Transport of organic carbon from the California coast to the slope region: A study of $\Delta^{14}C$ and $\delta^{13}C$ signatures of organic compound classes

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[1] Surface sediments along a transect from an abyssal site in the northeastern Pacific (Station M, 34°50′N, 123°00′W) to a small mountainous river on the California coast (Santa Clara River) were studied to investigate the sources and cycling of organic matter on the continental margin. Sediment samples were separated into organic compound fractions (extractable lipids, amino acids (THAA), carbohydrates (TCHO), and the acid-insoluble fraction), and their carbon isotope ratios were measured. The $\Delta^{14}C$ values of all the THAA and TCHO fractions were greater than −100‰, indicating relatively modern organic carbon (OC) source(s), and rapid cycling of these fractions. In contrast, the $\Delta^{14}C$ values of extractable lipids and the acid-insoluble fraction were distinctly lower than those of the THAA and TCHO fractions. The $\Delta^{14}C$ values of source OC to the sediments were estimated using a simple mixed layer model. These values were lower than the $\Delta^{14}C$ signatures of pre-industrial plankton suggesting input of both old OC and contemporary plankton to the margin sediments. The source of old OC at the 2000-m site was likely from laterally transported coastal sediment. The estimated low $\Delta^{14}C$ value of the transported OC suggests that old lipids and acid-insoluble material were selectively transported to the 2000-m site. The contribution of riverine POC to the margin sediments were estimated from $\Delta^{14}C$ and $\delta^{13}C$ values and indicate that relict OC exported by rivers was an important source of old lipids and acid-insoluble material to sedimentary OC on the shelf.

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1. Introduction

[2] Lateral transport is an important mechanism for controlling the composition of sedimentary organic carbon (SOC) on continental margins. Resuspension, lateral transport, and deposition are expected to enhance remineralization of more easily degradable components of SOC because of extended oxygen exposure time [*Hartnett et al.*, 1998; *Gélinas et al.*, 2001; *Aller and Blair*, 2004]. By this mechanism, more refractory components of SOC can be selectively transported to the deep ocean. Compound specific radiocarbon analyses have indicated that lateral advection of organic carbon (OC) is a widespread phenomenon [*Ohkouchi et al.*, 2002; *Mollenhauer et al.*, 2003]. However, studies of the lateral transport and its role in controlling biochemical compositions and isotopic signatures of SOC are far fewer than those examining vertical transport.

[3] The western coast of the United States is a tectonically active margin with a narrow continental shelf and steep slope; these characteristics may facilitate lateral transport of carbon relative to passive margins. Deposition of laterally transported OC on the slope of the California margin was suggested from a study of benthic remineralization and burial [*Jahnke et al.*, 1990; *Reimers et al.*, 1992]. Previous studies performed at the abyssal site, Station M (4100 m water depth, 220 km off the coast of central California) indicate that sinking and suspended particulate organic carbon (POC) contains resuspended SOC and river-exported POC despite the distance from land [*Bianchi et al.*, 1998; *Sherrell et al.*, 1998; *Smith et al.*, 2001].

[4] ^{14}C ages of sinking POC collected at 3450 m depth and deep suspended POC at Station M were much older than expected from their short turnover time, indicating that they contained ^{14}C-depleted (old) OC [*Druffel et al.*, 1998; *Hwang et al.*, 2004]. Studies of radiocarbon isotope signa-

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tures of organic compound classes (extractable lipids, THAA (total hydrolyzable amino acids), TCHO (total hydrolyzable neutral carbohydrates), and the acid-insoluble fraction of deep sinking POC at Station M revealed that old OC was present exclusively in extractable lipids and the acid-insoluble fraction) [*Wang et al.*, 1998; *Hwang and Druffel*, 2003]. Although not fully understood, selective incorporation of OC from dissolved organic carbon (DOC) and/or resuspended SOC were likely sources of the old OC to these organic fractions.

[5] Along an active margin, small mountainous rivers export relict OC from eroded bedrock [*Blair et al.*, 2003; *Masiello and Druffel*, 2001, *Komada et al.*, 2004]. Relict OC is refractory in the sense that it has survived at least one geological cycle of sedimentation-rock formation-mountain uplifting. In a companion paper, *Komada et al.* [2005] showed that OC exported by the Santa Clara River contained a high proportion of bitumen (organic solvent-extractable fraction of relict organic matter) and kerogen (relict organic matter that is not extracted by organic solvents). These are operationally similar to the extractable lipids and the acid-insoluble fractions, respectively. Therefore, relict OC from rivers may be a source of old OC observed in POC and sediments on the California margin.

[6] In this paper, we studied lateral transport of resuspended sediments and contribution of river-exported OC to the California margin sediment. We focused on different biogeochemical behavior of individual compound classes depending on their lability.

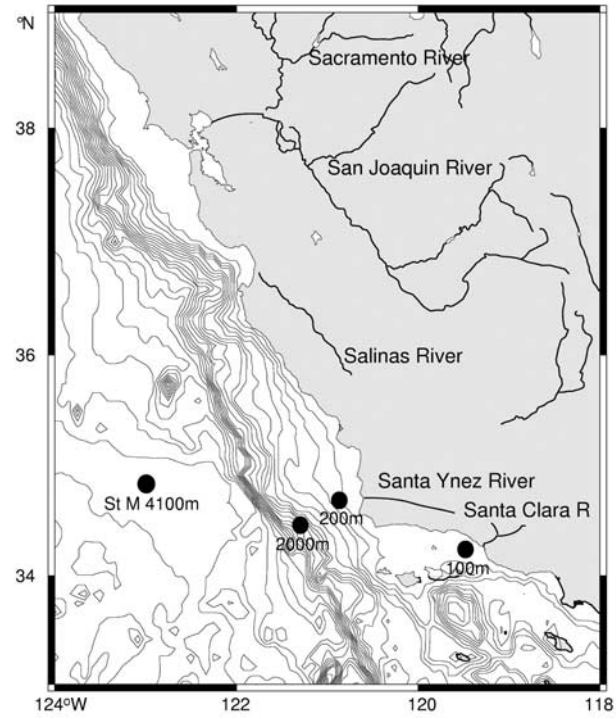

Figure 1. Sampling locations for sediments used in this study. The actual water depths at these stations (2000-m, 200-m, and 100-m sites) were 1866-m, 225-m, and 92-m from west to east. The location of Station M is also indicated.

2. Sample Collection and Analyses

[7] Sampling sites were chosen along an east-west transect between Station M and the mouth of the Santa Clara and Santa Ynez Rivers on the California margin (Figure 1). Sediments were collected at 1866 m (34°28′N, 121°19′W, hereinafter, 2000-m site) and 225 m (34°41′N, 120°53′W, hereinafter, 200-m site) water depths using a Multicorer during the MULVFS cruise aboard the R/V *New Horizon* in August 2001. Sediment was also collected at 92 m (34°15′N, 119°33′W, hereinafter, 100-m site) water depth using a Soutar box corer during the PULSE-40 cruise aboard the R/V *New Horizon* in June 2002. Sediment in the box core was subcored onboard ship using 3-inch diameter push cores and sectioned in 0.5 to 3 cm thicknesses. Samples were frozen at −20°C in pre-combusted glass jars. Upon returning to the laboratory at University of California, Irvine, the samples were thawed and either lyophilized or poisoned with saturated mercuric chloride solution then dried in air at 50°C. Dried samples were finely ground and stored frozen until analyses.

[8] For isotope analyses of total organic matter, each sediment sample was acidified with 1 mL of 3% phosphoric acid overnight in a quartz tube (Vycor, 9 mm outer diameter). Combustion of samples and cryogenic purification of the resultant CO_2 gas were performed using standard procedures [*Druffel et al.*, 1992]. Percent organic carbon (OC%) was determined by manometric measurement of the CO_2 produced. About 0.8 mgC was graphitized on a Co catalyst at 580°C for 8 hours using H_2 gas as the reductant [*Vogel et al.*, 1987].

[9] Samples from the tops of the sediment cores (0 to 1 cm) were separated into organic compound fractions: extractable lipids, THAA, TCHO, and the acid-insoluble fraction (see *Wang et al.* [1998] for more detail). Briefly, lipids were extracted using a mixture of methylene chloride and methanol (2:1 volume:volume) by ultrasonic treatment. About a half of the residue was hydrolyzed with 6N HCl for THAA extraction, and the other half was hydrolyzed with 72% then 1.2N H_2SO_4 for TCHO extraction. The hydrolyzates were eluted through ion exchange columns for separation of THAA and TCHO from each other. (Further analyses of THAA fraction isolated by this method proved that this fraction contained other minor compounds as well [*Quan*, 2005]. However, this method is valid for our purpose of separation of labile, hydrolyzable, amino acids-like material.) Any residue that remained after HCl-hydrolysis was defined as the acid-insoluble fraction. Each fraction was transferred into a quartz combustion tube (Vycor brand) and treated in the same way as for isotopic analyses of total organic matter. In addition to marine SOC, POC suspended near the mouth of the Santa Clara River was analyzed to determine the importance of riverine input of relict OC to the ocean [*Komada et al.*, 2005].

[10] Carbon isotope ratio measurements were performed at the Keck Carbon Cycle AMS Laboratory at the Univer-

Table 1. Measured Properties of Bulk Sedimentary Organic Carbon

Depth, cm	UCID Number	Total C $\delta^{13}C$, ‰	Total N, %	Total C, %	OC, %	Org. C $\delta^{13}C$, ‰[a]	Org. C $\Delta^{14}C$, ‰[a]
			100 m Water Depth, 34°15′N, 119°33′W				
0–0.5	5394	−20.0	0.13	1.5	1.2	−23.6, −23.6	−173
0.5–1	5395	−20.3	0.13	1.5	1.2	−23.8	−174
1–2	5396	−20.2	0.12	1.5	1.1	−23.9, −23.9	−150
2–4	5397	−20.1	0.12	1.6	1.2	−23.7	−175
4–6	5398	−20.0	0.13	1.6	1.2	−23.7	−182
6–8	5399	−20.1	0.12	1.5	1.1	−24.0	−218
8–10	5400	−20.1	0.11	1.4	1.1	−23.9	−217
10–13	5401	−19.8	0.11	1.5	1.1	−23.9	−229
13–16	5402	−19.7	0.11	1.5	1.1	−24.1	−247, −253
			200 m Water Depth, 34°41′N, 120°53′W				
0–0.5	5381	−16.0	0.08	0.8	0.5	−21.4	−202
0.5–1	5382	−16.2	0.08	0.9	0.6	−21.7	−216
1–1.5	5383	−16.5	0.08	0.9	0.6	−21.6, −21.6	−186
1.5–2	5384	−16.4	0.08	0.9			
2–2.5	5385	−16.4	0.06	0.7	0.6	−21.8	−215
2.5–3	5386	−16.1	0.07	0.9			
3–3.5	5387	−16.2	0.07	0.8	0.5	−21.9	−219
3.5–4	5388	−16.2	0.08	0.8			
4–4.5	5389	−16.3	0.07	0.9	0.5	−21.9	−214
4.5–5	5390	−16.3	0.07	0.8			
5–6	5391	−16.1	0.06	0.8	0.5	−21.9	−237
6–7	5392				0.6	−21.9	−208
7–8	5393	−16.6	0.08	0.9	0.6	−22.0	−228
			2000 m Water Depth, 34°28′N, 121°19′W				
0–0.2	5120	−15.7				−21.4	−141
0.2–0.5	5358	−15.8	0.38	4.2	2.5	−21.3	−166, −149
0.5–1	5359	−15.8	0.37	4.2	2.5	−21.5	−167, −163
1–1.5	5360	−15.9	0.37	4.1	2.5	−21.5	−194
1.5–2	5361	−15.8	0.37	4.2	2.5	−21.5	−190
2–2.5	5362	−15.7	0.36	4.2	2.5	−21.5	−187
2.5–3	5363	−15.5	0.36	4.1			
3–3.5	5364	−15.7	0.36	4.1	2.4	−21.4	−190
3.5–4	5365	−15.5	0.36	4.1			
4–4.5	5366	−15.4	0.36	4.1	2.4	−21.5	−206
4.5–5	5367	−15.4	0.35	4.0	2.3	−21.5, −21.5	−212
5–6	5368	−15.1	0.35	4.1	2.3	−21.4	−217, −218
6–7	5369	−15.0	0.34	4.0			
7–8	5370	−14.9	0.34	4.0	2.1	−21.3	−229, −225
8–9	5371	−14.5	0.32	4.0			
9–10	5372				2.1	−21.2	−244
10–11	5373	−14.4	0.32	4.0			
11–12	5374	−14.4	0.32	4.0	2.2	−21.3	−250
12–13	5375	−14.3	0.31	3.9			
13–14	5376	−14.5	0.32	3.9	2.1	−21.3, −21.3	−267, −270
14–15	5377	−14.3	0.31	3.9			
15–18	5378	−14.2	0.32	4.0	2.1	−21.3	−294
18–21	5379	−14.1	0.31	4.0	2.1	−21.1	−330
21–24	5380	−14.2	0.31	3.9	2.0	−21.1	−322, −320

[a]Where two values appear, splits were run.

sity of California, Irvine. Radiocarbon results are reported as $\Delta^{14}C$, which is per mil deviation of the $^{14}C/^{12}C$ ratio relative to a nineteenth century wood standard, corrected to $\delta^{13}C$ of −25‰. The average differences between the results of split CO_2 samples were 5‰ for $\Delta^{14}C$ (n = 7) and 0.05‰ for $\delta^{13}C$ (n = 5; Table 1). The $\Delta^{14}C$ and $\delta^{13}C$ values of the organic fractions were blank-corrected using the standard dilution method described by *Hwang and Druffel* [2005]. Blank correction for the $\Delta^{14}C$ values of organic fractions was small (on average, 6 ± 9‰), except for two small THAA samples (0.39 and 0.19 mgC, compared to the mass of blank carbon 0.09 mgC), which resulted in large total uncertainties (±27 and ±390‰, respectively; see Table 2).

3. Results and Discussion

3.1. Organic Carbon Content (OC%), $\Delta^{14}C$, and $\delta^{13}C$ Values of Total Organic Matter

[11] Percent OC of sediment at the three locations ranged from 0.5 to 2.5% (Table 1 and Figure 2a) in the upper 25 cm of the sediment column. The OC% values of sediment at the 100-m and 200-m sites were nearly constant with depth within 0.2% range. At the 2000-m site, OC% was 2.5%

Table 2. Yields and the Isotopic Signatures of the Organic Fractions of SOC[a]

Samples	Extractable Lipids			THAA			TCHO			Acid Insoluble		
	Percent of SOC	$\Delta^{14}C$, ‰	$\delta^{13}C$, ‰	Percent of SOC	$\Delta^{14}C$, ‰	$\delta^{13}C$, ‰	Percent of SOC	$\Delta^{14}C$, ‰	$\delta^{13}C$, ‰	Percent of SOC	$\Delta^{14}C$, ‰	$\delta^{13}C$, ‰
Riverine POC	10	−845 ± 6	−23.8 ± 0.1	1	−400 ± 390	n/a	4	−11 ± 15	−23.6 ± 1.2	48	−649	−24.4
100 m, 0–0.5 cm	8	−534 ± 6	−23.3 ± 0.1	7	12 ± 9	−19.8 ± 0.4	7	40 ± 8	−20.5 ± 0.4	51	−236	−24.7
100 m, 0.5–1 cm	7	−585 ± 6	−23.6 ± 0.1	2	43 ± 27	−19.7 ± 1.6	6	35 ± 9	−20.9 ± 0.5	50	−246	−24.8
200m, 0–0.5cm	n/a	n/a	n/a	4	−17 ± 19	−17.6 ± 1.0	6	−21 ± 11	−19.6 ± 0.5	46	−301	−22.4
200 m, 0.5–1 cm	6	−357 ± 6	−22.8 ± 0.1	4	−52 ± 28	−18.0 ± 1.5	5	−20 ± 12	−19.6 ± 0.6	55	−300	−22.8
2000 m, 0–0.2 cm	6	−311 ± 6	−23.3 ± 0.1	5	−93 ± 21	−17.6 ± 0.8	9	−78 ± 8	−19.1 ± 0.3	n/a	n/a	n/a
2000 m, 0.2–0.5 cm	5	−319 ± 6	−23.4 ± 0.1	6	−87 ± 10	−18.1 ± 0.3	8	−68 ± 6	−19.0 ± 0.2	49	−197	−22.2
4100 m, 0.2–0.5 cm	2	−404 ± 31	−23.4	18	−114 ± 19	−18.5	18	−94 ± 37	−16.9	49	−354 ± 9	−22.9

[a]Blank correction was performed using four, three, and four sets of processed standards (cod liver oil, glutamic acid, and D-glucose) for extractable lipids, THAA, and TCHO, respectively, following a method described by *Hwang and Druffel* [2005]. The acid-insoluble fractions were not blank-corrected because their masses were sufficiently large (>7 mgC) compared to that of blank carbon (<0.01 mgC). Data for the 4100-m site from *Wang et al.* [1998] are also shown for comparison. Here n/a means data not available.

from 0 to 2.5 cm, and then decreased gradually to 2.0% to 23 cm depth.

[12] The $\Delta^{14}C$ values for the bulk SOC at our three sites ranged from −140‰ to −330 ‰ (Figure 2b). At the 200-m site, the $\Delta^{14}C$ values did not show any discernable trend with depth. The $\Delta^{14}C$ values at the 100-m and 2000-m sites from the surface of the sediments to 4–5 cm depths were almost constant, and gradually decreased with depth below these depths. The $\Delta^{14}C$ values between 1 and 4 cm at the 2000-m site were virtually identical, indicating that this layer was well mixed. However, the $\Delta^{14}C$ values of the layer from the surface to 1 cm were significantly higher than those of the layer below. These fluctuations in $\Delta^{14}C$ values near the surface are discussed further in section 3.3.

[13] The $\delta^{13}C$ values of bulk SOC ranged from −24.0 to −21.0 ‰ (Figure 2c). These values are lower than those of marine phytoplankton [*Wang et al.*, 1998], but similar to those of sinking POC collected at 3450 m depth at Station M, (ranged from −21 to −23‰ [*Hwang et al.*, 2004]). The $\delta^{13}C$ values at the 100-m site (−23.5 to −25.0‰) were lower than the other sites by about 2‰. The $\delta^{13}C$ values at the 200-m site (−21 to −22‰) were slightly lower than those at the 2000-m site which were not different from those at Station M. Thus, judging from the bulk SOC $\delta^{13}C$ values, inclusion of terrestrial OC was apparent only at the 100-m and 200-m sites. The vertical distributions of $\delta^{13}C$ values were uniform within a 0.5‰ range at each site, indicating that selective remineralization of organic fractions of various $\delta^{13}C$ values was not significant.

3.2. Abundances, $\Delta^{14}C$, and $\delta^{13}C$ Values of the Organic Compound Fractions of SOC and Riverine POC

[14] Extractable lipids, THAA, and TCHO each accounted for 5 to 10% of the total SOC, and the acid-insoluble fraction accounted for about 50% of the SOC (Table 2). The extracted organic fractions accounted for 68 to 72% of total SOC. The abundances of THAA and TCHO did not show any apparent trend along the transect. However, the abundance of extractable lipids showed a decreasing trend from the coastal site to the deep ocean.

[15] The $\Delta^{14}C$ values of THAA and TCHO were similar, and higher than $\Delta^{14}C$ values of extractable lipids and the acid-insoluble fraction (Table 2 and Figure 3; the dotted lines connecting the symbols from site to site are to distinguish each organic fraction, and do not indicate interpolation of data). The differences are most prominent at the 100-m site where $\Delta^{14}C$ values of extractable lipids and the acid-insoluble fraction were 560 and 270‰ lower than the averages of THAA and TCHO, respectively. The $\Delta^{14}C$ values of THAA and TCHO in surface SOC at the 100-m site were positive, indicative of the presence of bomb ^{14}C and rapid cycling of carbon within these organic fractions. In contrast, low $\Delta^{14}C$ values of lipids and the acid-insoluble fraction indicate either slow cycling and/or existence of old carbon source.

[16] The $\delta^{13}C$ values of extractable lipids were lower than those of THAA and TCHO (Table 2 and Figure 4). This is partly because of different degrees of physiological fractionation during the synthesis of the compound classes by organisms [*Degens et al.*, 1968; *DeNiro and Epstein*, 1977; *Hayes*, 2001]. The $\delta^{13}C$ values of the acid-insoluble fraction were distinctly lower than those of THAA and TCHO, but were similar to those of extractable lipids. The same was observed for sinking POC at Station M [*Hwang and Druffel*, 2003].

[17] The $\Delta^{14}C$ values of the organic fractions of riverine POC indicate that there were at least two sources of distinctly different $\Delta^{14}C$ signatures (i.e., TCHO from a modern source and extractable lipids from relict OC). The $\delta^{13}C$ values also indicate the same: Despite the fact that the $\delta^{13}C$ values of lipids in organisms are significantly lower than those of THAA and TCHO because of physiological fractionation, the $\delta^{13}C$ values of the organic fractions of the river sample overlap with each other. This indicates that TCHO and extractable lipids originated from different sources. In synthesis, TCHO originated from modern terrestrial plants while extractable lipids originated from relict OC of marine-origin bedrock. This is reflected in higher abundance of extractable lipids (10%) than THAA (1%) and TCHO (4%). Normally, carbohydrates are the major component of terrestrial plants. Sources of riverine POC are discussed in more detail in the companion paper [*Komada et al.*, 2005].

[18] As was indicated by the bulk SOC $\delta^{13}C$ values, riverine input at the 100-m and 200-m sites is apparent for organic fractions as well. The $\Delta^{14}C$ values of lipids and $\delta^{13}C$ values of TCHO at the margin sites were intermediate

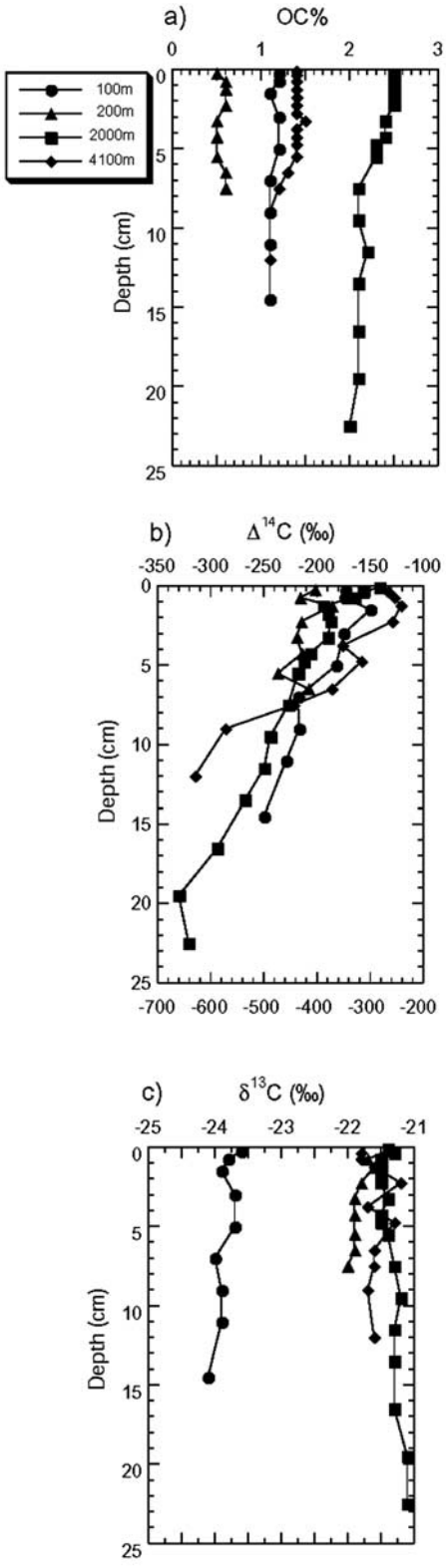

Figure 2. Vertical distributions of (a) OC%, (b) $\Delta^{14}C$ (note that the 4100-m site results are plotted on the bottom horizontal axis) and (c) $\delta^{13}C$ values of sedimentary organic carbon on the California margin. Previously reported data at the 4100-m site by *Wang et al.* [1998] are also shown for comparison.

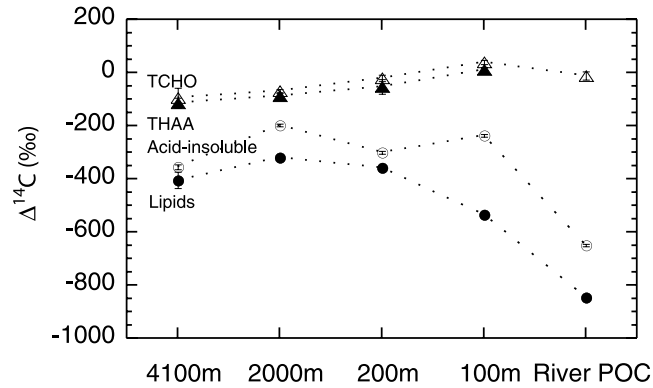

Figure 3. The $\Delta^{14}C$ values of the organic fractions (THAA, solid triangles; TCHO, open triangles; extractable lipids, solid circles; the acid-insoluble fraction, open circles) in the top 1 cm of sediment core (see Table 2). Where visible, vertical lines are total uncertainties from Table 2. The data for the 4100-m site (0.2–0.5 cm depth) are from *Wang et al.* [1998].

between the values at Station M and riverine POC, implying the possibility of two end-member mixing between marine POC and riverine POC (Figures 3 and 4).

3.3. Source OC to Sediments and Implications for Lateral Transport

[19] The $\Delta^{14}C$ values of core top SOC were all lower than those of pre-industrial plankton. Several processes contribute to old ^{14}C ages of SOC at the water-sediment interface. Bioturbation mixes younger SOC near the surface with older, deeper SOC. Input of pre-aged OC from land or allochthonous resuspended SOC, and selective removal of relatively ^{14}C-enriched organic fractions by dissolution, oxidation, and heterotrophic consumption after sedimentation can contribute to old ^{14}C ages. If selective mineraliza-

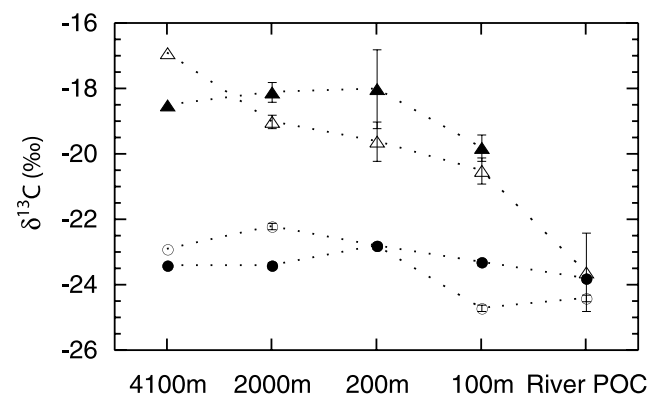

Figure 4. The $\delta^{13}C$ values of the organic fractions (THAA, solid triangles; TCHO, open triangles; extractable lipids, solid circles; the acid-insoluble fraction, open circles). Where visible, vertical lines are total uncertainties from Table 2. Data for the 4100-m site are from *Wang et al.* [1998]. See Figure 3 caption for sediment layer depth.

tion in the sediment column is minor, as indicated by little change in $\delta^{13}C$ with depth at our sites, then the effect of bioturbation can be factored out. Taking this approach, we estimated the $\Delta^{14}C$ signature of the source OC (i.e., OC supplied from the water column) from the sedimentation rate, the depth of the mixed layer (defined as the layer with uniform $\Delta^{14}C$ values near the water-sediment interface), and the $\Delta^{14}C$ value of SOC in the mixed layer using a simple mixed layer model. A comparison of the estimated $\Delta^{14}C$ values of the source OC to those of contemporary, plankton-derived POC would help to evaluate the relative contribution of laterally transported old OC across the margin.

[20] In our mixed layer model, complete homogenization was assumed in the fixed-depth mixed layer (i.e., rate of bioturbation is much higher than the sedimentation rate). Aging was assumed to be the only process that changed the $\Delta^{14}C$ values. In consequence, the age ($\Delta^{14}C$ values) of SOC is uniform throughout depth within the mixed layer. The time needed for sediment to accumulate to a thickness equivalent to that of the mixed layer was calculated by dividing the mixed layer depth with the sedimentation rate. A half of this value was subtracted from the age of SOC in the mixed layer to estimate the age of source OC. The age of SOC at the lower boundary of the mixed layer was used as the age of SOC in the mixed layer rather than averaging the observed ages of the SOC in the mixed layer. It was calculated by extrapolating the depth-^{14}C age relationship observed below the mixed layer. This way, more degree of freedom was obtained by using a larger number of data points. However, the ages calculated by two different methods were not statistically different.

[21] The sedimentation rate at each site was calculated by linear regression of the ^{14}C ages with corresponding sediment depths below the mixed layer, assuming that aging was the only process that changed the $\Delta^{14}C$ values below the mixed layer depths (5 ± 1, 3 ± 1, and 4 ± 0.5 cm at the 100-, 2000-, and 4100-m sites, respectively; the 200-m site was not considered because it was homogeneous within the sampling depth). The calculated sedimentation rates were 14 ± 3, 13 ± 1, and 1.2 ± 0.2 cm/kyr (uncertainties are standard errors of the regression) at the 100-, 2000-, and 4100-m sites, respectively.

[22] An example calculation of source OC at the 100-m site is as follows. The ^{14}C age at the lower boundary of the mixed layer (5 cm) calculated from linear regression (depth = 0.01404 × Age − 17.79) was 1600 ± 600 years. Half of the time needed for sedimentation of 5 cm (5 cm/(14 cm/kyr)/2 = 178 years) was subtracted from the ^{14}C age of the lower boundary of the mixed layer to calculate the ^{14}C age of OC at the top of the mixed layer, or source OC (1600 − 178 = 1422 years, which is equivalent to a $\Delta^{14}C$ value of −160 ± 60‰).

[23] The estimated $\Delta^{14}C$ values of the source OC to the sediments were −160 ± 60, −180 ± 20, and 40 ± 200‰ at the 100-, 2000-, and 4100-m sites, respectively. The uncertainties are propagated standard errors of the linear regression. The estimated $\Delta^{14}C$ values are lower than pre-industrial values of plankton (−70‰ [*Berger et al.*, 1966]) indicating that old OC was deposited in addition to plankton-derived contemporary OC at the 100-m and 2000-m sites. However, at the 4100-m site, the uncertainty for the estimated $\Delta^{14}C$ value was too large to allow for meaningful interpretation.

[24] At the 2000-m site, the most plausible source of the old OC is laterally transported SOC. At the 100-m site, relict OC from riverine POC can be another source of old OC (discussed in section 3.4) in addition to laterally transported SOC. Accumulation of the laterally transported SOC may be enhanced by selective remineralization of fresh sinking POC upon sedimentation [*Aller and Blair*, 2004]. A fraction of laterally transported SOC may be labile and remineralized selectively also [*Anderson et al.*, 1994].

[25] The estimated $\Delta^{14}C$ value of source OC provides a constraint on the contribution of laterally transported OC, assuming two sources of OC to the sediment: OC from contemporary plankton and laterally transported OC. At the 2000-m site, minimum contribution from lateral transport can be set at 12% by assigning −1000‰ as its $\Delta^{14}C$ value (−70‰ × (1 − x) + (−1000‰) × x = −180‰, x = the minimum fraction of OC from lateral transport = 0.12; pre-bomb $\Delta^{14}C$ value of plankton (−70‰) was used for a contemporary autochthonous end-member [*Berger et al.*, 1966]). More realistically, if we assume that only the refractory fraction of the laterally transported SOC from the shelf (e.g., the acid-insoluble fraction, $\Delta^{14}C$ = −300‰ as observed at the 200-m site) was accumulating at the 2000-m site, then about 50% of the SOC would be from lateral transport (−70‰ × (1 − x) + (−300‰) × x = −180‰, x = 0.48). This value is comparable to what *Reimers et al.* [1992] suggested. They argued that about 50% of the accumulated SOC on the central California margin (3000–4000 m depth range) was from lateral transport based on the discrepancies between sinking POC flux (estimated from primary productivity, water depth, and their relationships determined by *Martin et al.* [1987]) and the sum of benthic remineralization and burial.

[26] In any case, because the estimated value of the source OC (−180‰ at the 2000-m site) is most likely an average of modern sinking POC (−70‰) and old transported SOC, the $\Delta^{14}C$ value of the transported SOC must be much lower than −180‰. Thus the value is likely to be much lower than the $\Delta^{14}C$ values of bulk SOC at upstream sites where SOC may originate, indicating that fractions with low $\Delta^{14}C$ signatures (i.e., extractable lipids and the acid-insoluble fraction) were selectively transported to deeper locations. Remineralization of relatively younger labile fractions will lower $\Delta^{14}C$ values of transported OC.

[27] The estimated $\Delta^{14}C$ value of the source OC at the 2000-m site may help to understand the high $\Delta^{14}C$ values at the top 1-cm layer. The observed values for the 0–1 cm layer (−140 to −160‰) were significantly higher than the values below this depth (−190 ± 10‰) and the estimated value (−180 ± 20‰) of the source OC. A plausible explanation may be that relatively young SOC transported by a recent episodic event (such as mudslide or turbidity flow) may have formed a new top layer, and this spike of relatively young SOC had not been mixed with the underlying sediment completely. Certainly, mudslides

caused by earthquakes are possible in this area [*Murai et al.*, 2004].

3.4. Contribution of Riverine POC to the Margin Sediments

[28] The contribution of riverine POC was estimated using carbon isotope ratios assuming mixing between two end-members: marine POC and riverine POC. Our sampling sites most probably do not follow a transport path from the mouth of one specific river. Studies of clay mineralogy showed that fine-grained sediments in the California shelf were supplied from the adjacent rivers [*Griggs and Hein*, 1980; *Hein et al.*, 2003]. Hence it is logical to assume that the 100-m site was mainly influenced by the Santa Clara River [*Drake et al.*, 1972; *Thornton*, 1984], while the 200-m site was mainly influenced by the Santa Ynez River. However, by studying our transect, we would still be able to catch general features of transport of river-exported organic carbon from the California coast in the study area. The Santa Clara River is one of many similar systems along the coast of California [*Inman and Jenkins*, 1999; *Mertes and Warrick*, 2001].

[29] The $\delta^{13}C$ values were used to calculate the contribution of riverine POC to TCHO in SOC. Spatial variability of $\delta^{13}C$ values of organic fractions in plankton and the change in $\delta^{13}C$ values of the organic fractions during diagenesis in the sediment were assumed to be negligible within the study area. The $\delta^{13}C$ values of TCHO of core top SOC were slightly lower than those of THAA except at Station M, where the $\delta^{13}C$ value of TCHO was higher [*Wang et al.*, 1998] (Table 2 and Figure 4). We obtained lower yields for the TCHO fraction at our sites than was reported by *Wang et al.* [1998] at Station M. Thus we did not use the TCHO value at Station M for the calculation below for consistency of data. Instead we used the $\delta^{13}C$ value of TCHO at the 2000-m site as the marine end-member. Thus the estimate of riverine TCHO in SOC may be a lower limit of the actual value. A mass balance calculation shows that about 33 ± 13 and 13 ± 14% of the TCHO at the 100-m and 200-m sites, respectively, were from riverine POC. For example, at the 100-m site, the riverine component was calculated using the $\delta^{13}C$ values of TCHO in SOC at the 2000-m site, riverine POC, and SOC at the 100-m site from Table 2; $-19.0 \times (1 - x) - 23.6 \times x = -20.5$, x = fraction from riverine POC = 0.33.

[30] Because of a lack of $\delta^{13}C$ results for THAA in riverine POC, it was not possible to estimate the contribution of riverine POC for this fraction at the margin sites. However, the $\delta^{13}C$ values of THAA at the 200-m, 2000-m, and 4100-m sites were equal (Figure 4), indicating constant (more likely, negligible) contribution of riverine POC at those sites. Riverine input of THAA seems apparent only at the 100-m site. Considering the low concentration of THAA (1%) in riverine POC and the high concentration in sinking POC (about 20% [*Hwang and Druffel*, 2003]), it seems reasonable to observe more limited influence of riverine THAA than other organic fractions in SOC.

[31] Although $\delta^{13}C$ cannot be used to evaluate the contribution of riverine POC to SOC due to the similarity in $\delta^{13}C$ between the two end-members for extractable lipids and the acid-insoluble fraction, the large differences in $\Delta^{14}C$ between SOC and riverine POC can be used for these two fractions. However, the $\Delta^{14}C$ signatures of SOC are also subject to change through processes such as aging and incorporation of old carbon from DOC and resuspended sediments in addition to inclusion of riverine POC. Thus a method to isolate the effect of the inclusion of riverine POC is required to determine the marine end-member $\Delta^{14}C$ values. THAA appears to be the least influenced by riverine sources, as discussed before. Only the 100-m site appears to contain THAA from riverine POC. Although the THAA $\Delta^{14}C$ result for riverine POC is not available, it is expected to be similar to that of TCHO (i.e. modern, Figure 3). In this case, inclusion of riverine THAA at the 100-m site will not change the $\Delta^{14}C$ value of THAA in SOC significantly. Thus the THAA $\Delta^{14}C$ values can be used to represent the marine end-member.

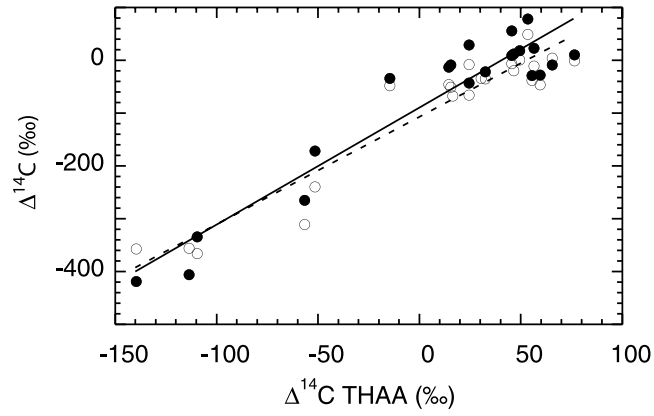

Figure 5. Correlations between $\Delta^{14}C$ values of THAA and extractable lipids (solid circles and solid line) or THAA and acid-insoluble fraction (open circles and dashed line) from plankton, sinking POC, detrital aggregates, sediment flocculation, and sediments at Station M [*Wang et al.*, 1998; *Hwang and Druffel*, 2003]. Correlation coefficients (r^2) were 0.90 for extractable lipids and 0.91 for the acid-insoluble fractions.

[32] We hypothesize that correlations exist between $\Delta^{14}C$ values of THAA and other organic fractions in the purely marine environment (i.e., no riverine POC) and thus the $\Delta^{14}C$ values of the marine end-member for extractable lipids and the acid-insoluble fraction may be estimated from those of THAA. As a preliminary attempt, we used the correlations among the $\Delta^{14}C$ values of THAA and the other fractions of plankton, sinking POC, detrital aggregates, sediment floc, and surface sediments at Station M, under the assumption that Station M suffices the above-mentioned condition. Where $\Delta^{14}C$ values of THAA decreased from plankton to sediment, those of extractable lipids and the acid-insoluble fraction decreased at a much faster rate. There are significant correlations between the THAA $\Delta^{14}C$ values and those of the associated lipids and between the THAA $\Delta^{14}C$ values and acid-insoluble fraction $\Delta^{14}C$ values (both $r^2 = \sim 0.9$, Figure 5).

[33] For a given $\Delta^{14}C$ value of THAA at each site on the margin, the marine end-member $\Delta^{14}C$ values of extractable

Table 3. Calculation of the Content of Riverine POC in Organic Fractions

	4100 m	2000 m	200 m	100 m	Riverine POC
		Extractable Lipids			
Observed $\Delta^{14}C$, ‰	−404 ± 31	−319 ± 6	−357 ± 6	−534 ± 6	−845 ± 6
Estimated marine end-member,[a] ‰		−282 ± 29	−205 ± 57	−63 ± 23	
Percent riverine POC[b]		7 ± 5	24 ± 9	60 ± 4	
		Acid Insoluble			
Observed $\Delta^{14}C$, ‰	−354 ± 9	−197 ± 10	−300 ± 10	−236 ± 10	−649 ± 10
Estimated marine end-member,[a] ‰		−284 ± 26	−213 ± 52	−83 ± 20	
Percent riverine POC[b]		(−24 ± 8)	20 ± 12	27 ± 4	

[a]The $\Delta^{14}C$ values were calculated from linear regressions: Extractable lipids $\Delta^{14}C = 2.2154 \times (\text{THAA } \Delta^{14}C) - 89.648$ and acid-insoluble $\Delta^{14}C = 2.0349 \times (\text{THAA } \Delta^{14}C) - 107.26$. The uncertainties are propagated standard errors of regressions.

[b]The contribution of riverine POC was calculated using a simple mass balance equation assuming two end-member mixing between marine sediments of the estimated $\Delta^{14}C$ values and riverine POC.

lipids and the acid-insoluble fraction were estimated from the linear regressions (Table 3). The observed $\Delta^{14}C$ values were lower than the estimated marine end-member values (except for the acid-insoluble fraction at the 2000-m site). The contributions of riverine POC for extractable lipids and the acid-insoluble fraction were calculated by a mass balance equation, assuming that the discrepancies between the estimated and observed values were caused by the input of riverine POC. The estimated $\Delta^{14}C$ values of the marine end-member and the calculated percentages of riverine POC are listed in Table 3. These estimates provide lower limits because Station M was assumed to be a purely marine environment; however, limited seasonal input of riverine POC has been suggested [*Smith et al.*, 2001; *Hwang et al.*, 2004].

[34] Using this method, the extractable lipids in SOC were calculated to contain the highest fraction of riverine POC, up to 60% at the 100-m site (Table 3) and zero at the 2000-m site. The contribution of riverine POC to the acid-insoluble fraction was about 20–30% on the shelf. The relative contributions of riverine POC to each organic fraction are in the order, lipids > acid-insoluble fraction ≈ TCHO > THAA.

4. Conclusions

[35] We conclude that lateral transport of OC on the California margin is an important process. The $\Delta^{14}C$ and $\delta^{13}C$ values of organic compound classes provide additional information on the sources and cycling of each compound class. The $\Delta^{14}C$ values of source OC to the sediments on the margin were estimated using a simple mixed layer model and vertical profiles of $\Delta^{14}C$ at the 2000-m site. The estimated $\Delta^{14}C$ value of source OC was lower than pre-industrial values for plankton. This indicates that old OC, most likely from laterally transported resuspended SOC, was accumulating at this site.

[36] Laterally transported SOC is expected to have lower $\Delta^{14}C$ values than those of SOC at its source locations. Selective remineralization of relatively younger, labile organic fractions during the lateral transport and/or after deposition will lower the $\Delta^{14}C$ value of total OC. Thus refractory material (i.e., extractable lipids and the acid-insoluble fraction) may be selectively transported to deeper locations.

[37] Contribution of riverine POC to SOC on the shelf was estimated using isotopic mass balances. We found that the relative contributions of riverine POC to each organic fraction are in the order: lipids > acid-insoluble fraction ≈ TCHO > THAA. These results show that relict OC from small mountainous rivers is an important component of SOC on the California margin.

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References

Aller, R. C., and N. E. Blair (2004), Early diagenetic remineralization of sedimentary organic C in the Gulf of Papua deltaic complex (Papua New Guinea): Net loss of terrestrial C and diagenetic fractionation of C isotopes, *Geochim. Cosmochim. Acta*, *68*, 1815–1825.

Anderson, R. F., G. T. Rowe, P. F. Kemp, S. Trumbore, and P. E. Biscaye (1994), Carbon budget for the mid-slope depocenter of the Middle Atlantic Bight, *Deep Sea Res., Part II*, *41*, 669–703.

Berger, R., R. E. Taylor, and W. F. Libby (1966), Radiocarbon content of marine shells from the California and Mexican west coast, *Science*, *153*, 864–866.

Bianchi, T. S., J. E. Bauer, E. R. M. Druffel, and C. D. Lambert (1998), Pyrophaeophorbide-a as a tracer of suspended particulate organic matter from the NE Pacific continental margin, *Deep Sea Res., Part II*, *45*, 715–731.

Blair, N. E., E. L. Leithold, S. T. Ford, K. A. Peeler, J. C. Holmes, and D. W. Perkey (2003), The persistence of memory: The fate of ancient sedimentary organic carbon in a modern sedimentary system, *Geochim. Cosmochim. Acta*, *67*, 63–73.

Degens, E. T., M. Behrendt, B. Gotthardt, and E. Reppmann (1968), Metabolic fractionation of carbon isotopes in marine plankton: II. Data on samples collected off the coasts of Peru and Ecuador, *Deep Sea Res.*, *15*, 11–20.

DeNiro, M. J., and S. Epstein (1977), Mechanism of carbon isotope fractionation associated with lipid synthesis, *Science*, *197*, 261–263.

Drake, D. E., R. L. Kolpack, and P. J. Fischer (1972), Sediment transport on the Santa Barbara–Oxnard Shelf, Santa Barbara Channel, California, in *Shelf Sediment Transport: Processes and Pattern*, edited by D. J. P. Swift et al., pp. 307–331, Dowden, Hutchinson and Ross, Stroudsburg, Pa.

Druffel, E. R. M., P. M. Williams, J. E. Bauer, and J. R. Ertel (1992), Cycling of dissolved and particulate organic matter in the open ocean, *J. Geophys. Res.*, *97*, 15,639–15,659.

Druffel, E. R. M., S. Griffin, J. E. Bauer, D. M. Wolgast, and X.-C. Wang (1998), Distribution of particulate organic carbon and radiocarbon in the

water column from the upper slope to the abyssal NE Pacific Ocean, *Deep Sea Res., Part II*, *45*, 667–687.

Gélinas, Y., J. A. Baldock, and J. I. Hedges (2001), Organic carbon composition of marine sediments: Effects of oxygen exposure on oil generation potential, *Science*, *294*, 145–148.

Griggs, G. B., and J. R. Hein (1980), Sources, dispersal, and clay mineral composition of fine-grained sediment off central and northern California, *J. Geol.*, *88*, 541–566.

Hartnett, H. E., R. G. Keil, J. I. Hedges, and A. H. Devol (1998), Influence of oxygen exposure time on organic carbon preservation in continental margin sediments, *Nature*, *391*, 572–574.

Hayes, J. M. (2001), Fractionation of the isotopes of carbon and hydrogen in biosynthetic processes, in *Stable Isotope Geochemistry, Reviews in Mineralogy and Geochemistry*, edited by J. W. Valley and D. R. Cole, pp. 225–278, Mineral. Soc. of Am., Washington, D. C.

Hein, J. R., J. S. Dowling, A. Schuetze, and H. J. Lee (2003), Clay-mineral suites, sources, and inferred dispersal routes: Southern California continental shelf, *Mar. Environ. Res.*, *56*, 79–102.

Hwang, J., and E. R. M. Druffel (2003), Lipid-like material as the source of the uncharacterized organic carbon in the ocean?, *Science*, *299*, 881–884.

Hwang, J., and E. R. M. Druffel (2005), Blank correction for $\Delta^{14}C$ measurements in organic compound classes of oceanic particulate matter, *Radiocarbon*, *47*, 75–87.

Hwang, J., E. R. M. Druffel, S. Griffin, K. L. Smith Jr., R. J. Baldwin, and J. E. Bauer (2004), Temporal variability of $\Delta^{14}C$, $\delta^{13}C$, and C/N in sinking particulate organic matter at a deep time series station in the northeast Pacific Ocean, *Global Biogeochem. Cycles*, *18*, GB4015, doi:10.1029/2004GB002221.

Inman, D. L., and S. A. Jenkins (1999), Climate change and the episodicity of sediment flux of small California rivers, *J. Geol.*, *107*, 251–270.

Jahnke, R. A., C. E. Reimers, and D. B. Craven (1990), Intensification of recycling of organic matter at the sea floor near ocean margins, *Nature*, *348*, 50–54.

Komada, T., E. R. M. Druffel, and S. E. Trumbore (2004), Oceanic export of relict carbon by small mountainous rivers, *Geophys. Res. Lett.*, *31*, L07504, doi:10.1029/2004GL019512.

Komada, T., E. R. M. Druffel, and J. Hwang (2005), Sedimentary rocks as sources of ancient organic carbon to the ocean: An investigation through $\Delta^{14}C$ and $\delta^{13}C$ signatures of organic compound classes, *Global Biogeochem. Cycles*, GB2017, doi:10.1029/2004GB002347.

Martin, J. H., G. A. Knauer, D. M. Karl, and W. W. Broenkow (1987), VERTEX: Carbon cycling in the northeast Pacific, *Deep Sea Res.*, *34*, 267–285.

Masiello, C. A., and E. R. M. Druffel (2001), Carbon isotope geochemistry of the Santa Clara River, *Global Biogeochem. Cycles*, *15*(2), 407–416.

Mertes, L. A. K., and J. A. Warrick (2001), Measuring flood output from 110 coastal watersheds in California with field measurements and SeaWiFS, *Geology*, *29*, 659–662.

Mollenhauer, G., T. I. Eglinton, N. Ohkouchi, R. R. Schneider, P. J. Müller, P. M. Grootes, and J. Rullkötter (2003), Asynchronous alkenone and foraminifera records from the Benguela upwelling system, *Geochim. Cosmochim. Acta*, *67*, 2157–2171.

Murai, L. Y., H. Greene, and S. N. Ward (2004), Trans-terrestrial landslides and impact on the marine environment: Big Sur coastline, California, *Eos Trans. AGU*, *85*(47), Fall Meet. Suppl., Abstract OS23B-1317.

Ohkouchi, N., T. I. Eglinton, L. D. Keigwin, and J. M. Hayes (2002), Spatial and temporal offsets between proxy records in a sediment drift, *Science*, *298*, 1224–1227.

Quan, T. M. (2005), Chemical characterization of dissolved organic matter (DOM) in seawater: Structure, cycling, and the role of biology, Ph.D. thesis, Mass. Inst. of Technol.–Woods Hole Oceanogr. Inst., Woods Hole, Mass.

Reimers, C. E., R. A. Jahnke, and D. C. McCorkle (1992), Carbon fluxes and burial rates over the continental slope and rise off central California with implications for the global carbon cycle, *Global Biogeochem. Cycles*, *6*(2), 199–224.

Sherrell, R. M., M. P. Field, and Y. Gao (1998), Temporal variability of suspended mass and composition in the northeast Pacific water column: Relationships to sinking flux and lateral advection, *Deep Sea Res., Part II*, *45*, 733–761.

Smith, K. L., R. S. Kaufmann, R. J. Baldwin, and A. F. Carlucci (2001), Pelagic-benthic coupling in the abyssal eastern North Pacific: An 8-year time-series study of food supply and demand, *Limnol. Oceanogr.*, *46*, 543–556.

Thornton, S. E. (1984), Basin model for hemipelagic sedimentation in a tectonically active continental margin: Santa Barbara Basin, California Continental Borderland, in *Fine-Grained Sediments: Deep Water Processes and Facies*, edited by D. A. V. Stow and D. J. P. Piper, pp. 377–397, Blackwell, Malden, Mass.

Vogel, J. S., D. E. Nelson, and J. R. Southon (1987), ^{14}C background levels in an accelerator mass spectrometry system, *Radiocarbon*, *29*, 323–333.

Wang, X.-C., E. R. M. Druffel, S. Griffin, C. Lee, and M. Kashgarian (1998), Radiocarbon studies of organic compound classes in plankton and sediment of the northeastern Pacific Ocean, *Geochim. Cosmochim. Acta*, *62*, 1365–1378.

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