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Evidence of old carbon in the deep water column of the Panama Basin from natural radiocarbon measurements

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Abstract. Radiocarbon ($\Delta^{14}\text{C}$) analyses were performed on sinking and suspended particulate matter, dissolved inorganic carbon (DIC), sediment and sediment fluff from a deep-water station in the Panama Basin. $\Delta^{14}\text{C}$ signatures for sinking particulate inorganic and organic carbon (PIC, POC) collected at 3354 meters depth were lower than surface DIC $\Delta^{14}\text{C}$ values, and higher than the inorganic and organic carbon from the sediment (SIC, SOC). We compare these data with those obtained for other Pacific and Atlantic sites and show that the gradient between surface DIC $\Delta^{14}\text{C}$ and deep suspended POC $\Delta^{14}\text{C}$ is the same irrespective of distance from the coast. This indicates that: 1) resuspended SOC is an equally important contributor to deep POC at locations close to and far from continental slopes, and/or 2) DOC sorption is a significant contributor for causing low $\Delta^{14}\text{C}$ values of deep POC.

Introduction

Seasonal fluxes of biogenic and lithogenic particles in the Panama Basin have been studied previously using sediment traps [Honjo, 1982; Honjo *et al.*, 1992]. Honjo (1982) deployed sediment traps at three depths (890, 2590, 3560 m) in 1980 to collect settling particles during 2-month increments. Two peaks of mass flux were found; they each occurred simultaneously at the three sediment trap depths. The first peak during February through March was coincident with a peak of primary production over the northern bight caused by upwelling that was induced by strong northerly winds over the Panama Isthmus. The second flux peak, during June through July, consisted primarily of a single species of coccoliths (*Umbellicospaera sibogae*). Total mass flux increased with depth at all time periods except during June through July. The flux of organic carbon and carbonate carbon decreased or remained the same with depth over the year. Honjo (1982) estimated that only a small amount of the lithogenic flux originated from the overlying surface waters. The majority of lithogenic particles, which consisted of a smectite clay (beidellite) found on the Pacific continental slope off Costa Rica, is probably resuspended from the slope and laterally transported to the Basin by the westerly undercurrent. Mucous that is prevalent during periods of high primary production aids vertical transport of fine lithogenic particles by scavenging and agglutinating them as they settle through the water column [Honjo, 1982]. The importance of carbon transport via lateral motion from the slope is less certain.

In order to further understand and quantify the major sources of particulate carbon in the oceanic water column in this region, we measured carbon isotope ratios ($\Delta^{14}\text{C}$, $\delta^{13}\text{C}$) in sinking particulate organic and inorganic carbon (POC, PIC), as well as suspended POC, surface sedimentary organic and inorganic carbon (SOC, SIC) and surface water dissolved inorganic carbon (DIC) collected from the Panama Basin in the eastern equatorial Pacific. The $\Delta^{14}\text{C}$ values of POC and PIC are post-bomb (>1958) but are lower than those of the DIC in the overlying surface waters. These data suggest a subsurface source or sources of carbon to the deep sea.

Oceanographic Setting and Methods

The site in the Panama Basin was located in the Coiba Deep (3700-4000 m depth), which lies between the southern edge of Coiba Ridge (1000-3000 m depth) and the northern edge of Malpelo Ridge (1000-3000 m depth, see Figure 1). The bottom flow at our site is less than that observed in other areas of the Panama Basin due to two sills about 500 m above the basin floor in the Coiba Deep [Stevenson, 1970; Wyrski, 1967]. Surface seawater samples were collected on 4, 6 and 26 January 1984 (Table 1). A hose attached to a Jabsco pump was lowered over the side of the ship to 1-2 m depth. The hose was flushed for a minimum of 5 minutes before filling a 55-gallon polyethylene drum with seawater. The DIC in seawater (concentration was 1816-1846 μM) was extracted aboard ship immediately after collection using a closed gas recirculation method [Linick, 1980]. The absorber solutions (NH_4OH and SrCl_2) were returned to the laboratory and processed to produce purified acetylene counting gas. The gas samples were counted in quartz, gas proportional beta counters (volumes of 0.75 and 1.5 L) for three, 2-day periods [Griffin and Druffel, 1985].

A PARFLUX Mark II, single-cup sediment trap [Honjo *et al.*, 1980] was deployed at 3354 m depth, 266 m above the bottom (3620 m), in the Panama Basin ($5^\circ 18' \text{N}$, $81^\circ 58' \text{W}$) from 26 January to 23 March 1984 (57 days). Two grams of solid HgCl_2 were placed in the trap collection cup (~2L volume) prior to deployment to minimize bacterial remineralization of trapped organic matter.

The sediment trap sample was refrigerated and returned to the lab. It was divided on 4-5 June 1984 into three size fractions, <63 μm , 63 μm -1 mm, and >1 mm, using brass sieves. A portion of the sample was poured into a 1 mm sieve and rinsed first with its own water and then with a small amount of distilled water (<5% of the total). This was repeated until all of the sample had been separated into three size fractions. Each size fraction was filtered through quartz fiber filter paper (0.8 μm pore diameter) and rinsed a minimum of two times with distilled water, and dried in an oven (40°C) overnight. There

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are two problems with these methods. First, the samples were stored for over 2 months prior to sieving and may have led to alteration of the sizes of individual particles. Second, the water was not tested for dissolved organic carbon (DOC) content, thus the amount of DOC lost, either to dissolution or cell lysis is unknown; this loss probably does not exceed 10% of each fraction. Thus, cellular organic carbon, likely young (high ^{14}C) with respect to other carbon sources, may have been lost from the three POC samples. The loss of younger carbon would leave the remaining POC lower in ^{14}C content (older ^{14}C age), but probably by not more than 20‰ in $\Delta^{14}\text{C}$.

A known amount of material was acidified with 2N HCl under vacuum to convert PIC to CO_2 . The residue was filtered, rinsed with distilled water and dried. Each sample, which now contained the organic carbon, was burned in a stream of purified oxygen to produce CO_2 . The larger samples were counted as CO_2 in a Cu, gas proportional beta counter (volume of 200cc) for three, 6-day periods. The smaller samples (AA# 1215, 1216, 2751) were sent to the U. of Arizona Tandem Accelerator Mass Spectrometry (TAMS) Facility for conversion to graphite and ^{14}C analysis [Jull *et al.*, 1986].

Sediment fluff was collected on Alvin dive #1537 (5°20'N, 81°55'W, 4 March 1984) from the top 1 cm of a sediment core (3-inch diameter, PVC core tube). The core was sampled by pushing it up through the PVC tube and slicing it with a spatula. Care was taken to sample the center of the slice to avoid contamination. The deeper sediment sample was homogenized from the section between 2 and 10 cm depth. The SIC and SOC fractions were prepared and counted as for the PIC and POC samples described above, with the smallest CO_2 sample (AA# 2010, see Table 1) analyzed using AMS techniques.

The suspended POC sample was collected on 6 January 1984 using an in situ pump [Bacon and Anderson, 1982] for 6 hours

Figure 1. Map of the Panama Basin showing bottom bathymetry and the collection sites for the sediment trap, sediment core (Alvin dive site) and suspended POC (pump).

at a depth of 2800 m (5°20'N, 81°55'W). The seawater (1550L) was filtered through a quartz fiber filter that had not been pre-fired (blank ≈ 0.45 ml CO_2). The filter was frozen at -20°C . It was then acidified, dried and combusted using standard techniques [Griffin and Druffel, 1985]. The CO_2 (2.58mgC) was converted to graphite and analyzed for ^{14}C .

The $\Delta^{14}\text{C}$ measurements were corrected as for geochemical samples without a known age [Stuiver and Polach, 1977]. The $\delta^{13}\text{C}$ value was measured for each sample using a VG Micromass 602E mass spectrometer at WHOI.

Results and Discussion

Measurements of DIC $\Delta^{14}\text{C}$ in surface seawater ranged from 81 to 94‰ (see Table 1). These values are slightly higher than two $\Delta^{14}\text{C}$ values obtained for annually banded coral samples that grew during 1979 and 1980 (74 and $73 \pm 4\%$ respectively) collected from Uva Island off the Pacific coast of Panama (8°N, 82°W, NE of our sampling site) [Druffel, 1987]. We have no data showing the seasonal variability of DIC $\Delta^{14}\text{C}$ at our site.

The $\Delta^{14}\text{C}$ values for PIC in the three size fractions of the sediment trap sample ranged from $-27 \pm 10\%$ ($<63\mu\text{m}$) to $55 \pm 14\%$ ($>1\text{mm}$) (6 sigma spread) (Table 1, Fig. 2) and values increased as the size of the sample particles increased. The two smaller sized PIC $\Delta^{14}\text{C}$ values were significantly lower than the surface water DIC $\Delta^{14}\text{C}$ values measured in surface seawater. The $\Delta^{14}\text{C}$ values for POC in the three size fractions of the sediment trap sample ranged from -28% ($63\mu\text{m}$ - 1mm) to 18% ($>1\text{mm}$) (4 sigma spread). All POC $\Delta^{14}\text{C}$ values were lower than the surface water DIC $\Delta^{14}\text{C}$ values. The range of the POC $\Delta^{14}\text{C}$ values was smaller and the values did not increase with size, in contrast to the PIC $\Delta^{14}\text{C}$ values (see Figure 2).

The suspended POC sample, from 2500 m depth, had a $\Delta^{14}\text{C}$ value of $5 \pm 20\%$. This value is $76 - 89\%$ lower than the surface DIC $\Delta^{14}\text{C}$ values and is equal to the $\Delta^{14}\text{C}$ values for the sinking POC fractions (see Figure 2).

Sediment fluff, the top 1 cm of the sediment, had a $\Delta^{14}\text{C}$ value of -133% for the SIC fluff and -179% for the SOC fluff. These values are much lower than the suspended POC, sinking POC and sinking PIC $\Delta^{14}\text{C}$ values. The $\Delta^{14}\text{C}$ value of SIC (2-10 cm) was 64% lower than that of the fluff SIC. The SOC and fluff SOC $\Delta^{14}\text{C}$ values are the same within error.

Table 1. Radiocarbon and $\delta^{13}\text{C}$ Measurements of Samples Collected at the Panama Basin Site.

WH# [AA#]	Type/ [Depth]	% total C in sample	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	$\pm$ ‰
<i>Surface Seawater</i>					
300	DIC [1 m depth]		-3.1	81	7
299	DIC [1 m depth]		1.1	90	4
298	DIC [2 m depth]		0.7	94	4
<i>Sinking Particles - Trap at 3354 m depth</i>					
[1215]	PIC $>1\text{mm}$	6	-2.7	55	14
411	PIC $63\mu\text{m}$ - 1mm	59	0.8	22	10
412	PIC $<63\mu\text{m}$	35	0.5	-27	10
[1216]	POC $>1\text{mm}$	8	-26.6	18	9
414	POC $63\mu\text{m}$ - 1mm	27	-21.5	-28	12
415	POC $<63\mu\text{m}$	65	-22.3	5	10
<i>Suspended Particles - In situ pump</i>					
[2751]	POC _{susp} 2800m		-	5	20
<i>Sediment</i>					
483	SOC Fluff 0-1cm		-21.1	-179	9
[2010]	SIC Fluff 0-1cm		-	-133	10
363	SIC 2-10cm		-1.9	-197	8
417	SOC 2-10cm		-20.4	-184	5

Figure 2. $\Delta^{14}\text{C}$ of the carbon pools from the Panama Basin site. DIC $\Delta^{14}\text{C}$ range was for surface waters (see Table 1), POC and PIC were sinking material from a 2-mo sediment trap collection at 266 mab (bottom depth 3620m), suspended POC was from 2800 m depth, and fluff and sediment SIC and SOC were from the underlying sediments. (See text for details.)

The most striking observation from our data is that nearly all POC and PIC $\Delta^{14}\text{C}$ values of samples we analyzed from the water column are intermediate between the high surface DIC $\Delta^{14}\text{C}$ values, and the low underlying sediment and sediment fluff values (Figure 2). These data indicate that the particles in the water column are not derived exclusively from the euphotic zone (0–200 m); instead, there is a source of old carbon to the deep ocean. This situation is similar to nearly all of the data collected so far from the Pacific and Atlantic Oceans (see below). The exception is Stn P (50°N, 145°W) in the Gulf of Alaska, where all of the sinking POC $\Delta^{14}\text{C}$ values of samples collected in 1982 were higher than surface DIC $\Delta^{14}\text{C}$ values, which indicated a source of ^{14}C -rich, terrestrially-derived carbon to this area of the deep NE Pacific [Druffel *et al.*, 1986].

It is also evident that the larger fractions of the sinking PIC (63 μm –1 mm, > 1 mm) in the Panama Basin have higher $\Delta^{14}\text{C}$ values than that in the smallest fraction (<63 μm). This likely is due to the fact that larger shells and tests originate from the high- ^{14}C surface waters, where they are produced, and fall quickly to the deep-sea. We envision that the smallest size fraction of inorganic carbon would be more likely to have been resuspended from slope sediments because of their small size and mass and transported into the water column.

The low $\Delta^{14}\text{C}$ values of SOC are due to bioturbation of fresh (post-bomb ^{14}C), newly-arrived carbon down into the sediment mixed layer (0–10 cm) where dilution with already buried, older (low- ^{14}C) carbon takes place. A comparison between the fluff SOC $\Delta^{14}\text{C}$ value ($-179 \pm 9\text{‰}$) in the Panama Basin and those found at Station M ($-200 \pm 10\text{‰}$, [Wang *et al.*, 1996]) and the Santa Monica Basin (SMB) site (-10‰ , [Williams *et al.*, 1992]) demonstrates that there is younger, post-bomb material (> -70‰) present in the SMB, where there is little or no bioturbation of the sediments due to anoxic conditions.

The organic fractions of nearly all of the samples studied had lower $\Delta^{14}\text{C}$ values compared to their inorganic counterparts. This suggests that there is preferential association of old organic carbon with particles studied here. Two sources of old organic carbon that could be responsible are DOC (dissolved organic carbon), which has a $\Delta^{14}\text{C}$ value of

about -525‰ in the deep Pacific [Bauer *et al.*, 1992; Williams and Druffel, 1987; Williams *et al.*, 1992], and SOC that is resuspended either locally or laterally advected off the continental shelf and slope and transported to the deep ocean.

The $\Delta^{14}\text{C}$ values reported here are compared to those from other sites. First, the DIC $\Delta^{14}\text{C}$ values in the Panama Basin (81–94‰) are slightly higher than those measured from Station M (34°50'N, 123°00'W, 25 m depth) in the NE Pacific (average = 68 ± 9 , $n=12$) between 1991 and 1995 [Masiello *et al.*, 1997], lower than the surface values found at a North Central Pacific site (31°N, 159°W, 3m) in June/July 1987 (average = 132‰ , $n=16$) and the same as that measured in the SMB in October 1987 (5 m depth, 33°45'N, 118° 54'W, 94‰)[Williams *et al.*, 1992]. Second, the $\Delta^{14}\text{C}$ value of suspended POC ($5 \pm 20\text{‰}$) from 2800 m depth is similar to the average value ($-6 \pm 13\text{‰}$, $n=4$) obtained for samples from Stn M at 2500 m depth collected from Feb 1992 and July 1993 [Druffel *et al.*, 1996]. Therefore, the $\Delta^{14}\text{C}$ gradients between average surface DIC values and average suspended POC values in mid-depth regions (2500–2800 m) for the Panama Basin and Station M are virtually identical (83‰ and 74‰, respectively), as were those at the N. Central Pacific and the Santa Monica Basin sites (84‰ and 83‰, between surface and mid-depth, 3000m and 510m, respectively). Two locations in the N. Atlantic, the Middle Atlantic Bight (MAB) and off Bermuda, also reveal similar surface-to-deep gradients (see Figure 3). These depth gradients are similar, irrespective of distance from the continental rise and slope.

Based on these constant gradients, Druffel *et al.* (1996, 1997) postulated that a major process causing lower $\Delta^{14}\text{C}$ values of deep suspended and sinking POC could be sorption (or biological incorporation) of “old” DOC onto particulate matter. Though it cannot be demonstrated with certainty, it is possible that part of the $\Delta^{14}\text{C}$ gradient between surface DIC and deep suspended POC at our Panama Basin site is due to DOC sorbed onto the POC. To lower the $\Delta^{14}\text{C}$ of suspended POC in the Panama Basin from the average DIC $\Delta^{14}\text{C}$ value (88‰) in the surface to the observed value of 5‰ would require the addition of 13% DOC ($\Delta^{14}\text{C} = -525\text{‰}$). For sinking POC, 15% DOC would be needed to lower $\Delta^{14}\text{C}$ of sinking POC from 88‰

Figure 3. $\Delta^{14}\text{C}$ differences ($\Delta\Delta^{14}\text{C}$) between surface DIC and deep suspended POC values for six locations, versus each station's distance from the closest continental shelf. (Panama Basin (PB), this work; Stn M (NEP), [Druffel *et al.*, 1996]; Santa Monica Basin (SMB), [Williams *et al.*, 1992]; North Central Pacific (NCP), [Druffel *et al.*, 1992]; N. Atlantic (NA), [Druffel *et al.*, 1992]; Middle Atlantic Bight (MAB), [Bauer and Druffel, 1998]).

to the average observed value of -3‰ (weighted as to the mass of size fractions listed in Table 1).

A second process that is likely responsible for the low POC $\Delta^{14}\text{C}$ values is sediment resuspended into the water column. Honjo (1982) reported that lithogenic particle fluxes increased with depth in the water column in the Panama Basin, however, organic and inorganic carbon fluxes remained the same or decreased with depth. This does not discount the possibility that there may have been net loss of surface-derived organic and inorganic carbon which were replaced by laterally transported lithogenic particles that had old organic and inorganic carbon sorbed to it. If we assume that resuspended sediment fluff was the source of the old organic and inorganic carbon which had $\Delta^{14}\text{C}$ signatures of -179‰ and -133‰, respectively (Table 1), and the average surface DIC $\Delta^{14}\text{C}$ signature (88‰) was equal to the surface-derived POC, then the fraction of total sinking POC ($\Delta^{14}\text{C}$ = -3‰) and sinking PIC ($\Delta^{14}\text{C}$ = 7‰) that was composed of surface sediment would have been 34% organic and 37% inorganic carbon, respectively. Likewise, in the case of the suspended POC, 31% of its organic carbon would have originated as resuspended SOC to obtain its $\Delta^{14}\text{C}$ value of 5‰, had the old carbon been from resuspension.

Of the two proposed mechanisms that could account for the lower suspended and sinking POC $\Delta^{14}\text{C}$ values, resuspended sediment likely accounts for at least part of it. Deep, lateral currents can be > 15 cm/sec in this region, strong enough to cause resuspension of surficial sediments from topographic highs such as the Coiba Ridge to the north and the Malpelo Ridge to the south [Honjo et al., 1982]. Other studies have reported the dominance of lateral transport in the mid-slope region of the MAB off the eastern U.S. coast [Anderson et al., 1994]. On the other hand, the similarity of the surface to deep gradient in $\Delta^{14}\text{C}$ (DIC minus POC) between the Panama Basin and all other sites studied (N. Central Pacific, NE Pacific, SMB, Middle Atlantic Bight, N. Atlantic), irrespective of their distance from the continental shelf/slope (Figure 3), indicates that resuspended material is likely not the sole source of old carbon to deep suspended POC and sinking POC pools. Incorporation of DOC onto the POC is a likely source of old carbon, though its importance needs to be quantified.

A possible way to pull apart these two signals is to use the $\Delta^{14}\text{C}$ differences between the sinking PIC and sinking POC samples as an indicator of how much resuspended sediment is likely contributing to the trap material. The average sinking PIC $\Delta^{14}\text{C}$ value (7 ± 14 ‰, weighted as per mass in each fraction) is 10‰ higher than the average sinking POC $\Delta^{14}\text{C}$ value (-3 ± 18 ‰); this difference is smaller than the 46‰ difference observed between the fluff SIC and fluff SOC $\Delta^{14}\text{C}$ values. The fact that the inorganic carbon $\Delta^{14}\text{C}$ values are higher in both the sinking particulate matter (though not significantly) and the sediment fluff supports the assertion, though does not provide conclusive proof, that there is a resuspended sediment component of the sinking particles.

A way to resolve this is to measure the isotopic signatures of the organic matter associated with the lithogenic particles separately from that associated with the phytodetritus that originates in the euphotic zone. This would require obtaining new samples, however.

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