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J Hwang

ERM Druffel

S Griffin

KL Smith

RJ Baldwin

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Authors

J Hwang, ERM Druffel, S Griffin, KL Smith, RJ Baldwin, and JE Bauer

Temporal variability of Δ^{14}C, δ^{13}C, and C/N in sinking particulate organic matter at a deep time series station in the northeast Pacific Ocean

Jeomshik Hwang, Ellen R. M. Druffel, and Sheila Griffin
Department of Earth System Science, University of California, Irvine, California, USA

Kenneth L. Smith Jr. and Roberta J. Baldwin
Marine Biology Research Division, Scripps Institution of Oceanography, University of California,
San Diego, La Jolla, California, USA

James E. Bauer
School of Marine Science, College of William and Mary, Gloucester Point, Virginia, USA

[1] A 6-year time series of Δ^{14}C, δ^{13}C, and C/N measurements in deep sinking particulate organic matter (POM) is presented for an abyssal site, Station M in the northeast Pacific Ocean. The Δ^{14}C values revealed that sinking POM at 3450 m depth (650 m above bottom) contained old carbon despite its presumed short transit time in the water column. The isotopic and chemical properties of the sinking POM varied with time and appear to be controlled by more than one major process. In 1993, 1994, and late 1996, isotopic signatures and C/N molar ratios indicate negligible or vertically homogeneous influence of resuspended particles from the bottom or particles laterally transported from the margin to the study site. However, during early 1995 and 1998, Δ^{14}C values were lower than those during other periods and C/N values at three deep depths were not equal, indicating that the study site was influenced by resuspended sediments more severely than during other periods. During mid-1995 to mid-1996, δ^{13}C values decreased abruptly while Δ^{14}C values increased slightly, and C/N values were extremely high (up to $\sim$80) at 50 and 600 m above bottom; these results suggest input of degraded, modern, terrestrial organic matter. The periods of anomalous isotopic signatures, as well as vertically heterogeneous C/N values [*Smith et al.*, 2001], were correlated with high discharge periods of California rivers with a time lag of 2 to 4 months. The correlation suggests that regional meteorological events are important in controlling the biogeochemical properties of particles at Station M by varying the intensity of resuspension and transport of organic matter from the continental margin. *INDEX TERMS:* 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4806 Oceanography: Biological and Chemical: Carbon cycling; 4860 Oceanography: Biological and Chemical: Radioactivity and radioisotopes; 4863 Oceanography: Biological and Chemical: Sedimentation; *KEYWORDS:* lateral advection, POM, radiocarbon

1. Introduction

[2] A major fraction of the particulate organic matter (POM) sinking to the deep ocean originates from primary production in the overlying surface waters, with a transition time of 1 to 2 months [*Deuser and Ross*, 1980; *Honjo*, 1982]. The flux of sinking POM (as particulate organic carbon, POC) is greatly attenuated during its vertical transport, where only a few percent of the organic carbon produced in surface waters reaches the ocean floor [*Martin et al.*, 1987; *Wakeham et al.*, 1997]. However, processes modifying sinking POM are not well understood. Sinking POM may exchange with suspended POM by physically or biologically mediated aggregation-disaggregation [*Cho and Azam*, 1988; *Smith et al.*, 1992] and with dissolved organic matter (DOM) by sorption-desorption [*Druffel et al.*, 1992; *Henrichs and Sugai*, 1993; *Kepkay*, 1994; *Chin et al.*,
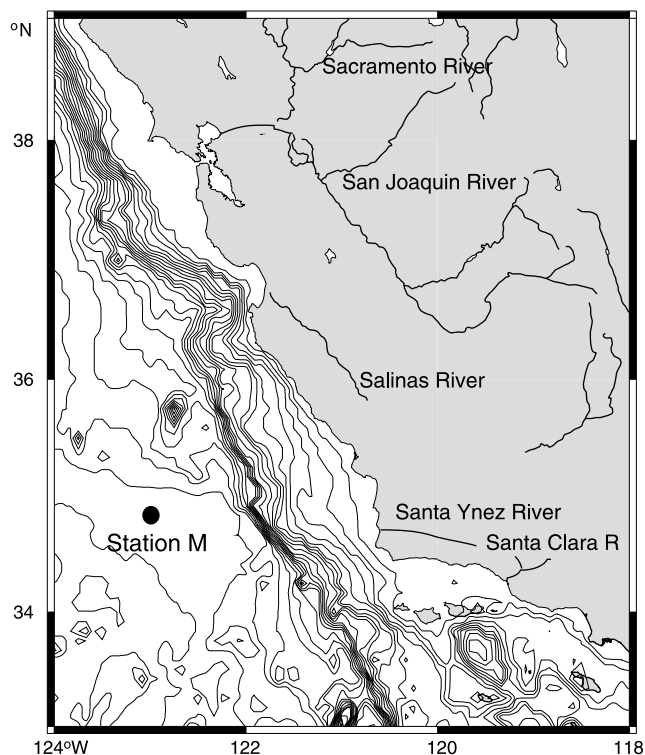
Figure 1. Map of the California coast and locations of Station M and four associated river systems.

1998], which may be facilitated by mucous or gels present on some particles [*Passow and Alldredge*, 1995]. Dissolved inorganic carbon (DIC) may further be incorporated into microorganisms associated with sinking POM via anapleurotic reactions [*Rau et al.*, 1986], a direct use of bicarbonate ion from surrounding water to produce organic compounds in energy generation cycles. Laterally transported terrestrial organic matter or resuspended sedimentary organic matter (SOM) can also be an important source of sinking POM and suspended POM on continental margins [*Walsh et al.*, 1981; *Biscaye et al.*, 1994; *Bauer and Druffel*, 1998; *Liu et al.*, 2000].

[3] Carbon isotope ratios are effective tools for studying biogeochemical processes of organic matter in the ocean [*Druffel and Williams*, 1992]. The $\Delta^{14}C$ signature (per mil deviation of the $^{14}C/^{12}C$ ratio relative to a nineteenth century wood standard) is a good tracer for identifying carbon sources to sinking POM because potential carbon sources have different $\Delta^{14}C$ signatures and turnover times from those of plankton, a major source of sinking POM. Marine DOM in the deep ocean has distinctively low $\Delta^{14}C$ values (from −390‰ in the Atlantic Ocean to −550‰ in the northeast Pacific Ocean) [*Druffel et al.*, 1992; *Bauer et al.*, 1998]. Surface SOM has low $\Delta^{14}C$ values (e.g., <−200‰ on the California margin [*Druffel et al.*, 1998]). In addition, rivers export organic carbon of various $\Delta^{14}C$ signatures to the coastal ocean [*Hedges et al.*, 1986; *Raymond and Bauer*, 2001; *Raymond et al.*, 2004]. Especially, suspended POM from small mountainous rivers

contain a significant amount of old organic carbon from eroded bedrock in addition to modern organic carbon [*Kao and Liu*, 1996; *Masiello and Druffel*, 2001; *Blair et al.*, 2003; *Komada et al.*, 2004]. The $\delta^{13}C$ signature may be used to differentiate marine OC and terrestrial OC from C-3 plants due to their distinct $\delta^{13}C$ signatures [*Degens*, 1969; *Meyers and Lallier-Vergès*, 1999].

[4] Comprehensive studies of biological, physical, and chemical properties in the water column and the sediment have been carried out at Station M since 1989 [*Druffel et al.*, 1996; *Smith et al.*, 2001]. Here, we report a 6-year time series of $\Delta^{14}C$, $\delta^{13}C$ and C/N measurements of sinking POM collected as a part of the larger Station M studies [*Smith et al.*, 2001]. We used the time series data to study carbon sources to sinking POM and processes that control the properties of sinking POM.

2. Study Site Characteristics and Sample Analyses

[5] Station M (34°50′N, 123°00′W, water depth of 4100 m) is located 50 km west of the base of the continental rise, 220 km off the coast of central California (Figure 1). The site lies within the southward flowing California Current in the surface. Near the coast, both the seasonal countercurrent at the surface in fall and winter and the subsurface undercurrent, mainly confined on the continental slope, flow northward along the California coast [*Lynn and Simpson*, 1987, and references therein].

[6] The flux of particulate mass at 600 m above bottom (mab) at Station M is positively correlated with an upwelling index [*Bakun*, 1973] that is a proxy for primary production, with a time lag of approximately 50 days [*Baldwin et al.*, 1998]. This indicates that primary production in the overlying surface waters is the major source of the sinking POM. Input of resuspended SOM to POM at Station M is apparent from $\Delta^{14}C$ measurements [*Druffel et al.*, 1998], pyrophaeophorbide-*a*, a degradation product of chlorophyll-*a* [*Bianchi et al.*, 1998], and the aluminum content in suspended POM [*Sherrell et al.*, 1998]. The high C/N values of sinking POM observed at 50 mab suggest that terrestrial OC reaches Station M [*Smith et al.*, 2001], despite its distance from the coast.

[7] Sinking particles were collected using a single conical sediment trap deployed at 650 mab along with two other sediment traps (600 mab and 50 mab [*Smith et al.*, 2001]) on a single mooring. The benthic mixed layer has been reported to reach up to 80 mab with an average height of 45 mab at Station M [*Beaulieu and Baldwin*, 1998]. The 0.25 m² opening of the cone was covered with a 1 × 1 cm baffle to reduce turbulent flow. Polyethylene collection bottles were attached to a sequencer at the bottom of the cone and programmed to sample in 10-day increments. The bottles were filled with seawater collected from the same depth that the sediment trap was moored. The water was filtered with a precombusted quartz filter (142 mm diameter Whatman ultrapure QMA, 0.8 μm pore diameter) and poisoned with mercuric chloride to a final concentration of 3 mM. The sediment traps were retrieved and redeployed every 13–14 weeks. Samples for carbon isotopic measure-

ments were collected from July 1993 to the end of 1998 with a hiatus from October 1996 to November 1997. The sediment trap failed to collect samples from mid-June to late October 1994 because of presumed clogging due to extremely high flux [*Baldwin et al.*, 1998].

[8] Retrieved sample bottles were kept on ice until processing. Swimmers, organisms that were alive when trapped, were removed manually using forceps from the sample under an illuminated magnifying glass. Each sample was filtered on precombusted quartz filters (Whatman QMA, 47 mm diameter, 0.8 μm pore size) by applying gentle vacuum. Multiple filter pads were used for large samples. Filtered samples were kept frozen at −20°C. The entire layer from a portion of the filter was scraped off to minimize sampling bias. Each sample was dried in an oven (<55°C for 12–24 hours), crushed in a glass vial with a glass rod and frozen until analysis. In order to determine the flux of sinking POC from our samples, it would have been necessary to dry all of the filter pads from a given sample; to facilitate future sampling, we instead left the remainder frozen. We used POC flux into the 600 mab trap published by *Smith et al.* [2001].

[9] A CHN analyzer (Carlo Erba) was used for total carbon (organic plus inorganic carbon) and total nitrogen content determination. For organic carbon content, a few milligrams of each sample were acidified in a silver boat with incremental amounts of sulfurous acid (H_2SO_3, certified grade) until the total volume of acid was 400 μL [*Verardo et al.*, 1989]. The acidified sample was dried after each addition of acid. After addition of about 150 μL, bubbles were not observed. Organic carbon content of each acidified sample was determined using the same CHN analyzer. The relative standard deviations (i.e., coefficient of variation = [1 standard deviation × 100]/mean) of duplicate sample analyses were 2% for organic carbon and 4% for total nitrogen.

[10] Organic carbon content of the 650 mab trap determined by this method agreed with that determined by manometric measurement of CO_2 gas produced by combustion of samples for isotope measurements (the difference between two methods is 0.0 ± 0.3%, n = 125). The organic carbon contents of samples from 600 and 50 mab (previously published by *Smith et al.* [2001]) were determined from the difference between total carbon content measured using a CHN analyzer and inorganic carbon content measured using a Coulometrics Carbon Analyzer. Despite the fact that organic carbon content was determined by two different methods, organic carbon to total nitrogen molar ratios (C/N) from the three trap depths are virtually identical during most of the study, with the exception of short periods during 1995 and 1996. Four samples from the 650 mab trap, including two samples collected when C/N values of 50 mab trap samples were the highest, were analyzed for total carbon and total nitrogen contents independently at the Virginia Institute of Marine Science. The C/N values calculated using these total nitrogen contents were not different from the University of California, Irvine, results within the analysis error (the difference was 0.6 ± 0.2).

[11] For isotope ratio determination of organic carbon, about 30 mg of each sample was weighed in a silver boat,

fsput into a 9-mm OD quartz tube (Vycor brand), acidified with 1 mL of 3% phosphoric acid (certified grade), and allowed to stand overnight. The sample was then dried under vacuum with CuO, flame-sealed, and combusted at 850°C for 2 hours [*Druffel et al.*, 1992]. Water vapor was removed from resultant CO_2 gas cryogenically using isopropyl alcohol/dry ice traps. The volume of the gas was determined by measuring the pressure in a known volume. About 750 μgC of each CO_2 sample was used for a $\Delta^{14}C$ measurement, and about 100 μgC was used for a $\delta^{13}C$ measurement. The CO_2 gas was reduced to graphite on a cobalt catalyst using H_2 gas at 580°C for 8 hours [*Vogel et al.*, 1987]. Isotope ratio analyses were performed either at the National Ocean Sciences AMS Facility at Woods Hole Oceanographic Institution or the Keck Carbon Cycle AMS Laboratory at the University of California, Irvine. Reproducibility (1 standard deviation) of duplicate POM analyses was ±4–8‰ for $\Delta^{14}C$ and ±0.1‰ for $\delta^{13}C$. The $\Delta^{14}C$ and $\delta^{13}C$ values of three samples from the 50 mab trap were also analyzed for comparison with the results from the 650 mab trap.[1]

3. Results and Discussion

3.1. POC Flux

[12] The POC fluxes into the 50 mab and 600 mab traps were reported by *Smith et al.* [2001], and were temporally correlated with each other (r = 0.80, P < 0.001). For this study, we used the POC flux into the 600 mab trap as a proxy for the flux into our 650 mab trap to compare with our isotopic and chemical data.

[13] Briefly, POC flux reached a maximum of 26 mgC m^{-2} d^{-1} in June 1993 (Figure 2a). In summer 1994, a POC flux as high as in 1993 was observed in the 50 mab trap; unfortunately, the sediment traps at 650 mab and 600 mab failed to collect samples because of assumed "clogging" of the baffle by large-sized aggregated particle masses [*Baldwin et al.*, 1998]. In 1995 and 1996, there were no prominent peaks in POC flux. In late 1997 and early 1998, POC flux remained low (<5 mgC m^{-2} d^{-1}), likely due to a strong El Niño event that caused low productivity in the northeast Pacific [*Chavez et al.*, 2002]. In late 1998, POC flux was high (11 mgC m^{-2} d^{-1}) and was associated with a La Niña event [*Chavez et al.*, 2002].

3.2. $\Delta^{14}C$ Measurements of Sinking POM: Sources of Carbon

[14] The $\Delta^{14}C$ values obtained for samples collected in 10-day intervals from June 1993 through December 1998 ranged from about −80 to +40‰ (Figure 2b). The $\Delta^{14}C$ values in early 1995 and during 1998 were lower than for other periods. Large and rapid temporal variability was reflected at times with variations of larger than 16‰ (2 sigma) between two consecutive samples; for example, in April 1995, $\Delta^{14}C$ values decreased by 70‰ from the previous 10-day sample.

[15] Most sinking POM samples had post-bomb $\Delta^{14}C$ values (>−50‰) confirming a short turnover time

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[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gb/2004GB002221.
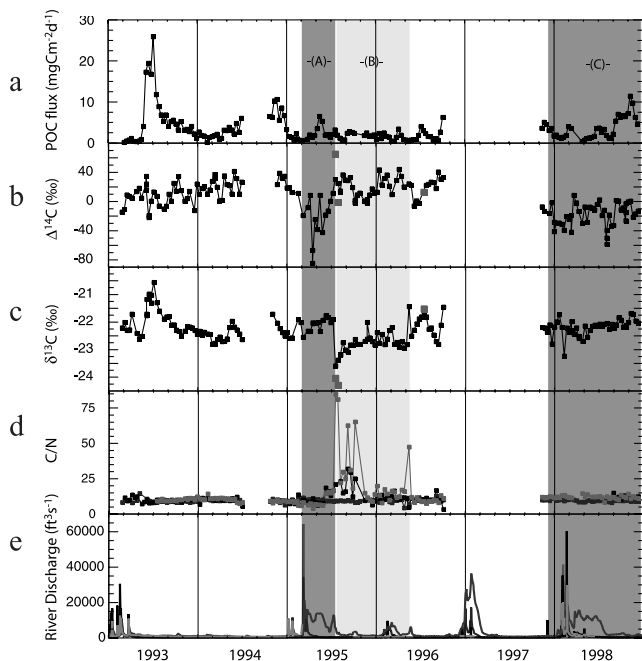
Figure 2. Time series data of sinking POM at Station M. The study period was divided into normal periods (no shading) and three special periods (A, B, and C) according to anomalous values of $\Delta^{14}C$, $\delta^{13}C$, and C/N values. (a) POC flux into the sediment trap moored at 600 mab. (b) $\Delta^{14}C$ values of sinking POM. Red squares are the results from three 50 mab samples. One standard deviation of duplicate analyses is 8‰ (error bars not shown). (c) The $\delta^{13}C$ values of sinking POM. One standard deviation of duplicate analyses is 0.1‰ (error bars not shown). (d) C/N molar ratios at 650 mab (blue, this study), 600 mab, and 50 mab (black and red, respectively [*Smith et al.*, 2001]). (e) Discharge rate of the San Joaquin River (brown, USGS station number 11274000), the Salinas River (blue, station number 11152500), the Santa Ynez River (pink, station number 11133500), and the Santa Clara River (black, station number 11114000). River discharge data were downloaded from USGS web site (http://waterdata.usgs.gov/nwis/discharge). There are hiatuses in the Santa Clara River data (October 1993 to September 1995) and the Santa Ynez River data (March 1992 to September 1992, April 1993 to December 1993, February 1994 to December 1994, March 1995 to September 1995, June 1996 to January 1998, June 1998 to December 1998). See color version of this figure at back of this issue.

(<30 years). However, $\Delta^{14}C$ values of sinking POM are lower than those of plankton (59–81‰ [*Wang et al.*, 1998]) and surface DIC measured at Station M from 1992 to 1998 (40–80‰ [*Masiello et al.*, 1998; E. R. M. Druffel and S. Griffin, unpublished data, 2004]). These data indicate that plankton from the overlying water was not the only source of sinking POM. Sinking POM must have acquired old carbon, because aging during its vertical transport is far too small to account for this vertical gradient in $\Delta^{14}C$. A vertical gradient was also observed in $\Delta^{14}C$ of suspended POM at Station M

[*Druffel et al.*, 1996] and at very remote locations where the influence of resuspended sediments was likely to be negligible [*Druffel and Griffin*, 1998]. The mechanisms suggested to explain this vertical gradient included sorption of DOM onto POM, incorporation of DOM by bacterial heterotrophy, and incorporation of DIC via anapleurotic reactions that produce organic compounds. Incorporation of DOM is likely responsible, at least partly, for low $\Delta^{14}C$ values of sinking POM at Station M [*Hwang*, 2004, chap. 6].

[16] If $\Delta^{14}C$ of sinking POM reflects mainly the temporal variability of $\Delta^{14}C$ of DIC in surface waters, then POM $\Delta^{14}C$ is expected to be high in El Niño years and low in non-El-Niño years. Upwelling of low $\Delta^{14}C$ subsurface water is suppressed during El Niño years, resulting in surface waters with $\Delta^{14}C$ values that are higher than during non-El-Niño years. However, a correlation between the $\Delta^{14}C$ values of sinking POM and El Niño-Southern Oscillation at this site is not apparent from these data. In contrast, sinking POM $\Delta^{14}C$ values were lower in 1998, a strong El Niño year, than during earlier years. This indicates that the original $\Delta^{14}C$ signatures were altered significantly after POM left the surface. The variability of sinking POM $\Delta^{14}C$ values (about 80‰) is greater compared to those of DIC in surface waters (~40‰) [*Masiello et al.*, 1998; E. R. M. Druffel and S. Griffin, unpublished data]. This suggests that processes exist to cause larger variability in sinking POM $\Delta^{14}C$ other than physical processes at the surface, associated with changes in water masses.

[17] One potential carbon source to sinking POM is organic matter that is advected laterally to the Station M water column. Lateral advection of resuspended sediment from the California margin has been documented by several investigators [*Druffel et al.*, 1998; *Sherrell et al.*, 1998; *Bianchi et al.*, 1998; *Smith et al.*, 2001]. The $\Delta^{14}C$ values of the surface sediments from the continental rise and slope are around −250‰ [*Druffel et al.*, 1998]. The 80‰ variability in sinking POM $\Delta^{14}C$ (−40 to 40‰) can be accounted for by incorporation of less than 30% resuspended SOM into sinking POM using simple isotopic mass balance (40‰ × (1 − x) + (−250‰) × x = −40‰, where x = the fraction of carbon from DOM in sinking POM = 0.28).

[18] Laterally transported material may contain young terrestrial OC and/or old carbon from eroded bedrock from rivers. Rivers near Station M (except the San Joaquin River) do not have well-developed estuaries and therefore export particles directly into the coastal ocean. A fraction of riverine POM may be exported as suspended POM beyond the continental shelf and then incorporated into sinking POM. During the flood of the Eel River in January 1995, only 25% of the exported sediment formed a recognizable deposit on the shelf [*Wheatcroft et al.*, 1997], implying that the other portion may have been dispersed over other parts of the continental margin. The Salinas, the Santa Ynez, and the Santa Clara Rivers are characterized as small mountainous rivers [*Inman and Jenkins*, 1999] and expected to export low $\Delta^{14}C$ OM because of a large inclusion of relict OM [*Kao and Liu*, 1996; *Masiello and Druffel*, 2001; *Blair et al.*, 2003; *Komada et al.*, 2004]. As an example, *Komada et al.* [2004] showed that suspended POM ($\Delta^{14}C$ values ranging from −232 to −544‰) in the Santa Clara River stream near the
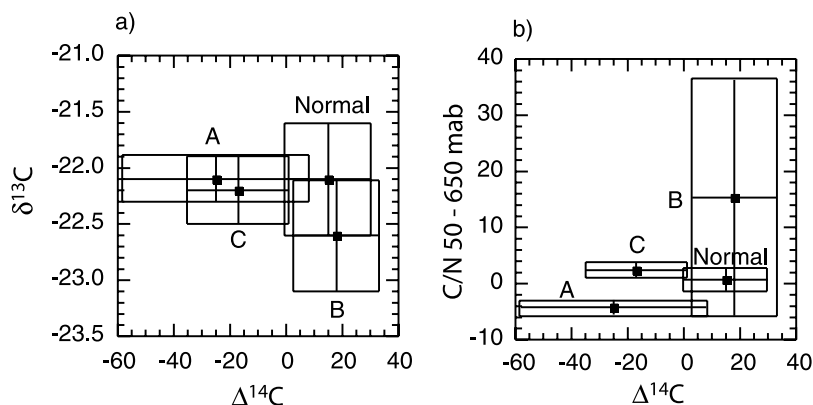
Figure 3. Property to property plots of (a) $\delta^{13}C$ versus $\Delta^{14}C$ values and (b) the difference between C/N in the 50 mab and C/N in the 650 mab trap samples versus $\Delta^{14}C$ values. The time series was divided into four periods (A, B, C, and normal) in accordance with the deviation of $\Delta^{14}C$, $\delta^{13}C$, and C/N values. The error bars are 1 standard deviation.

ocean was a mixture of ancient shale OM ($\Delta^{14}C$ values $<-885‰$) and modern soil OM ($\Delta^{14}C$ ranging from 45 to 122‰ at the surface). Sediments on the California shelf near the Santa Clara and the Santa Ynez Rivers appear to contain a significant amount (>20% of lipids and the acid-insoluble organic fraction) of old carbon from those rivers [Hwang, 2004]. Resuspended SOM from the shelf may also contain petroleum from natural seeps as sources of low $\Delta^{14}C$ OM [Wilson et al., 1974; Bauer et al., 1990].

3.3. Potential Causes of Variability in $\delta^{13}C$ Values for Sinking POM

[19] The $\delta^{13}C$ values of sinking POM ranged from -23.5 to $-20.5‰$ (Figure 2c). Except for the two short periods in mid-1993 and mid-1995, $\delta^{13}C$ values varied by less than 2‰. The degree of $\delta^{13}C$ fractionation during photosynthesis is a function of environmental factors, primarily pCO_2 in seawater and available light [Rau et al., 1992; Thompson and Calvert, 1994; Laws et al., 1995; Rost et al., 2002]. Because primary production affects pCO_2 levels near the producers, there is a positive correlation between $\delta^{13}C$ values of the phytoplankton and primary production (and therefore, sinking POC flux) [Deuser et al., 1968; Deuser, 1970; Rau et al., 1992]. The Station M data show a correlation ($r = 0.76$, $P < 0.001$, $n = 69$) between sinking POC flux and $\delta^{13}C$ values only during 1993, late 1994, and late 1996; this implies that during other periods, either pCO_2 was not depleted enough to cause detectable enrichment of ^{13}C or $\delta^{13}C$ values were modified by other processes. An abrupt decrease in $\delta^{13}C$ in summer 1995 that did not accompany significant change in POC flux is not likely to be caused by biological activity in surface waters.

[20] Sources other than plankton-derived POM from the overlying surface waters are considered to explain the variability of $\delta^{13}C$ values that is not correlated with POC flux. Unlike $\Delta^{14}C$ values, input of organic carbon from DOM, resuspended SOM, and relict OM from rivers will not cause significant change in POM $\delta^{13}C$, because their $\delta^{13}C$ signatures are similar to those of sinking POM (-21 to $-23‰$ [Bauer et al., 1998; Druffel et al., 1998]). However, terrestrial OC from C-3 plants has significantly

lower $\delta^{13}C$ values (-22 to $-34‰$ [Trumbore and Druffel, 1995; Meyers and Lallier-Vergès, 1999]); therefore incorporation of terrestrial organic carbon may be a cause of the variability.

3.4. Molar Ratio of Organic Carbon to Total Nitrogen (C/N)

[21] Molar C/N ratios of sinking POM at 650 mab at Station M were constant, ~10 during all sampling periods (Figure 2d). Generally, C/N values of sinking POM in the deep ocean are higher than the Redfield ratio for phytoplankton [Knauer et al., 1979; Loh and Bauer, 2000], and our data are consistent with this observation. Selective degradation of N-rich proteins in the water column may be a reason for this difference.

[22] The C/N values at 650 mab (this study) were compared with those of Smith et al. [2001] for 600 and 50 mab (Figure 2d). In 1993 and 1994, C/N values from all depths (10 ± 2) were similar, indicating that input of allochthonous OM was either negligible or affected all three traps equally. However, C/N values at 600 mab and 50 mab show dramatically different patterns from those at 650 mab in other periods. In early 1995, C/N values at 600 mab (9 ± 2) and 50 mab (7 ± 1) were slightly lower than those at 650 mab (11 ± 1). In July–November 1995 and January–May 1996, C/N values of POM at 50 mab and 600 mab were extremely high ($25–80$), while those at 650 mab remained unchanged (9 ± 1). Conversely in 1998, C/N values at 600 and 50 mab (12 ± 1) were slightly higher than those at 650 mab (10 ± 1). Extremely high C/N values also suggest that there were sources of OC other than plankton-derived OC from the overlying waters. The variation of the difference in C/N values among the traps suggests that the height of vertical reach of the allochthonous OC varied with time.

3.5. Periods of Anomalous Properties of Sinking POM

[23] The periods during which C/N values at three depths disagree coincide with those when $\Delta^{14}C$ and/or $\delta^{13}C$ values at 650 mab are anomalous. In accordance with the deviation of $\Delta^{14}C$, $\delta^{13}C$, and C/N values, the time series was divided into four periods (Figures 2 and 3: (1) normal periods: March

Table 1. Previously Reported Δ^{14}C, δ^{13}C, and C/N Values of the Organic Matter Sources at Locations Near the Study Site and the Direction of Change (in Parentheses) of These Properties When Sinking POM Incorporates Organic Matter From These Sources

	Δ^{14}C	δ^{13}C	C/N
DOM in the deep Pacific Ocean[a]	−550 (down)	−21 to −22 (no change)	18
Resuspended marine sediment on the California Margin[b]	−250 (down)	−22 (no change)	8–9 (no change)
Organic matter from the Santa Clara River[c]	−430 (down)	−22 (no change)	11 (no change)
Organic matter from terrestrial plants[d]	>0 (up)	−24 (down)	>10 (up)

[a]*Druffel et al.* [1992], *Bauer et al.* [1998], and *Loh and Bauer* [2000].
[b]*Wang et al.* [1998] and *Druffel et al.* [1998].
[c]*Masiello and Druffel* [2001].
[d]*Meyers and Lallier-Vergès* [1999].

1993 to June 1994, November 1994 to February 1995, and May 1996 to October 1996; (2) period A: February 1995 to May 1995; (3) period B: May 1995 to May 1996; and (4) period C: December 1997 to December 1998. The normal period is defined as that when δ^{13}C values are linearly correlated with sinking POC flux, and C/N values at all three depths are equal (Figure 3). The Δ^{14}C and δ^{13}C values for the 50 mab samples (red squares in Figures 2b and 2c) were similar to those of 650 mab samples only in the normal period (July 1996). Sinking POM in this period appears minimally influenced by allochthonous OC, and is therefore assumed to be representative of open ocean POM. Period A is defined by low and variable Δ^{14}C values (−25 ± 33‰) and significant variability in C/N among samples at three depths (Figure 3b). Period B is defined by low δ^{13}C values (−22.6 ± 0.5‰), normal or slightly elevated Δ^{14}C (18 ± 15‰), and large differences in C/N values among samples at three depths. Period C is similar to period A except that C/N values at 650 mab were lower than those at 600 and 50 mab (Figure 2d).

[24] We considered three processes that might be responsible for the variability of the isotopic signatures and the C/N values of sinking POM during these periods: (1) input of resuspended SOM from local or shelf/slope sources; (2) input of old OM from land via rivers; and (3) input of young OM from terrestrial plants via rivers. Resuspended SOM may also contain OC from small mountainous rivers as discussed in section 3.2. Previously reported Δ^{14}C, δ^{13}C, and C/N values of the potential organic carbon sources at locations close to the study site, and the direction of change of these properties when sinking POM includes organic matter from these sources, are listed in Table 1.

[25] The rapid decrease in Δ^{14}C values during period A requires one or more processes that can occur over a 10-day time period. Incorporation of resuspended SOM is one possible mechanism, because of the low Δ^{14}C values (−250‰) for SOM but similar δ^{13}C values in SOM relative to sinking POM. The C/N value for SOM was around 10 in surface sediment at Station M in 1995 [*Smith et al.*, 2001] and around 8 in a slope site in 2001 [*Hwang*, 2004].

[26] During period B, C/N values at 50 and 600 mab were extremely high, while those at 650 mab remained unchanged (9 ± 1). In the mid-July 1995 sample, when the C/N value at 50 mab was the highest (85), the δ^{13}C value decreased from −21.9 to −23.6‰, while Δ^{14}C values increased by 20‰. This δ^{13}C value is the lowest observed during the entire study period. High C/N and high/normal Δ^{14}C values combined with low δ^{13}C values indicate the presence of modern,

terrestrial organic matter. The isotopic signatures of sinking POM from the 50 mab trap when C/N values were the highest (June 1995) showed an even stronger signal (red squares in Figures 2b and 2c). The Δ^{14}C and δ^{13}C values were 66‰ and −24.0‰, respectively.

[27] The dominant terrestrial vegetation (>99%) in most California watersheds is C-3 plants [*Still et al.*, 2003]. The δ^{13}C values of surface soil OC in the Santa Ynez basin ranged from −27 to −28‰ [*Komada et al.*, 2004]; thus incorporation of terrestrial OC into sinking POM will lower δ^{13}C values. The small mountainous rivers are not likely the source of the modern terrestrial OC, unless plant debris is separated from relict OC during transport due to the differences in their physical properties. However, the San Joaquin River has a relatively large drainage basin (19,024 km^2), 32% of which is cropland and pasture [*Saleh et al.*, 2003] and is likely to export modern plant material during the rainy seasons.

[28] It is interesting that the C/N values of POM at 650 mab remained constant (∼9) during Event B, and did not appear to reflect the input of terrestrial OC as did the isotopic signatures and the C/N values of the samples from the deeper traps (Figure 2d). However, C/N is not a conservative property in the sense that C and N can be degraded at different rates. In addition, C/N values cannot be treated linearly as in a simple mass balance equation. For example, a 50:50 mixture by weight of two POM pools with the same OC content but different C/N values (80C/1N versus 80C/10N) will have a C/N value of 14.5 instead of 44. Therefore, unlike isotopic signatures, the change of C/N by mixing with other POM may be small in comparison.

[29] Period C was similar to period A, except that C/N values at 50 and 600 mab were higher than those at 650 mab during this period. Low Δ^{14}C (−20‰) and normal δ^{13}C values of sinking POM may suggest incorporation of resuspended SOM into POM. The C/N values of resuspended SOM may also vary with time. For example, *Smith et al.* [2001] reported an increase in C/N from 8 in 1990 to about 12 in 1996, and the highest value (∼19) was observed in 1998 in SOM at Station M. Therefore the same process of SOM incorporation as in period A may have caused the observed vertical distribution of C/N values.

3.6. Potential Mechanisms of Lateral Transport of Resuspended SOM

[30] *Smith et al.* [2001] reported previously that temporal peaks in C/N at 50 mab were correlated with the San Joaquin River discharge with a time lag of about 4 months.

We compared periods of high discharge rates of four rivers close to the study site with the periods of anomalous properties of sinking POM (Figure 2e). Discharge rates in 1992/1993 winter were relatively low, and only a small difference in C/N values at 650 and 600 mab was observed in early 1993. In winter 1993/1994, river discharge rates were very low, and our data show negligible input of resuspended SOM. The high river discharge rates in 1995 and in 1998 correlate with anomalous properties of sinking POM with a time lag of 2 to 4 months. Although a cause-effect relationship between river discharge and anomalous properties of sinking POM cannot be confirmed at this point, river discharge is apparently related with the driving force of lateral transport of resuspended SOM and/or riverine POM. Regional weather may thus be an important controlling factor influencing the properties of sinking POM at Station M. Winter storms may enhance resuspension of sediments; however, wind speed recorded at a buoy station (National Data Buoy Center, station 46023, data not shown) during the study period did not show a clear pattern of high wind in winter.

[31] The mechanism of lateral transport, especially to the deep water column, in the study area is not well understood. One potential mode of lateral transport to Station M is lateral dispersion along isopycnal surfaces, and then vertical transport via gravity. Another potential mode is lateral flow along the ocean floor as a thick nepheloid layer. When river water contains a high enough particle load its density may exceed that of seawater, and a hyperpycnal plume or margin plume can develop [*Imran and Syvitski*, 2000; *Wheatcroft*, 2000]. Hyperpycnal plumes have been observed from small mountainous rivers such as the Eel River and the Santa Clara River [*Wheatcroft et al.*, 1997; *Mertes and Warrick*, 2001; *Warrick*, 2002]. *Warrick* [2002] showed that over 99% of the discharge by the Santa Clara River might be hyperpycnal. He also showed schematically that thick bottom nepheloid layers initiated by hyperpycnal plumes could move farther to the outer shelf than the hyperpycnal plumes [*Warrick*, 2002]. The signal of resuspended SOM or terrestrial OM was strongest in the 50 mab trap, suggesting that this mode of lateral advection is a more plausible mechanism of OM transport to our site.

4. Implications for the Carbon Cycle

[32] It has been suggested that a large fraction of OM produced on continental shelves may be transported to slope waters and sediments [*Walsh et al.*, 1981; *Bauer and Druffel*, 1998; *Bauer et al.*, 2001]. The results of programs such as SEEP I and II suggested that a very small fraction (much smaller than 5%) of the primary production on the eastern U.S. shelf was exported to the continental slope [*Biscaye et al.*, 1994]. However, other reports suggest that a significant amount of OC (9 ± 6% of primary production of the coastal ocean) is transported from the continental margins to the ocean basin [*Bauer and Druffel*, 1998; *Bauer et al.*, 2001; *Liu et al.*, 2000, and references therein]. Sediment reworking by resuspension on the Southern California Shelf was indicated by low $\Delta^{14}C$ values of SOM in spite of high sedimentation rates [*Santschi et al.*, 2001; *Hwang*, 2004]. Higher OC content (3%) in the sediment was observed at a continental rise site (3800 m water

depth) than at other sites of different water depths between Station M and the California coast (4100, 2000, 500, 200, and 100 m water depths [*Druffel et al.*, 1998; *Hwang*, 2004]). This site may be a deposition center of OC, implying that OC transport from the shelf is a persistent phenomenon in the continental slope near Station M.

[33] Nearly 20% of oceanic primary production takes place in coastal oceans [*Martin et al.*, 1987; *Hedges*, 1992; *Liu et al.*, 2000], and this value is expected to increase because of human activities, such as enhanced input of nutrients. Sediment resuspension and transport appear to be enhanced by coastal storms and river discharge in winter seasons in the California coast. The correlation between OC transport and weather implies that OC transport may be different in the future as a response to the global climate change. Our results imply that change in OC transport from the margins to the deep ocean in relation with regional weather should be considered for better prediction of future change in global carbon cycling.

[34] The transport of OC has an implication for paleoclimatology as well. Interpretation of paleo-temperature proxies requires that the compounds in a sediment horizon have the same temporal and spatial origin. However, our results suggest that care should be taken in interpreting the paleochronological data. Displacement by resuspension, advective transport, and then deposition of pre-aged organic compounds can cause large offset in the ages between time proxies and temperature proxies [*Ohkouchi et al.*, 2002].

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R. J. Baldwin and K. L. Smith Jr., Marine Biology Research Division, Scripps, Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093, USA. (rbaldwin@ucsd.edu; ksmith@ucsd.edu)

J. E. Bauer, School of Marine Science, College of William and Mary, Gloucester Point, VA 23062, USA. (bauer@vims.edu)

E. R. M. Druffel, S. Griffin, and J. Hwang, Department of Earth System Science, University of California, Irvine, Irvine, CA 92697, USA. (edruffel@uci.edu; sgriffin@uci.edu; jeomshik@uci.edu)
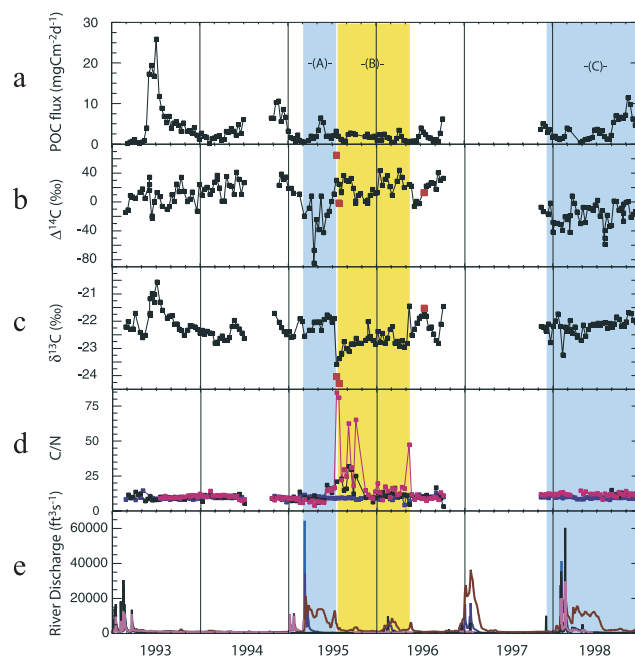
Figure 2. Time series data of sinking POM at Station M. The study period was divided into normal periods (no shading) and three special periods (A, B, and C) according to anomalous values of $\Delta^{14}C$, $\delta^{13}C$, and C/N values. (a) POC flux into the sediment trap moored at 600 mab. (b) $\Delta^{14}C$ values of sinking POM. Red squares are the results from three 50 mab samples. One standard deviation of duplicate analyses is 8‰ (error bars not shown). (c) The $\delta^{13}C$ values of sinking POM. One standard deviation of duplicate analyses is 0.1‰ (error bars not shown). (d) C/N molar ratios at 650 mab (blue, this study), 600 mab, and 50 mab (black and red, respectively [*Smith et al.*, 2001]). (e) Discharge rate of the San Joaquin River (brown, USGS station number 11274000), the Salinas River (blue, station number 11152500), the Santa Ynez River (pink, station number 11133500), and the Santa Clara River (black, station number 11114000). River discharge data were downloaded from USGS web site (http://waterdata.usgs.gov/nwis/discharge). There are hiatuses in the Santa Clara River data (October 1993 to September 1995) and the Santa Ynez River data (March 1992 to September 1992, April 1993 to December 1993, February 1994 to December 1994, March 1995 to September 1995, June 1996 to January 1998, June 1998 to December 1998).