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Penetration of anthropogenic carbon into organic particles of the deep ocean

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[1] In the late 1980s, bomb ¹⁴C was present in suspended particulate organic carbon (POC) from the North Central Pacific (NCP) and Sargasso Sea (SS) throughout most of the water column, demonstrating that deep POC had exchanged with atmospheric CO₂ in the past 30 years. Upon reoccupation of these sites in 1999 and 2000, respectively, we observed that the Δ¹³C values of suspended POC were lower than those measured a decade earlier. This demonstrates that anthropogenic CO₂ from fossil fuel and biomass burning has penetrated a major organic matter pool in the deep ocean. Δ¹⁴C measured in the suspended POC showed similar or higher values in the deep Sargasso Sea and decreased values in the deep NCP compared to those measured previously. We use a box model to show that the differences in the radiocarbon results are likely due to the presence of resuspended sediment that is laterally advected from the continental margin to the deep Sargasso Sea.


1. Introduction

[2] The primary source of suspended POC in the deep open ocean is believed to be marine phytoplankton derived from CO₂ fixation in surface waters [Hedges et al., 1997]. Evidence in support of this includes the similarity of δ¹³C values of POC (−20.5 to −22‰) to those of marine plankton (−18 to −20‰), and the low levels of isotopic and molecular indicators of terrestrial organic matter [Williams and Gordon, 1970; Meyers-Schulte and Hedges, 1986]. The radioactive form of carbon (¹⁴C, half-life = 5730 years) is used to determine the residence times of carbon pools in the ocean. In 1989, suspended POC Δ¹⁴C values, which ranged from +140‰ in the surface to −90‰ in the deep Sargasso Sea [Druffel et al., 1992; Druffel and Williams, 1990], were much higher than those in dissolved organic carbon (DOC). Values higher than −50‰ indicate the presence of bomb ¹⁴C. Previous studies of suspended POC in the North Pacific Ocean and Sargasso Sea [Druffel et al., 1992; Druffel and Williams, 1990] revealed a decrease of Δ¹⁴C values with depth, suggesting that there was an ‘old’ source of carbon to deep sea POC. In the present study, we used δ¹³C and Δ¹⁴C measurements to track the penetration of both anthropogenic and bomb carbon into the water column on a decadal time scale.

2. Methods

[3] Samples were collected from the NCP site (31°N, 159°W, bottom depth at 5770 m) during 26 May to 12 June 1999 and from the SS site (31°50′N, 63°30′W, bottom depth at 4500 m) during 14 to 29 June 2000. The NCP site is 1000 km north of Hawaii; the surface waters flow eastward. The SS site is 100 km southeast of Bermuda, where the input of particles to the water column from the island is minimal [Deuser and Ross, 1980]. Previously, the NCP and SS sites were occupied from 6 June to 3 July 1987 and 29 May to 20 June 1989, respectively [Druffel et al., 1992].

[4] Suspended POC was collected using modified, in situ Yentsch pumps [Williams et al., 1980] deployed for 2–6 hours. Depending on the concentration of suspended POC, 600–11,000 liters of seawater were filtered through four, 142 mm diameter, pre-combusted (500°C) quartz fiber filters (Whatman ultra pure QM-A 0.8-μm pore diameter) mounted in PVC holders. The unrisen filters, along with blank filters and filters placed under the top filter used to assess the efficiency of the top filter, were folded and frozen in cleaned glass jars at −20°C. At UCI, samples were thawed, rolled up and placed into a double quartz tube with 4 ml of 1% phosphoric acid overnight to rid the sample of inorganic carbon (to pH <2.5). The samples were dried under vacuum, combusted to CO₂ and converted to graphite; δ¹³C was measured on a subsample of the CO₂.

[5] The Δ¹⁴C and δ¹³C measurements from the 1999 and 2000 cruises were made at the National Ocean Sciences Accelerator Mass Spectrometer (NOSAMS) at Woods Hole Oceanographic Institution and at the W. M. Keck Carbon Cycle AMS Laboratory at UCI. δ¹³C values were determined at NOSAMS and UCI. The suspended POC Δ¹⁴C measurements for the NCP and SS cruises were reported as geochemical samples without known age according to standard techniques [Stuiver and Polach, 1977] and have an overall uncertainty of ±7‰. The overall uncertainty of the δ¹³C measurements, made on splits of the CO₂ produced from the closed-tube combustions, was ±0.1‰. The concentrations of suspended POC at the two sites were similar,
3. Results and Discussion

In 1999, \(\delta^{13}C\) in NCP suspended POC (Figure 1a) varied from a high of \(-21.5\%\) (at 50 mab, meters above bottom, 5720 m depth) to a low of \(-26.0\%\) (at 150 m). Samples between 900 m and 4200 m in 1999 had \(\delta^{13}C\) values that were lower than the 1987 values from the same depths. The average of the five (5) differences \((\delta^{13}C_{1987} - \delta^{13}C_{1999})\) was \(0.4 \pm 0.3\\%\), which is larger than the uncertainty of the individual measurements \((\pm 0.1\%)\). In 2000 at SS, \(\delta^{13}C\) values ranged from a high of \(-20.4\%\) (at 4000 m) to a low of \(-24.0\%\) (at 100 m). At 600 m and deeper, \(\delta^{13}C\) values were lower during 2000 than those at the same depths during 1989. The average of the eight (8) differences was \(0.6 \pm 0.3\%\), which is also larger than the uncertainty of the individual measurements.

The \(\delta^{13}C\) values of suspended POC in the upper 200 m at both sites were lower than those in deep waters, likely due to preferential utilization of labile compounds whose \(\delta^{13}C\) values are high (e.g., amino acids and sugars) [Jeffrey et al., 1983]. The \(\delta^{13}C\) values of suspended POC at NCP were 1.0–1.5\% lower at NCP than those at SS (Figures 1a and 1b), in part, because DIC \(\delta^{13}C\) values in surface waters were lower in the North Pacific than in the North Atlantic [Kroopnick, 1985]. Additionally, higher \(\delta^{13}C\) values for plankton are expected in SS surface waters based on lower equilibrium \(CO_2(aq)\) concentrations than in the NCP [Rau et al., 1991].

[8] The suspended POC \(\Delta^{14}C\) values obtained for the 1999 cruise to the NCP site ranged from a high of \(112\%\) (at 150 m) to a low of \(-15\%\) (at 4200 m, Figure 2a). Values of \(\Delta^{14}C\) decreased with depth to about 3200 m and then were relatively constant \((-3 \pm 12\%)\) between 3600 m and 5720 mab. The 1999 values were lower than the 1987 values at all depths sampled (Figure 2a). The average of \(\Delta^{14}C\) differences between the two cruises at ten (10) depths was \(32 \pm 15\%\). Differences were larger between 0 and 1000 m depth and below 3200 m, and smaller at mid-depths (1800–

Figure 1. \(\delta^{13}C\) values (\%) of suspended POC for two cruises each to (a) the NCP (31°N, 59°W, 1987 and 1999), and (b) SS (31.5°N, 63.5°W, 1989 and 2000) sites. The sampling depths were determined using meters wire out and observed wire angle (for depths <3000 m); a pinger was used on deeper deployments. These methods resulted in an uncertainty of about 2–3\% in the depth assignments.

Figure 2. \(\Delta^{14}C\) values (\%) of suspended POC for two cruises each to (a) the NCP, and (b) SS sites. The difference between duplicate \(\Delta^{14}C\) measurements from separate filters from the same deployment to 20 m depth was 10\%, and those for four separate deployments to the same depths (3 m, 20 m, 900 m and 1800 m) were 7\%, 6\%, 17\% and 8\%, respectively (all for 1999 and 2000 cruises). All duplicates but one (17\% value) were within ±2 sigma (14\%) of the total uncertainty.
3200 m). The decrease of $\Delta^{14}C$ in suspended POC with time coincides with the reduction since the early 1970s of $\Delta^{14}C$ in dissolved inorganic carbon (DIC) in subtropical surface waters. It is the $\Delta^{14}C$ in surface DIC that determines the $\Delta^{14}C$ signature of photoautotrophs and hence POC in the euphotic zone [Druffel, 1987; Williams and Druffel, 1987].

[9] In the SS during 2000, suspended POC $\Delta^{14}C$ values ranged from a high of 100% (at 50m) to a low of -162%o (at 4450m, 50 mab) (Figure 2b). Values decreased with depth throughout the entire water column, with the largest decrease (134%) occurring between 3200m and 3995m. No such decrease was seen in the NCP data, however, it has been seen off the west and east coasts of the U.S. [Druffel et al., 1998; Bauer and Druffel, 1998]. In 2000, differences of $\Delta^{14}C$ values in the SS were an average of 26 ± 9% (n = 5) lower in the upper 200m than in 1989, but higher by 15 ± 8%o (n = 6) between the depths of 600m and 3200m (Figure 2b). In 2000, the $\Delta^{14}C$ values at 3995m and 3600m were 44% and 31% lower, respectively, than those in 1989.

[10] A previous study using Th isotopes [Bacon and Anderson, 1982] reported that the turnover times of suspended mineral particles in the water column were <5–10 years. Though suspended POC is only 0.1–3% the abundance of DOC in seawater, the presence of bomb $^{14}C$ in the POC fraction (>50%) demonstrates a decadal residence time for POC, two orders of magnitude shorter than the 4000 to 6000 $^{14}C$ year residence times reported for bulk DOC in the deep sea [Williams and Druffel, 1987; Bauer et al., 1992].

[11] The most likely explanation for the decrease of deep (>200 m depth) suspended POC $\delta^{13}C$ values over the decade of this study (Figure 1) is the input of excess CO$_2$ from fossil fuel and biomass burning to the oceans. Although we cannot eliminate the possibility of seasonal influences as a contributing cause of the isotopic changes, they are minimized because: 1) all of our sampling was done during the same time of year (June), and 2) sea surface temperature changes, which have been shown to correlate with changes in export production [Laws et al., 2000], were minimal (+2°C) at our sites during the occupations. The $\delta^{13}C$ signature of the anthropogenic CO$_2$ is ~20% lower than pre-anthropogenic atmospheric CO$_2$, and has caused atmospheric CO$_2$ $\delta^{13}C$ values to decrease by 1.1% over the past four decades [Keeling et al., 1979; Ciais et al., 1995]. This has resulted in a decrease of upper ocean DIC $\delta^{13}C$ values by 0.4–0.6‰ in the Pacific [Quay et al., 1992; McNichol and Druffel, 1992] from the early 1970s to the early 1990s. If the decreases of $\delta^{13}C$ values in the deep suspended POC pool at SS are due exclusively to anthropogenic CO$_2$, this would account for 3% (0.6‰/20‰) of the suspended POC below 450m depth. This does not include the anthropogenic CO$_2$ that was incorporated into the organic C cycle via photosynthesis, and has since been remineralized to DIC.

[12] The $\Delta^{14}C$ values of CO$_2$ in the atmosphere, and hence in the surface ocean, were lower during 1999 and 2000 than a decade earlier because of the enhanced Suess effect with time [Suess, 1953], and to dilution of atmospheric CO$_2$ by exchange with low $\Delta^{14}C$ CO$_2$ in the surface ocean. However, we observe contrasting trends with time of the $\Delta^{14}C$ of deep POC from the two sites that indicate distinct sources to and/or cycling of deep suspended POC in each ocean.

[13] In the NCP, lower $\Delta^{14}C$ in the suspended POC pool in 1999 indicates that much of the new, bomb $^{14}C$ that had been present in deep waters in 1987 had been remineralized by 1999 and replaced by more recent POC with lower $\Delta^{14}C$ values (Figure 2a). In contrast, $\Delta^{14}C$ values in the suspended POC pool in the SS were slightly higher in 2000 compared to those in 1989 (between 600m and 3200m) indicating that there may have been a delayed or smaller relative input of bomb $^{14}C$ to the deep suspended POC pool as compared to that in the NCP.

[14] We developed a simple box model of $\Delta^{14}C$ for suspended POC in the deep ocean; the sources are sinking POC from recent primary production and sorption of deep DOC onto suspended particles. Steady state was assumed for the amount of suspended POC per unit area in the deep ocean, [POCsusp]; decay of $^{14}C$ from 1950 to 2000 was assumed to be negligible. We calculated the $\Delta^{14}C$ values for suspended POC in one-year time steps (using Equation 1 below) while varying $k_1$ and $k_2$ (yr$^{-1}$) to obtain the best fit to the two average values measured at each deep-sea site (Figure 3):

$$\frac{d(\Delta^{14}C_{POCsusp})}{dt} = k_1(\Delta^{14}C_{POCsink}) + k_2(\Delta^{14}C_{DOC}) - (k_1 + k_2)(\Delta^{14}C_{POCsusp})$$

(1)

where: $k_1$ = (flux of POCsink into POCsusp)/[POCsusp], $k_2$ = (flux of DOC into POCsusp)/[POCsusp], and $\Delta^{14}C_{DOC}$ in the deep NCP and SS are -525‰ and -390‰, respectively [Druffel et al., 1992].

[15] The best fit to the NCP data was obtained using a $k_1$ for POCsink of 0.1 yr$^{-1}$ and a $k_2$ for DOC of 0.018 yr$^{-1}$; the combined turnover time of POCsusp (= 1/(k1 + k2)) is 8.5 years. Assuming the concentrations of suspended POC in the SS and NCP are similar, new production in the SS is 30% lower than in the NCP ($k_1 = 0.067$ yr$^{-1}$) [Michaels et al., 1994; Emerson et al., 1997], and DOC is sorbed to POC at the same rate in both oceans ($k_2 = 0.018$ yr$^{-1}$), the model results (not shown in Figure 3) are much higher than the observed SS values.
A third source of old carbon to the deep suspended POC in the SS is laterally advected, resuspended sediment (POC_{SOC}). Transport of resuspended sediment from the northeastern U.S. margin to the Bermuda rise has been reported using isotopic [Ohkouchi et al., 2002; Bauer and Druffel, 1998] and physical evidence [Laine et al., 1994]. A $\Delta^{14}C$ measurement of POC_{SOC} from the U.S. continental slope was $-400\%$ in April 1994 [Bauer and Druffel, 1998].

To fit the observed data, $k_3(\text{flux of SOC into POC}_{sus})/(\text{POC}_{sus})$ is about 0.007 (see Figure 3). The addition of another source of old carbon does not change the shape of the trend, so we still cannot simulate the observed data as well as we can for the NCP. This might be because the resuspension events are episodic, and their strength varies with time (for example, resuspension may have been stronger in 1989 than in 2000).

4. Conclusions

The decrease of $\delta^{13}C$ in suspended POC from the 1980s to the 1990s suggests that anthropogenic CO$_2$ has permeated the organic carbon of the deep open ocean. Detection of the anthropogenic signal in deep-ocean suspended POC is facilitated by its low concentration and more rapid turnover (i.e., decades) than other, much larger carbon pools (e.g., DOC or DIC). We observed that $\Delta^{14}C$ values in suspended POC were lower in the 1990s in the NCP than 12 years earlier, whereas those in the SS stayed the same or increased with time. Using a box model, we show that the average turnover time of bulk suspended POC in the deep sea is about 8–10 years. Overall lower $\Delta^{14}C$ values in the deep SS were attributed to laterally advected organic carbon from surface sediments of the continental margin. These findings emphasize the critical importance of decadal-scale time-series measurements for assessing changes in deep ocean biogeochemical processes. Also critical to our understanding of atmospheric/ocean coupling is the role of oceanic organic matter in sequestering excess CO$_2$, especially considering the likely scenario of two times the preanthropogenic level of atmospheric CO$_2$ that is anticipated within the next fifty to one hundred years [Climate Change 2001-IPCC Report, 2001].

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References


