

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

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Received 11 April 2005; received in revised form 19 October 2005; accepted 21 October 2005

Abstract

Incorporation of ¹⁴C-depleted (old) dissolved organic carbon (DOC) on/into particulate organic carbon (POC) has been suggested as a possible mechanism to explain the low $\Delta^{14}\text{C}$ -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 ¹⁴C. *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 $\Delta^{14}\text{C}$ 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 ¹⁴C-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 $\Delta^{14}\text{C}$ 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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Keywords: Particulate organic carbon; Dissolved organic carbon; Sorption; Radiocarbon; Organic compound classes; Carbon cycle; Atlantic Ocean; Sargasso Sea

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 ($\Delta^{14}\text{C}$, per mil deviation of the $^{14}\text{C}/^{12}\text{C}$ ratio relative to a nineteenth century wood standard, corrected to $\delta^{13}\text{C}$ 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 $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ -POC with depth.

One suggestion for the vertical gradient in $\Delta^{14}\text{C}$ of suspended POC is the incorporation of ^{14}C -depleted (old) DOC into POC pool (Druffel and Williams, 1990). The $\Delta^{14}\text{C}$ of DOC is so low that incorporation of a relatively small fraction of deep DOC ($\sim 14\%$ of total POC mass with a $\Delta^{14}\text{C}$ of -525‰ in the Pacific) would be sufficient to decrease $\Delta^{14}\text{C}$ 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- $\Delta^{14}\text{C}$ 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 $\Delta^{14}\text{C}$ 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 ($31^{\circ}50'\text{N}$, $63^{\circ}30'\text{W}$). 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 ($0.1\ \mu\text{M}$ suspended POC, Druffel et al., 2003) relative to the DOC concentration ($43\ \mu\text{M}$, Druffel et al., 1992).

Plankton material used for inoculation was collected by a surface plankton net tow ($335\ \mu\text{m}$ mesh size, mostly zooplankton) during previous cruises. The plankton material was acidified in 3% HCl solution overnight to remove inorganic carbon, dried at $50\ ^{\circ}\text{C}$ 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 = $66\ \mu\text{M}$). 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 $54\ \mu\text{M}$) to eliminate biological activity and assess physical sorption only. All incubation vessels were maintained in the dark at room temperature,

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