationship Between $\Delta^{14}C$ and $\delta^{13}C$ of DOC at Station M

The $\delta^{13}C$ of DOC at station M (Figure 4) showed a surprising amount of temporal variability, especially in surface and near-bottom waters (approximately 2‰ in both cases). This range in surface waters is attributable to the variability in $\delta^{13}C$ of the sources of DOC that contribute to the bulk pool at a given depth. Source variations in $\delta^{13}C$ can be due to differential inputs from isotopically heavy marine versus isotopically light terrestrial organic matter, or from fractionation effects arising from the rate of photosynthesis within marine waters. Variations in $\delta^{13}C$ of the suspended POC at station M [*Druffel et al.*, 1996] were as high as 4‰ in surface waters and 1–2‰ in deeper waters and likely reflect natural variation in the range of $\delta^{13}C$ in marine organic matter produced in this region. Terrestrial sources of isotopically light organic matter to this region are unlikely to be significant given the paucity of riverine inputs to this part of the North American west coast and of terrestrial organic matter to the Pacific in general [*Meyers-Schulte and Hedges*, 1986; *Opsahl and Benner*, 1997]. We thus speculate that the variation in $\delta^{13}C$ of DOC for this site is related to the similar (or greater) variation in POC resulting from fractionation effects during primary production of living and nonliving particles.

The variability of $\delta^{13}C$ of DOC in surface and mesopelagic waters is accompanied by concomitantly high relative variabil-

ity in $\Delta^{14}C$ (Figure 7), even though $\delta^{13}C$ and $\Delta^{14}C$ are not directly related in these samples. This is interpreted to mean that DOC having variable ^{14}C ages can have a range of $\delta^{13}C$ values, and that the two isotopes cannot be used to predict one another, unlike the situation in regions such as the Middle Atlantic Bight where inputs of low $\delta^{13}C$ terrestrial material are simultaneously enriched in ^{14}C [Guo et al., 1996; also J. E. Bauer and E. M. Druffel, Ocean margins as sources of ^{14}C-depleted organic carbon to the open ocean, submitted to Nature, 1997; J. E. Bauer et al., manuscript in preparation, 1998]. Below 1600-m depth at station M, however, the amount of variability in $\Delta^{14}C$ is much lower than in surface and mesopelagic waters, even though variability in $\delta^{13}C$ is similar (Figure 7). This suggests that the ^{13}C identity of DOC is retained while the ^{14}C identity is lost, perhaps due to the rapid utilization of any young, ^{14}C-enriched, labile DOC that may be injected to the deep ocean here, or as a result of the increasingly smaller amounts of ^{14}C-enriched DOC injected to the deepest parts of the ocean due to particle dissolution, etc.

4.3. Analysis and Interpretation of DOC and $\Delta^{14}C$-DOC Profiles

If the bulk of deep ocean DOC consists of persistent (on timescales of 10^2-10^4 years), refractory background material at station M, then additions of recently produced, ^{14}C-enriched DOC to this background should result in a shift in the deep DOC $\Delta^{14}C$ profiles (Figure 3a). Using an average DOC concentration of 38 μM and $\Delta^{14}C$ value of $-547\%o$ at station M for depths ≥ 1600 m, we calculate that 1.5 μM of recently produced "modern" (i.e., $\sim +70\%o$ [Druffel et al., 1996]) material would need to be added to this background DOC in order to observe a significant (i.e., $\geq \pm 2\sigma$, or $\sim 10\%o$) shift in the $\Delta^{14}C$ of the total DOC pool. That is, very small amounts (1.5 μM or more) of recent material derived from surface primary production would need to be added to the deep DOC pool via particle dissolution in order to detect significant shifts in the $\Delta^{14}C$ of the DOC pool. In more variable surface (25 m) waters the input would need to be ~ 2.5 μM DOC using average values of 70 μM DOC and $-238\%o$ for $\Delta^{14}C$. In both surface and deep waters the range of observed DOC concentrations over the course of the study was in excess of that needed to cause the predicted shifts. Thus dissolution of POC (or any other mechanism of DOC input to the deep ocean)
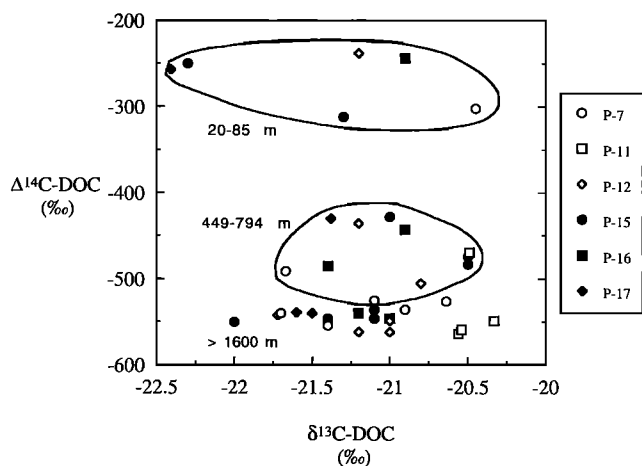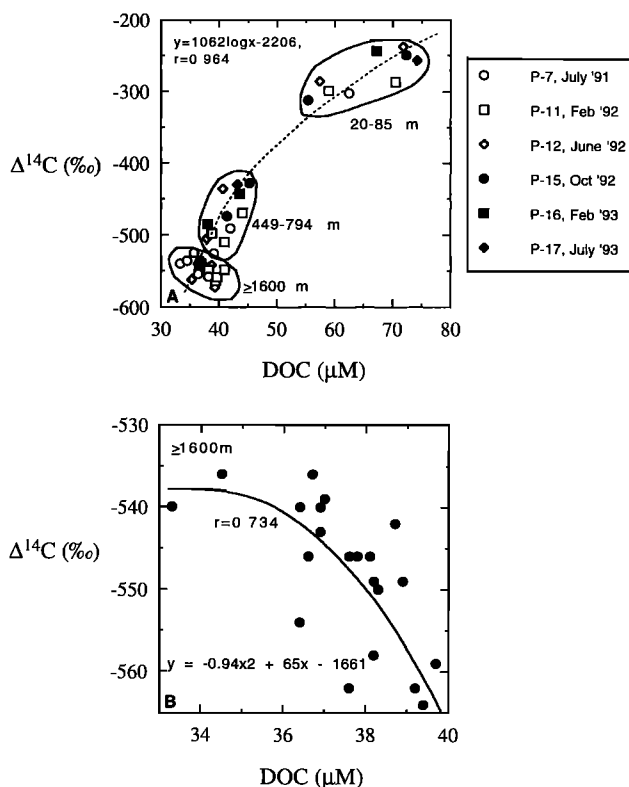

Figure 8. (a) Correlation between $\Delta^{14}C$ and DOC concentration for samples collected from all depths for data shown in Figures 2 and 3 and Table 3. (b) Correlation between $\Delta^{14}C$ and DOC concentration for samples collected from ≥ 1600-m depth. Values from Pulse 11 at 2500 m and Pulse 7 and 11 at 4100 m (~ 1 m above seafloor) are not included (see Table 3).

provides a viable means of altering $\Delta^{14}C$ in the deep DOC pool.

Overall, $\Delta^{14}C$ values are an increasing function of DOC concentration when plotted for all depths and sampling times at station M (Figure 8a). The scarcity of $\Delta^{14}C$ values between ~ -310 and $-430\%o$ is a result of depths between 85 and ~ 450 m not being sampled routinely in this study. Three general groupings of these data can be discerned: upper mixed layer (20–85 m), intermediate depths (~ 450 and 700 m), and deep ocean (≥ 1600 m) (Figure 8a). Plotted separately (not shown), the mixed layer shows a significant positive correlation ($r = 0.808$, $p \leq 0.01$, $n = 9$, slope $= 3.3\%o$ μM^{-1}) between $\Delta^{14}C$ and DOC concentration. This reflects the depth-dependent gradients in both DOC and $\Delta^{14}C$, which are a function of the relative proportions of recent, labile material supplied to each of the mixed layer depths (25 and 85 m). It is apparent that the input of ^{14}C-enriched labile material is dissipated over very small (85 m $-$ 25 m = 60 m) depths (Figures 3b and 8a).

A significant positive correlation ($r = 0.745$, $p \leq 0.01$, $n = 10$) is also seen between $\Delta^{14}C$ and DOC concentration for ~ 450 and 700 m depths (Figure 8a). However, the slope of this fit, $9.6\%o$ μM^{-1}, is greater than that for the mixed layer, indicating that smaller changes in DOC concentration result in correspondingly larger changes in $\Delta^{14}C$ at mesopelagic depths. If the DOC added to these depths is all modern (i.e., $\sim +70\%o$), then the greater slope is largely due to the effects of the mixing of this modern material with proportionally less
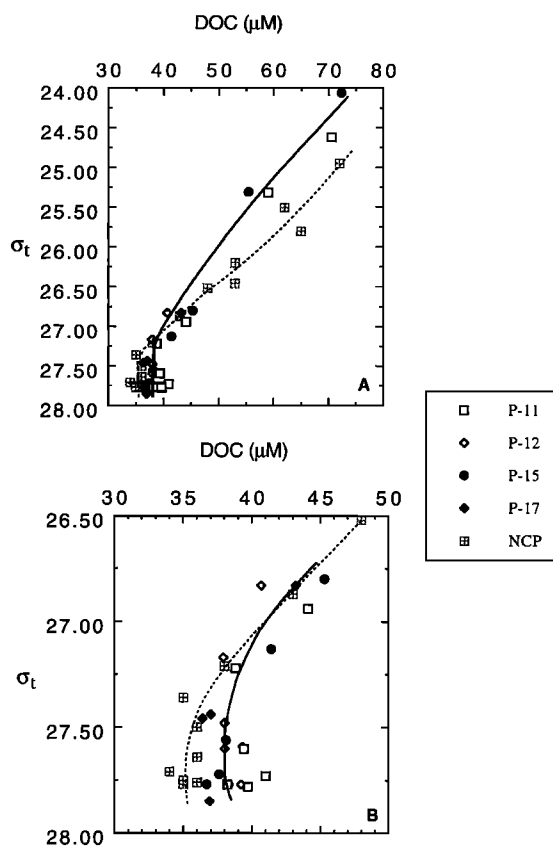

Figure 7. Relationships between $\Delta^{14}C$ and $\delta^{13}C$ of DOC at station M.

Figure 9. Concentrations of DOC station M and the NCP plotted as a function of (a) σ_t for all depths at both sites and (b) $\sigma_t \geq 26.50$ (depths $\geq$450 m) at both sites. Lines of best fit to the station M and NCP data are added. Note that not all station M values of DOC are plotted (see Table 3) due to the absence of corresponding temperature and/or salinity measurements in many cases.

[14]C-depleted DOC than in the mixed layer. For example, if 5 μM DOC of $\Delta^{14}C$ = +70‰ mixed with 39 μM DOC of $\Delta^{14}C$ = −525‰ (e.g., from ∼700 m), we would observe a net shift of +68‰ in the $\Delta^{14}C$ of the bulk DOC pool. The corresponding calculation for mixing the same amount of modern DOC with seawater from 85 m (55 μM, $\Delta^{14}C$ = −325‰) would result in a shift of only +33‰. The narrower range in DOC concentrations observed at intermediate depths is also indicative of the smaller quantities of recent DOC injected to these depths. These observations of the positive relationship between $\Delta^{14}C$ and DOC in the upper ocean support the model finding of *Druffel et al.* [1992] that the upper ocean contains both ^{14}C-depleted background material and ^{14}C-enriched material derived from recent surface production [*Williams and Yentsch*, 1976; *Moller-Jensen*, 1983].

In contrast to mixed layer and intermediate depths, samples from ∼1600 m and deeper reveal a significant ($p \leq 0.01$) inverse second-order correlation (r = 0.748, $p \leq 0.01$) between deep ocean $\Delta^{14}C$ values and DOC concentrations (Figure 8b), indicating that either (1) inputs of DOC to the deep ocean in this region are of older, ^{14}C-depleted material or (2) mechanisms that remove DOC are selective for ^{14}C-depleted material, leaving behind more ^{14}C-enriched DOC. The proximity of station M to the eastern Pacific continental margin provides one means whereby potentially older, [14]C-

depleted sedimentary organic material (either resuspended POC or pore water DOC) may be laterally advected off the shelf and slope [*Anderson et al.*, 1994; *Churchill et al.*, 1994; *Falkowski et al.*, 1994] and a fraction incorporated into the water column DOC pool. A similar mechanism is believed to affect both water column DOC and POC of the Middle Atlantic Bight (J. E. Bauer et al., manuscript in preparation, 1998). However, previous investigations of the $\Delta^{14}C$ of surficial sediment and pore water dissolved organic carbon [*Bauer et al.*, 1995] indicate that $\Delta^{14}C$ values are much greater (with correspondingly younger ^{14}C ages) than deep ocean DOC. Therefore this mechanism for introducing greater amounts of ^{14}C-depleted DOC to station M waters may be limited or at least localized in nature. We speculate that selective adsorption of more hydrophobic, ^{14}C-depleted DOC onto organic [*Druffel et al.*, 1996] or inorganic [*Mayer*, 1994; *Keil et al.*, 1994] particle surfaces, especially during high-particle-flux periods, could also lead to the observed relationship between $\Delta^{14}C$ and DOC in the deep ocean station M.

4.4. Comparison of Station M With the North Central Pacific

Values of the $\Delta^{14}C$ of DOC in the eastern North Pacific were consistently and significantly lower than at a site in the north central Pacific examined previously by *Druffel et al.* [1992] (Figures 3a and 3b). This offset in $\Delta^{14}C$ was accompanied by concomitantly higher DOC concentrations at nearly all depths at station M compared to the NCP (Figures 2a and 2b). Because some part of the offsets between station M and the NCP could be due to differences in isopycnal depths between the two sites, especially at depths above the main thermocline, we have replotted both DOC concentrations and $\Delta^{14}C$ signatures at the two sites as a function of σ_t (Figures 9 and 10, respectively). This procedure "normalizes" depth-dependent differences in DOC concentration and $\Delta^{14}C$ resulting from differences in isopycnal depths.

Concentrations of DOC can be seen to be generally greater in the NCP than station M for σ_t <∼26.50 (Figures 9a and 9b). In the region of σ_t ∼26.75−27.25 (Figure 9b) concentrations at both sites were similar, but at σ_t > ∼27.25, deep ocean values at station M in all cases exceeded those of the NCP. $\Delta^{14}C$ values of DOC, like DOC concentrations, are greater in the NCP than at station M for σ_t < ∼26.50 (Figure 10a). For σ_t > ∼27.50, $\Delta^{14}C$ values at station M were lower than those from deep NCP waters (Figure 10b). Although these data sets are not extensive and the offsets between station M and the NCP are not large, it appears that subtle but real differences may exist in both the concentrations and $\Delta^{14}C$ of the North Pacific central gyre and this region of its eastern margin. The general conclusion regarding these differences is that DOC concentrations are greater, and $\Delta^{14}C$ values are concomitantly higher, in the NCP relative to station M for waters above the lower part of the main thermocline. In the deep water column, station M DOC concentrations exceed those in the NCP, while $\Delta^{14}C$ values are lower than those in the NCP. These data suggest that while the upper water column of the central gyre may be a source of ^{14}C-enriched DOC relative to station M, the deep water column of station M may be a source of ^{14}C-depleted DOC to other areas of the North Pacific.

If we assume that the elevated DOC in station M deep waters is due to greater dissolution of POC and that it has a lower $\Delta^{14}C$ due to upwelled DIC, we can calculate the $\Delta^{14}C$ of

surface seawater DOC based on a two-component vertical mixing model. Assuming that $\Delta^{14}C$ of surface DOC is a mixture of 54% $((39\ \mu M/72\ \mu M)\times100)$ deep DOC $(^{14}C = -550\%o)$ and 46% newly formed DOC from photosynthetic DIC fixation $(^{14}C = +70\%o)$, then the $\Delta^{14}C$ of the bulk DOC in surface water is $-269\%o$. This value agrees well with the average observed $\Delta^{14}C$ of $-263 \pm 25\%o$ at 20–25 m (Table 3). *Druffel et al.* [1992] did a similar calculation for the NCP and obtained good agreement with the observed surface $\Delta^{14}C$ of $-155\%o$ for DOC. These examples demonstrate that DOC $\Delta^{14}C$ values are consistent with a vertical mixing model with two components, one being old, recycled deep DOC and the other being young DOC with a turnover time of less than 40 years (i.e., postbomb). The issue of how rapidly surface-derived organic carbon (DOC and/or POC) alters the $\Delta^{14}C$ of DOC in the deep ocean will be resolved by the reoccupation of sites that have undergone significant shifts in the $\Delta^{14}C$ of surface water DIC (i.e., decreasing bomb signal), thus changing the $\Delta^{14}C$ of surface-derived (i.e., source) organic carbon.

There are three possible explanations for the observed differences in the profiles from these two locations. First, there may be regional differences in the $\Delta^{14}C$ of the source materials to these waters. Lateral movement of materials (i.e., POC and DOC) outward from the margin toward the deep abyssal ocean at station M may impart a qualitative (i.e., isotopic) difference to the DOC or its precursor materials. However, because of the nonuniform offsets in DOC concentrations throughout the water column between these two sites (Figures 2a and 2b), the $\Delta^{14}C$ signatures of material advected from the margin would need to vary widely as a function of depth in order to derive the observed offsets in the $\Delta^{14}C$ profiles from the two locations (Figures 3a and 3b). Furthermore, surficial sediment (0- to 10-cm depth) porewater DOC as well as solid phase sediment organic carbon (SOC) in this general region have been found to be uniformly enriched in ^{14}C with respect to water column DOC in both margin (Santa Monica Basin) and hemipelagic sediments [*Bauer et al.*, 1995]. Thus unless older, more deeply scoured sediments are prevalent in certain regions of the shelf and slope, lateral movement of surficial sediment DOC and SOC would tend to result in more, rather than less, ^{14}C enrichment of DOC at station M.

Second, changes in the $\Delta^{14}C$ of surface DIC fixed into living biomass will influence the $\Delta^{14}C$ of the resultant nonliving organic carbon (i.e., DOC and POC) pools. The average summer (June 1992 and 1993) $\Delta^{14}C$ of surface (25- to 85-m depth) DIC at station M (average $\Delta^{14}C \approx 70\%o$ [*Druffel et al.*, 1996] was approximately 50%o lower than in NCP surface seawater in June 1987 (average $\Delta^{14}C = 120\%o$ [*Druffel et al.*, 1992]). At least part of the station M–NCP difference is due to the 4-year interval between sampling in the NCP (1987) and the start of our sampling at station M in 1991. This resulted in a decrease in the $\Delta^{14}C$ of surface (~20- to 100-m depth) ocean DIC in both the NCP and at station M of approximately 20–30%o [*Druffel et al.*, 1996]. Station M is also influenced seasonally by coastal upwelling which advects lower $\Delta^{14}C$ DIC from subsurface layers into shallow surface waters. This upwelling effect could account for approximately 15–20%o of the total $\Delta^{14}C$ variability noted at station M during the period of sampling [*Berger et al.*, 1966]. The low $\Delta^{14}C$-DIC at station M is transformed into living POC via photosynthetic carbon fixation, and it is possible that this summer signal is transferred through the POC to the DOC pool. Thus the lower overall $\Delta^{14}C$ of station M DOC (Figure 3a) may result in part from the fixation of low

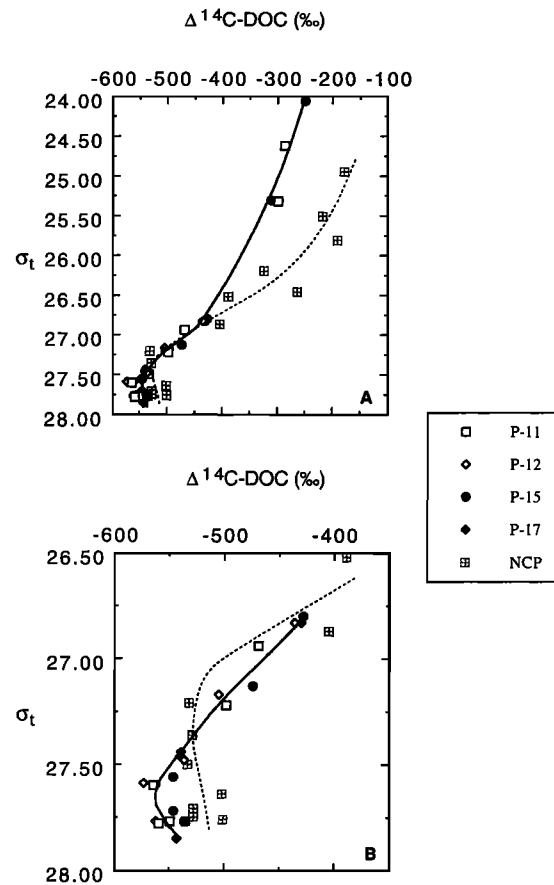**Figure 10.** $\Delta^{14}C$ values of DOC at station M and the NCP plotted as a function of (a) σ_t for all depths at both sites and (b) $\sigma_t \geq 26.50$ (depths $\geq$450 m) at both sites. Lines of best fit to the station M and NCP data are added. Note that not all station M values of $\Delta^{14}C$ are plotted (see Table 3) due to the absence of corresponding temperature and/or salinity measurements in many cases.

$\Delta^{14}C$-DIC and its transfer into both surface and deep water DOC at station M.

A third possibility is that differences in the magnitude of sinking and/or suspended POC fluxes between the NCP and station M help to control the observed average concentration and isotopic differences in DOC. Although low at most times of the year, deep sinking POC fluxes at station M can also be quite high (up to 20 mg C m^{-2} d^{-1}) on a seasonal basis (Table 1). This compares to typical sinking POC fluxes for the oligo-trophic NCP of ~1–2 mg C m^{-2} d^{-1} [*Smith*, 1992; *Smith et al.*, 1992]. Likewise, suspended POC concentrations are up to 3–4 times higher at station M than at the NCP site in both surface (20–25 m) and deep ($\geq$900 m) waters [*Druffel et al.*, 1992; 1996]. These greater concentrations and fluxes of suspended and sinking POC at station M may affect both concentrations and $\Delta^{14}C$ values of DOC by mechanisms such as dissolution and solubilization of organic matter from the POC, adsorption of the more hydrophobic DOC components (both solubilized and adsorbed components may also have distinct $\Delta^{14}C$ signatures from the bulk DOC [*Schiff et al.*, 1991; *Trumbore et al.*, 1992]), and differential utilization of solubilized and adsorbed DOC components by microheterotrophs.

The principal ramification of possibilities two and three is that the steady state concentrations and $\Delta^{14}C$ values of DOC

are to a first approximation controlled by vertical transport processes and that these are dominated by the strong summer flux of POC to the deep ocean at station M. Assuming that the primary means of organic matter transport is vertical (i.e., horizontal transport is insignificant), and the difference in the $\Delta^{14}C$ profiles of DOC in the NCP and at station M is due primarily to the difference in $\Delta^{14}C$ of surface DIC (and, consequently, surface organic matter) at the two locations, then we conclude that the surface $\Delta^{14}C$ signal is manifested in the deep DOC pool on timescales of at most 4–6 years (i.e., the time between NCP and station M sampling). If, on the other hand, horizontal transport from the shelf and slope to station M is more important, then temporal differences in $\Delta^{14}C$ of DIC could be manifested on shorter timescales. Time series measurements of the $\Delta^{14}C$ in suspended POC profiles show that significant short-term (months) shifts in these profiles occur [*Druffel et al.*, 1996] and strongly suggest that lateral transport of slope and shelf derived material occurs during summer periods station M. However, such vertical and horizontal transport mechanisms may play an important role in the removal (i.e., via and adsorptive or "stripping" mechanism) of at least a fraction of DOC from the water column as well.

5. Summary and Conclusion

Changes in the concentrations and $\Delta^{14}C$ of DOC at a time series station in the eastern North Pacific could not be differentiated exclusively on the basis of short-term (seasonal) variations in POC fluxes to the deep ocean. However, significant long-term (i.e., years) changes in both concentrations and $\Delta^{14}C$ values were observed. These changes were especially pronounced at mesopelagic (~450 and 700 m) depths, in proximity to the oxygen minimum. At mixed layer and mesopelagic depths, positive relationships were found between $\Delta^{14}C$ and DOC concentrations at station M, primarily reflecting diminishing vertical inputs of "recent" DOC through the main thermocline. At abyssal depths (≥ 1600 m) this relationship was reversed, and $\Delta^{14}C$ was negatively correlated with DOC concentrations. Hence, while small adsorptive or other losses from the DOC pool may significantly alter the $\Delta^{14}C$ of the much smaller POC pools [*Druffel et al.*, 1996], we do not observe a direct seasonal-scale effect of POC flux rate on the corresponding DOC pool. Instead, the deep ocean DOC pool appears to be controlled by longer-term inputs (POC dissolution, lateral advection) and losses (selective adsorption and/or "stripping out" of DOC during periods of elevated POC flux rates) resulting from the combined effects of interactions with organic and inorganic particles as well as other sources and sinks which have yet to be quantified. We hypothesize that differences in the DOC pools between the seasonally productive eastern North Pacific and the oligotrophic north Central Pacific arise from qualitative and quantitative differences in the sources and sinks of DOC between the two regions, as well as from the interactions between DOC and both organic and inorganic particles in the water column.

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