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Incorporation of aged dissolved organic carbon (DOC) by oceanic particulate organic carbon (POC): An experimental approach using natural carbon isotopes

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Abstract

Incorporation of ^{14}C-depleted (old) dissolved organic carbon (DOC) on/into particulate organic carbon (POC) has been suggested as a possible mechanism to explain the low Δ^{14}C-POC values observed in the deep ocean [Druffel, E.R.M., Williams, P.M., 1990. Identification of a deep marine source of particulate organic carbon using bomb [14]C. Nature, 347, 172–174.]. A shipboard incubation experiment was performed in the Sargasso Sea to test this hypothesis. Finely ground dried plankton was incubated in seawater samples from the deep Sargasso Sea, both with and without a biological poison ($HgCl_2$). Changes in parameters such as biochemical composition and carbon isotopic signatures of bulk POC and its organic compound classes were examined to study the roles of sorptive processes and biotic activity on POC character. Following a 13-day incubation, the relative abundance of the acid-insoluble organic fraction increased. Abundances of extractable lipids and total hydrolyzable amino acids decreased for both treatments, but by a greater extent in the non-poisoned treatment. The Δ^{14}C values of POC recovered from the non-poisoned treatment were significantly lower than the value of the unaltered plankton material used for the incubation, indicating incorporation of ^{14}C-depleted carbon, most likely DOC. The old carbon was present only in the lipid and acid-insoluble fractions. These results are consistent with previous findings of old carbon dominating the same organic fractions of sinking POC from the deep Northeast Pacific [Hwang, J., Druffel, E.R.M., 2003. Lipid-like material as the source of the uncharacterized organic carbon in the ocean? Science, 299, 881–884.]. However, the Δ^{14}C values of POC recovered from the poisoned treatment did not change as much as those from the non-poisoned treatment suggesting that biological processes were involved in the incorporation of DOC on/into POC.

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1. Introduction

Most particulate organic carbon (POC) in the open ocean is produced by photosynthesis using dissolved inorganic carbon (DIC) as its precursor in the surface ocean. Only a small fraction of POC produced by photosynthesis reaches the deep ocean (Martin et al.,

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1987; Wakeham et al., 1997). The POC is believed to reach the abyssal seafloor within approximately two months of its production (Deuser and Ross, 1980; Honjo, 1982).

Natural abundance radiocarbon signatures ($\Delta^{14}C$, per mil deviation of the $^{14}C/^{12}C$ ratio relative to a nineteenth century wood standard, corrected to $\delta^{13}C$ of $-25‰$; Stuiver and Polach, 1977) have been applied to studies of the sources, sinks, and cycling of marine POC in several studies (Williams and Druffel, 1987; Druffel et al., 1992; Williams et al., 1992). A major conundrum of these isotope data is the observed decrease of 50‰ to 100‰ in $\Delta^{14}C$ for both suspended and sinking POC with depth (Druffel et al., 1992; Druffel and Williams, 1990). If surface-produced POC was the only source of POC to deep waters and was transported to the deep ocean on time scales of months, as for sinking POC (Deuser and Ross, 1980; Honjo, 1982), to several years, as for suspended POC (Bacon and Anderson, 1982; Druffel et al., 2003), then there should be no discernible gradient in $\Delta^{14}C$-POC with depth.

One suggestion for the vertical gradient in $\Delta^{14}C$ of suspended POC is the incorporation of ^{14}C-depleted (old) DOC into POC pool (Druffel and Williams, 1990). The $\Delta^{14}C$ of DOC is so low that incorporation of a relatively small fraction of deep DOC (~14% of total POC mass with a $\Delta^{14}C$ of $-525‰$ in the Pacific) would be sufficient to decrease $\Delta^{14}C$ of suspended POC from 60‰ (surface water value) to $-20‰$ (at 3450 m depth, Druffel et al., 1998a). Another mechanism suggested is incorporation of low-$\Delta^{14}C$ DIC by either chemoautotrophy or anapleurotic reactions (direct use of bicarbonate ion to produce citric acid cycle intermediates that are drawn from the cycle for syntheses of other compounds) at depth by organisms associated with particles and aggregates (Rau et al., 1986). Finally, incorporation of old, resuspended sediments into the suspended POC may be a dominant mechanism on continental margins and surrounding slope regions (Bauer and Druffel, 1998; Druffel et al., 1998a; Sherrell et al., 1998; Hwang et al., 2004). However, the $\Delta^{14}C$ depth gradient is also observed at remote sites (e.g., North Central Pacific, Sargasso Sea), indicating that resuspended material is unlikely to be the only source of old POC, especially at depths 1–2 km above bottom (Druffel et al., 1998b).

Several studies suggest that incorporation of DOC on/into particles does occur in the ocean. Sorption of DOC onto mineral particles was observed in laboratory experiments (Hedges, 1977; Wang and Lee, 1993) and has been suggested as a way of preserving labile organic matter (Keil and Hedges, 1993; Mayer, 1994).

Spontaneous formation of particulate organic matter microgels from dissolved organic matter polymers in filtered seawater has also been reported (Chin et al., 1998). Highly sticky surface of transparent exopolymer particles (TEP) facilitates particle aggregation (Passow and Alldredge, 1995), implying that particles of similar properties as TEP may help the incorporation of DOC.

In the present study, an incubation experiment was conducted to better evaluate the process of carbon exchange between DOC and POC pools in open ocean waters. Changes in biochemical composition and isotopic signatures of bulk POC and its component organic compound classes were used to demonstrate that incorporation of DOC on/into POC does occur and should be considered in models of oceanic carbon fate and transformations.

2. Methods

An incubation experiment was performed during the SarC cruise in the Sargasso Sea in summer (June 9–July 11) 2000, aboard the *R/V Knorr*. Deep Sargasso Sea water was collected from 1500 m depth (31°50'N, 63°30'W). The water was drained from Niskin bottles directly into six 19-l polycarbonate vessels. Polycarbonate vessels used for the experiment had been filled with distilled water and were used after removing distilled water without further cleaning. Vessels of this type have been shown to be clean and do not add (due to leaching) or remove (due to sorption to the vessel walls) any measurable DOC to the stored water samples (J. Bauer, unpublished data). The seawater was not filtered because the POC concentration at this depth was very low (0.1 μM suspended POC, Druffel et al., 2003) relative to the DOC concentration (43 μM, Druffel et al., 1992).

Plankton material used for inoculation was collected by a surface plankton net tow (335 μm mesh size, mostly zooplankton) during previous cruises. The plankton material was acidified in 3% HCl solution overnight to remove inorganic carbon, dried at 50 °C and ground to a fine powder. Thirty milligrams of the plankton material ($50 \pm 0.2\%$ organic carbon content) was added to each of four vessels to simulate POC (resultant POC concentration=66 μM). Two additional vessels without plankton added were used as controls. A subset (vessels #3, #4 and #6) of the six total incubation vessels was poisoned with 3.8 ml of saturated mercuric chloride solution (final concentration of $HgCl_2$ was 54 μM) to eliminate biological activity and assess physical sorption only. All incubation vessels were maintained in the dark at room temperature,

about 22 °C. It is likely that both microbial activity and abiotic sorption were enhanced at room temperature relative to in situ temperature (3–5 °C) and the effects of incubation were more easily observable in a shorter time period. Although biotic activity may not be representative of actual in situ processes, our experiment is meaningful to study the general potential features of POC transformation by biotic and abiotic activity. Duplicate, unfiltered 10-ml sub-samples of the water from each vessel were collected daily for DOC monitoring and frozen until analysis. The vessels were shaken vigorously in an upright position twice a day, including once immediately after sub-sampling.

At the end of the 13-day incubation, water from the vessels was filtered through pre-combusted quartz-fiber filters (Whatman QMA, 47 mm, 0.8 μm nominal pore size) using a peristaltic pump and pre-cleaned silicone tubing. During the filtration, water samples were collected for isotope analyses of DIC and DOC. Filtration of each non-poisoned sample took about 90 min due to an abundance of apparent mucous particles following incubation. In contrast, POC from poisoned vessels appeared unaltered and filtration of the poisoned water samples took 30 min or less. Filtered samples were kept frozen until analysis.

A fraction (a quarter to a half) of each filter was combusted to determine the amount of POC and isotopic signatures of bulk POC. Recovery of POC determined by this method may have a large uncertainty because of uneven distribution of particles on the filters, as observed visually. Lipids, total hydrolyzable amino acids (THAA), total hydrolyzable neutral carbohydrates (TCHO), and the acid-insoluble fraction were extracted from the plankton material used for inoculation following the method described by Wang et al. (1998). However, only lipids, THAA, and the acid-insoluble fraction were extracted from recovered POC samples because of the small amount of material collected on the filters. Extracted organic fractions were combusted following the standard procedures for carbon isotope ratio measurements described in Druffel et al. (1992). The amount of each organic fraction was determined by measurement of the pressure of CO_2 gas produced by sealed tube combustion. The $\Delta^{14}C$ values were analyzed at the Keck Carbon Cycle AMS laboratory of the University of California, Irvine (analytical standard deviation $< \pm 5‰$). The $\delta^{13}C$ values were analyzed using a Finnigan Delta plus isotope ratio mass spectrometer at the Keck laboratory (analytical standard deviation $< \pm 0.1‰$). Isotopic signatures were blank-corrected following the standard dilution method described by Hwang and Druffel (2005). Subsamples for

DOC monitoring were analyzed with a Shimadzu TOC 5000A (analytical standard deviation $= \pm 2$ μM). All DOC analytical runs included periodic measurements of deep ocean seawater and low-carbon water community reference materials for establishing analytical accuracy and instrument blanks (Sharp et al., 2002). The measured values of these reference waters agreed at all times with the community consensus values reported by Sharp et al. (2002).

3. Results and discussion

3.1. Changes in concentrations and isotope signatures of bulk POC and organic fractions

Concentrations of DOC collected for daily monitoring had a high temporal variability ranging between 50 and 110 μM (data not shown). Increases in DOC concentration by 60 μM above the initial value at times cannot be explained by dissolution of the added POC because it would require 100% dissolution of the added POC. The high variability is likely caused by the inclusion of variable amounts of fine suspended particles into the subsamples because the samples were not filtered, and the results were not meaningful as DOC concentrations.

The POC concentrations in both poisoned and non-poisoned incubations decreased over the time course of the experiment. A greater amount of POC was recovered from the poisoned vessels (57% and 27% recovery for vessel #3 and #4, respectively) than the non-poisoned vessels (16% and 23% recovery for vessel #1 and #2, respectively, Table 1) by the end of the experiment. The average loss of POC in duplicate incubation treatments was equivalent to 38 ± 10 μM for the poisoned and 53 ± 3 μM for the non-poisoned treatments (data not shown). The results for the poisoned treatment suggest that POC was converted to DOC by non-biotic processes. The smaller recovery for the non-poisoned treatment suggests consumption of POC by microorganisms in addition to loss by physical processes. Unfortunately, samples collected at the end of the incubation for DOC concentration and $\Delta^{14}C$ measurement were lost.

By the end of the incubation, the concentrations of lipids and THAA in POC had decreased, while those of the acid-insoluble fraction increased (Table 1 and Fig. 1a). These changes in concentrations are larger for the non-poisoned (#2) treatment than for the poisoned treatment (#3) (Fig. 1a). This compositional change is consistent with observations of decreasing relative abundances of amino acids, carbohydrates, and lipids,

Table 1
Biochemical and isotopic composition of plankton and POC recovered from each vessel at the end of the incubation

Sample	Bulk POC			Abundances (%)				Δ^{14}C (‰)[a]				δ^{13}C (‰)[b]			
	Recovery (%)	Δ^{14}C (‰)	Δ^{13}C (‰)	Lipids	THAA	TCHO	Acid-insol.	Lipids	THAA	TCHO	Acid-insol.	Lipids	THAA	TCHO	Acid-insol.
Plankton material		74 ± 5 (2)[c]	−20.5	22 ± 1 (4)	54 ± 8 (4)	5 ± 1 (4)	3 ± 1 (4)	42 ± 8 (3)	79 ± 22 (2)	95 ± 11 (2)	34 ± 21 (4)	−24.7 ± 0.2 (3)	−18.5 ± 0.2 (3)	−19.1 ± 0.2 (3)	n.d.
POC #1 (non-poisoned)	16	−52 ± 9 (2)	−23.4					−163 ± 60							
POC #2 (non-poisoned)	23	8 ± 5 (2)	−22.3	10	23	n.d.	20	−227 ± 39	110 ± 26	n.d.	−91 ± 25	n.d.	−18.7 ± 0.5	n.d.	−24.7
POC #3 (poisoned)	57	48 ± 7 (2)	−21.2	19	34	n.d.	12	13 ± 7	86 ± 6	n.d.	16 ± 10	−24.8 ± 0.1	−18.9 ± 0.1	n.d.	−23.9
POC #4 (poisoned)	27	41 ± 20 (2)	−19.9												

n.d.=not determined.

[a] The Δ^{14}C values of lipids, THAA and TCHO were blank-corrected using the standard dilution method described by Hwang and Druffel (2005) by processing small sized standards. The acid-insoluble fractions were not blank-corrected. Instead, large uncertainties were given considering the worst case, i.e., when Δ^{14}C of blank carbon was −1000‰.

[b] The δ^{13}C values of lipids, THAA and TCHO were blank-corrected. The acid-insoluble fractions were not blank-corrected. However, the uncertainties are <1‰.

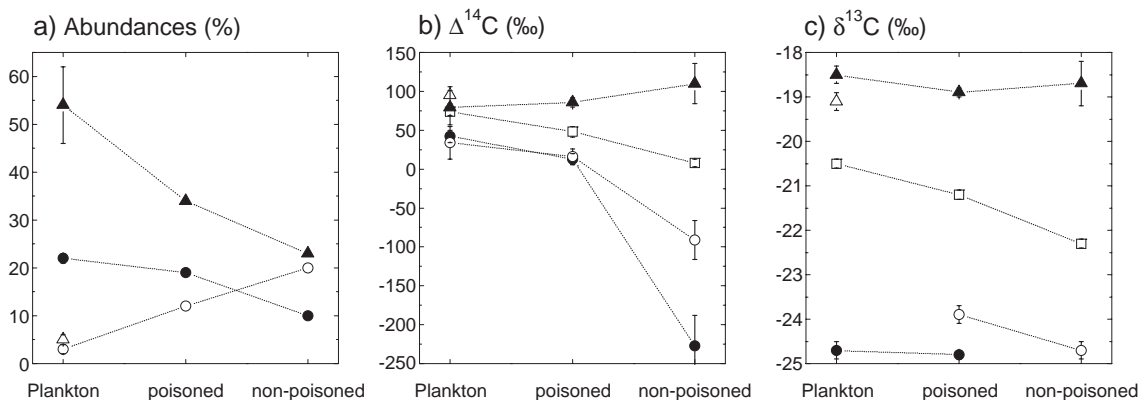[c] In parentheses are numbers of replicate analyses.

Fig. 1. a) Abundances (%), b) $\Delta^{14}C$ values (‰), and c) $\delta^{13}C$ values (‰) for the bulk forms and each organic fraction of plankton material used for the incubation, and POC recovered from vessel #3 (poisoned), and vessel #2 (non-poisoned) at the conclusion of each incubation (THAA, solid triangles; TCHO, open triangles; lipids, solid circles; the acid-insoluble fraction, open circles; Bulk OC, open squares). Carbohydrate data are available only for plankton material (only lipids, THAA, and the acid-insoluble fraction were extracted from recovered POC samples because of the small amount collected on the filters).

and increase in the acid-insoluble (or uncharacterized) fraction, in oceanic sinking POC as a function of depth (Wakeham et al., 1997). Thus, our findings may suggest selective preservation as a possible mechanism for accumulation of the acid-insoluble fraction.

The $\Delta^{14}C$ values of bulk POC recovered following the incubation were significantly lower ($-52‰$ to $+48‰$) than those of initial plankton material ($+74‰$, Table 1). However, the decrease was much larger for the non-poisoned treatment ($66–126‰$ decrease) than for the poisoned treatment ($26–33‰$ decrease). The $\Delta^{14}C$ values of individual organic fractions of the plankton material spanned a range of about $60‰$ (Table 1 and Fig 1b). By the end of the incubation, the $\Delta^{14}C$ values of THAA did not change significantly for either the poisoned or non-poisoned treatments. In contrast, the $\Delta^{14}C$ values of the lipids ($-227‰$ to $+13‰$) were much lower than the initial value ($42‰$). The $\Delta^{14}C$ values of the acid-insoluble fraction also decreased during the incubation. The range of the $\Delta^{14}C$ values of the individual organic fractions for the non-poisoned treatment was over $300‰$ at the conclusion of the incubation. These results are consistent with the observation that old carbon was present mainly as lipids and the acid-insoluble fraction, and the observed negative correlation between the range of $\Delta^{14}C$ values of individual organic fractions and the $\Delta^{14}C$ value of the corresponding bulk OC at Station M in the northeastern Pacific (Wang et al., 1998; Hwang and Druffel, 2003). The range of $\Delta^{14}C$ values among the organic fractions for the poisoned treatment was larger than that for the plankton material, but not as large as that observed for the non-poisoned treatment.

This suggests that incorporation of aged carbon occurs preferentially for lipids and the acid-insoluble fraction and biological activity enhances this process.

The $\delta^{13}C$ values of the bulk POC decreased over the course of the incubation (Table 1 and Fig. 1c). The decrease is greater for the non-poisoned treatment (1.8–2.9‰) than for the poisoned treatment ($-0.6–0.7‰$). In contrast, the $\delta^{13}C$ values of THAA did not change during the incubation. Although the data are not complete for comparison, the $\delta^{13}C$ values of lipids and the acid-insoluble fraction also did not appear to show a significant trend (Fig 1c).

Our results show that the $\delta^{13}C$ value of bulk POC changes as its biochemical composition changes. The decrease in the relative abundances of amino acids and carbohydrates, whose $\delta^{13}C$ values are higher than lipids (and the acid-insoluble fraction), may cause a decrease in the $\delta^{13}C$ value of bulk POC. As an alternative explanation, the observed 1‰ to 2 ‰ decrease in $\delta^{13}C$ of the bulk POC may also arise by incorporation of organic matter with considerably different $\delta^{13}C$ values from the bulk POC. However, the absence of change in $\delta^{13}C$ for the individual organic fractions suggests that the decrease was more probably caused by relative changes in the different biochemical components (i.e., selective preservation of organic components whose $\delta^{13}C$ values are lower than that of the bulk POC).

3.2. Potential processes occurring during POC incubation

The observed changes for the poisoned treatment are assumed to be a result of only physical processes such

as hydrolysis and cell lysis. Amino acids and carbohydrates are expected to remain in particulate form more than hydrophobic lipids do. For example, partition coefficients [(g sorbate/g sediment)/(g sorbate/ml solution)] for alanine and lysine were reported to be much smaller than those of n-eicosane and melanoidins (Henrichs, 1995). This is consistent with our observations that the concentration of THAA decreased from 54% to 23% while that of lipids only decreased from 22% to 19% (Table 1, Fig. 1a). The increase in the concentration of the acid-insoluble fraction may be at least partly the result of selective accumulation. The decrease in $\delta^{13}C$ values of the bulk POC (Fig. 1c) can be explained by selective loss of THAA. However, the relatively low $\Delta^{14}C$ value ($16 \pm 10‰$) of the acid-insoluble fraction suggests that it acquired aged carbon. Physical aggregation of DOC on/into particles is one potential mechanism for explaining the low $\Delta^{14}C$ values. Sorption of hydrophobic lipids from the DOC pool may be responsible for the slight decrease in $\Delta^{14}C$ of lipids in the POC.

For the non-poisoned treatment, only about 20% of the POC added was recovered (Table 1), and thus heterotrophic consumption of POC appeared to be occurring in addition to the abiotic processes mentioned above. Loss of labile THAA and lipids was more conspicuous than for the poisoned treatment (Table 1, Fig. 1a). In addition to the loss of POC by physical and biological processes, acquisition of old carbon is also more prominent than for the poisoned treatment.

Potential sources of old carbon to POC suggested in previous studies are incorporation of DOC, DIC, and resuspended sediments. Because the experiment was performed in a semi-closed system (except the exchange between DIC and atmospheric CO_2), some potential sources can be eliminated. First, incorporation of suspended POC in the water sample (concentration=0.09 μM, $\Delta^{14}C=45‰$; Druffel et al., 2003) is not a significant source of the old carbon here. Second, although our results do not rule out incorporation of DIC to produce POC, it is unlikely to be the main mechanism. A mass balance calculation using $-66‰$ as the $\Delta^{14}C$ value of DIC at 1500 m depth in the Sargasso Sea (Druffel and Griffin, unpublished data), indicates that about 70% of the recovered POC would need to be derived from DIC [$74 \times (1-x) + (-66 \times x) = -22‰$, where $-22‰$ is the average of the $\Delta^{14}C$ values of POC from the vessels #1 and #2; x=fraction from DIC=0.69]. The incubation vessels were not closed systems because we opened them for subsampling once per day and $\Delta^{14}C$ values of DIC collected at the end of the incubation rose to an average of $-34 \pm 5‰$ in all 4 vessels (Druffel and

Griffin, unpublished data). Consequently, 70% is a conservative estimate of the fraction of POC that may have been incorporated from DIC assuming this mechanism occurs. Furthermore, incorporated DIC would be predicted to contribute old carbon to all organic fractions (Rau et al., 1986 and references therein), which is not consistent with our observation.

The most plausible source of the old carbon is DOC, whose $\Delta^{14}C$ value in the deep water used for incubations was $-390‰$ (Druffel et al., 1992). A mass balance calculation shows that about 20% of recovered POC would need to be derived from DOC [$74 \times (1-x) + (-390 \times x) = -22$, $x=0.21$] to account for the observed $\Delta^{14}C$-POC values at the end of the incubation. This would be equivalent to a 3 μM decrease in the DOC concentration. In the oceanic water column, about 14% of the POC has been suggested to be comprised of sorbed DOC (Druffel and Williams, 1990). However, these values may not be directly comparable to the present findings because our experimental conditions (such as POC concentration) were different from the natural conditions. Furthermore, a fraction of added POC may have been converted to DOC to make the age of DOC younger than that of the initial DOC. If this were the case, the actual amount of incorporated DOC would be larger.

The observed low $\Delta^{14}C$ values of lipids and the acid-insoluble fraction support the DOC sorption hypothesis. Extractable lipids and the molecularly uncharacterized fraction of high molecular weight DOC were reported to have significantly lower $\Delta^{14}C$ values than protein-like and carbohydrate-like fractions (Loh et al., 2004). Therefore, incorporation of these components of the DOC would lower the $\Delta^{14}C$ values of the lipid and the acid-insoluble fractions of POC. A mass balance calculation indicates that the observed experimental findings could arise if ~30% of POC lipids was derived from DOC lipids [$42 \times (1-x) + (-830‰ \times x) = -227‰$, $x=0.31$, where x=proportion of lipids in POC sorbed from DOC, $-830‰$ was used as $\Delta^{14}C$ value of DOC lipids (Loh et al., 2004)]. This amount is equivalent to 0.4 μM of DOC (31% of recovered lipids as POC), which is about 1% of DOC.

Biological activity may enhance the incorporation of DOC on/into POC by changing certain properties of the particle surface. Particles recovered at the end of the incubation from the non-poisoned treatment were visibly coated with a transparent mucous. Diatoms excrete colloidal products that are the source of transparent exopolymer particles [TEP, Passow and Alldredge (1995)]. The TEP forms a sticky, mucous matrix that may facilitate the aggregation of particles and possibly

additional sorption of DOC. Although the material observed in our non-poisoned samples during filtration may not be the same as TEP, it is reasonable that it may have enhanced sorption of DOC onto the surface of the particles.

4. Summary

Radiocarbon analysis is an effective tool for studying the incorporation of DOC into POC because of the large difference in $\Delta^{14}C$ signatures between the two pools. The decrease in $\Delta^{14}C$ of recovered POC was much larger for the non-poisoned treatment than for the poisoned treatment, suggesting that biological activity enhanced the incorporation of DOC, likely by making particle surfaces more hydrophobic and surface-active. The old carbon that was incorporated was comprised predominantly of extractable lipids and acid-insoluble material, which is consistent with previous observations that the same organic fractions of sinking POC had much lower $\Delta^{14}C$ values than hydrolyzable amino acids and carbohydrates (Hwang and Druffel, 2003). The $\delta^{13}C$ values of bulk POC in the non-poisoned treatment decreased likely because of selective degradation of organic fractions enriched in ^{13}C, such as hydrolyzable amino acids.

Although this experiment demonstrates that incorporation of old DOC is a potential mechanism for lowering the $\Delta^{14}C$ of POC, it is not possible to say at this time that this is the exclusive or dominant mechanism operating in situ in the oceans. Studies of the formation mechanisms and properties of organic gels in the ocean and their role in connecting the DOC and POC pools (see a review by Verdugo et al., 2004) may shed additional light on our understanding the interactions between these two primary forms of marine organic matter.

Acknowledgements

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