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14C activity of dissolved organic carbon fractions in the north-central Pacific and Sargasso Sea

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that there is very much less H_2 in the bulge than is suggested by CO observations. The CS observations of Bally et al.[1] suggest that the former is the correct interpretation. Thus, in the bulge, the cosmic-ray nucleons do not seem to make a significant contribution to the gas pressure. This is consistent with our interpretation that the synchrotron observations imply a cosmic-ray electron density close to the local value.

The inference that the gas in the central regions of the Galaxy is under higher pressure leads to several observational consequences. Most of these are predictions, but some are suggested by existing data. (1) It will not be possible to find any lines of ^{13}CO unambiguously associated with the Galactic Centre with linewidths narrower than ~ 10 km s^{-1}, regardless of the resolution used to observe them. (2) The volume density of the H I in the galactic bulge is at least 10^2–10^3 everywhere in the bulge, and most probably exists only in thin sheets around the molecular clouds. (3) Measurements of Zeeman splitting in OH and H I should show field strengths of ~ 100 μG in gas unambiguously associated with the bulge. Such gas can be identified by its large radial velocities in absorption against the Sgr A and other continuum sources. (4) The scale height of the X-ray emitting gas is ~ 500–1,000 pc. (5) In the disk of the Milky Way, the ratio of high-density molecules to CO mapped within a constant CO surface brightness contour should be proportional to the stellar surface density of the disk and should decrease with galactocentric radius. The reason for this is that in the disk, the diffuse H I is the hydrostatic component with the highest pressure because of its large scale height and high surface density at all distances outside the bulge. Because the stellar surface density falls off much more rapidly than the scale height increases[38], the total gas pressure must fall monotonically with galactic radius. (6) For a given ionizing flux, H II regions should have higher emission measures (higher surface brightness) in the inner Galaxy than in the outer Galaxy; the emission measure scales as the square of the ambient gas density. In fact, the brightest H II regions are seen in the molecular ring of the Galaxy where the gas pressures should have their highest values in the disk[39]. (7) Supernova remnants in the galactic bulge should spend much less time in the 'snowplough' phase. Thus, there should be few large old remnants and there should be a much higher efficiency in transferring the kinetic energy of the supernova to the interstellar medium.

These arguments should be valid not only in the bulge of the Milky Way, but also in bulges of other galaxies and in elliptical galaxies. If there is an ambient hot, diffuse component filling these galactic bulges, then hydrostatic equilibrium and the deep potentials of these galaxies imply that the gas in the central regions of galaxies is under very high pressure[40]. X-ray observations show that spirals and ellipticals frequently have such hot, high-pressure gas in their nuclei[41]. This leads to additional predictions. (1) The molecular gas in the bulge regions of galaxies should have a higher ratio of molecules such as CS, HCN and HCO$^+$, relative to CO and ^{13}CO, than is found in their disks. In fact, high ratios have recently been found in the centres of many galaxies[42,43], suggesting that this picture is correct, but it remains to be shown that these ratios are significantly higher than is found in the disks of the galaxies, and that the observed ratios are correlated with central pressure. (2) The ratio of high-density molecules to CO should be a function of Hubble type and hot gas pressure. Dwarf irregular galaxies should have small abundances of high-density molecules relative to CO. In spite of the relatively weak lines of CO found in giant elliptical galaxies, they should have among the highest ratio of high-density molecules to CO if they have extended X-ray emission. If individual clouds mapped with interferometers can be observed, these clouds should have relatively broad lines commensurate with the large ambient pressures for the gas. (3) The inner regions of the molecular disk in the Cen A host galaxy NGC5128 should have high internal velocity dispersions and high dense gas molecular abundances. ☐

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^{14}C activity of dissolved organic carbon fractions in the north-central Pacific and Sargasso Sea

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RADIOCARBON measurements of dissolved organic carbon (DOC) oxidizable by ultraviolet irradiation (DOC_{uv}) yielded apparent ages of $\sim 6,000$ yr in the deep waters of the oligotrophic north-central Pacific gyre[1]. Recent reports of a potentially larger pool of DOC as measured by high-temperature catalytic combustion (DOC_{htc}) using discrete injections of sea water[2,3] have led to speculation that 'younger', more recently produced DOC could contribute significantly to overall oceanic organic carbon fluxes, owing to its suspected greater biological lability[4–6]. Here we present a comparison of $\Delta^{14}C$ (the deviation in parts per thousand from the ^{14}C activity of nineteenth-century wood)[7] of the DOC_{htc}, DOC_{uv} and humic substances in profiles from the oligotrophic north-central Pacific and Sargasso Sea. For each ocean, the $\Delta^{14}C$ values of all three fractions are remarkably similar, yielding no

evidence for a component of DOC that is cycled through the system on timescales shorter than several thousands of years. We observe an age difference between the two oceans of ~2,000 yr for the deepest DOC, which can largely be accounted for by differences in the $\Delta^{14}C$ of the DOC sources to the deep basins, and by the different deep-water circulation patterns and transit times in the two oceans.

Here we use the term DOC to mean that fraction of the organic carbon which passes a Whatman GF/C glass-fibre filter (nominal pore size 1.0 μm), thus including colloidal organic carbon and traces of carbon associated with small bacteria, viruses and organic particles. A total of 27 analyses of sea water from depths of 3 to 5,700 m in the north-central Pacific (Eve-1 cruise; 31° 00′ N, 159° 00′ W; June 1987) and 34 analyses from 3 to 4,450 m in the Sargasso Sea (Hydros-6 cruise; 31° 50′ N, 63° 30′ W; May 1989) were made on samples collected with clean, stainless steel Gerard barrels and filtered directly into clean 4-l bottles which were frozen at −20 °C. Before analysis, samples were thawed, acidified to pH 2.5 with H_3PO_4 and

sparged with carbon-free N_2 or O_2 to remove inorganic carbon. The DOC in the sea water was then oxidized by either standard ultraviolet irradiation (1,200 W for 6 h)[1], high-energy ultraviolet irradiation (2,400–3,600 W for 2–3 h), or continuous-injection HTC oxidation using Co/CoO-coated alumina or 2% (by weight) Pt-coated zeolite catalysts[8]. Separate subsamples were also analysed by HTC using discrete, 100-μl injection volumes. Humic substances (humic plus fulvic acids) were obtained by sequentially extracting sea water acidified with HCl to pH 2 on XAD-2 and XAD-4 macroreticular resins and collecting the base-soluble (0.1 M NaOH) fraction of the eluate[9,10]. The recovered, desalted material was then oxidized to CO_2 by sealed-tube combustion[11]. All samples were analysed for $\Delta^{14}C$ by accelerator mass spectrometry (AMS).

The efficacy of continuous-injection HTC combustion for quantitatively oxidizing DOC and allowing accurate determination of its ^{14}C content was demonstrated by redissolving humic substances, isolated from 50 and 3,200 m at the Sargasso Sea site, in ultra-high-purity artificial seawater at concentrations
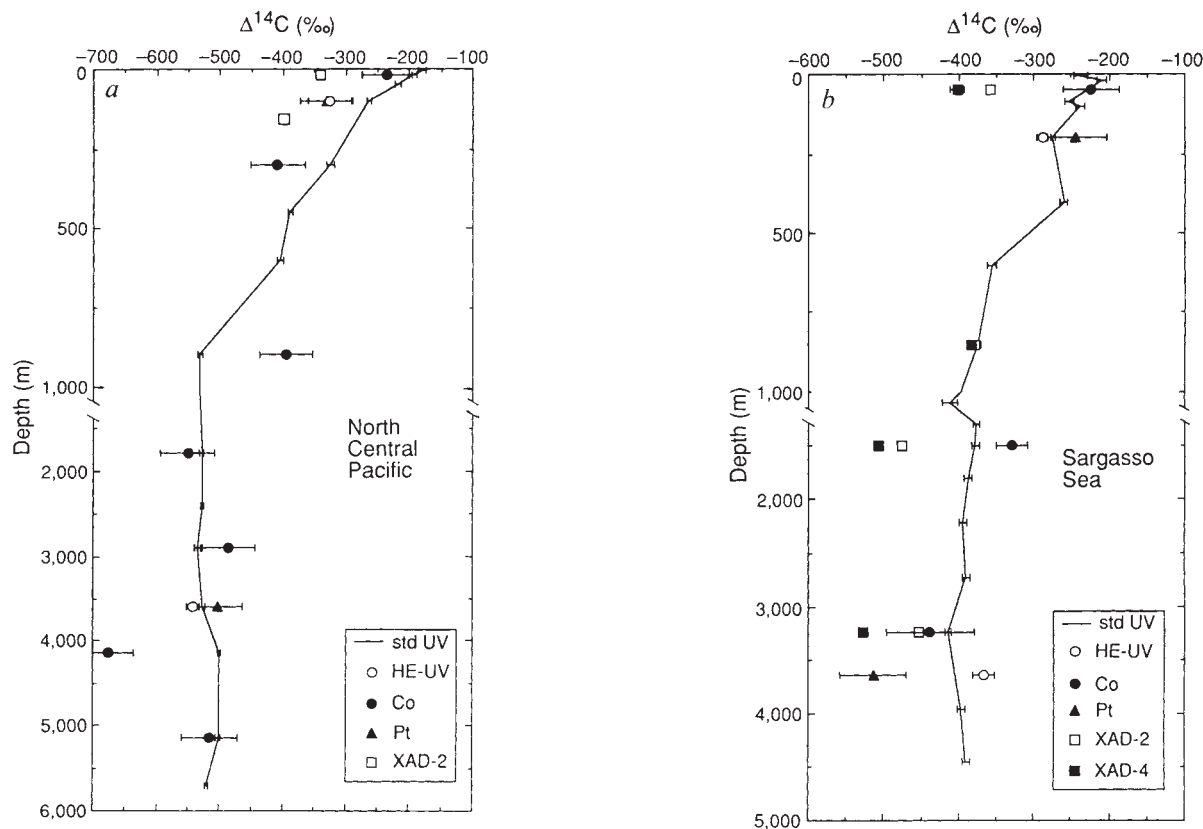

FIG. 1 Profiles of $\Delta^{14}C$ values of DOC measured for sea water from (a) the north-central Pacific (31° 00′ N, 159° 00′ W; June 1987) and (b) the Sargasso Sea (31° 50′ N, 63° 30′ W; May 1989). Values of $\Delta^{14}C$ for DOC_{uv} from the Pacific were previously reported[24]. All $\Delta^{14}C$ values are corrected to a $\delta^{13}C$ value of −25‰ (ref. 7). The $\delta^{13}C$ values of DOC_{uv} were determined directly on sample CO_2, whereas that of DOC_{htc} was assumed to be −21‰. Horizontal bars represent total cumulative error, including that for AMS counting statistics, blank correction and replicate analysis. Errors for $\Delta^{14}C$ values of DOC_{htc} are large because of subtraction of experimental blanks and their associated $\Delta^{14}C$. Standard ultraviolet (std UV) oxidations followed previous methodology[1]. High-energy ultraviolet (HE-UV) oxidations used similar techniques but with smaller sample volumes (650 ml) irradiated for shorter periods of time (2 h) at higher energies (2,400–3,600 W). The system blank for all ultraviolet oxidations was <2% of the sample size. The HTC oxidations consisted of continuous injection of seawater samples onto either Co/CoO-on-alumina or 2% Pt-on-zeolite catalysts at 900 °C, using ultra-high-purity (UHP) oxygen as the carrier gas[29]. Each HTC oxidation of ~100 ml of sea water required ~3–3.5 h. The blank due to carrier-gas flow (no water injection) averaged 22 ± 8% of total carbon collected during a sample run.

The average blank attributable to injection of water during HTC oxidations was 1.4 ± 2.5 μg C h^{-1} and was attained by continuously injecting UHP distilled water through the system for 12–18 h (total volume ~400–500 ml) before sample analysis. The mean $\Delta^{14}C$ value of blanks for carrier gas only over all runs was −441 ± 167‰ compared with a mean $\Delta^{14}C$ value of −430 ± 200‰ for continuous injection of UHP distilled water. The CO_2 evolved from each oxidation was collected either cryogenically for ultraviolet oxidations or with a synthetic zeolite molecular sieve for HTC oxidations[25], purified and quantified on a vacuum extraction line and flame-sealed in a 6-mm Pyrex tube. The $\Delta^{14}C$ measurements were made at Lawrence Livermore National Laboratory or University of Arizona AMS facilities following the conversion of sample CO_2 to graphite targets[26,27]. The $\Delta^{14}C$ values of humic substances isolated from the north-central Pacific were determined previously[12] (K. Meyers-Schulte and J. Hedges, personal communication) and are presented for comparison. In the Sargasso Sea, the XAD-2 isolates of humic substances are defined as having higher average molecular weight and hydrophobicity than the XAD-4 isolates. Note difference in depth scales between sites and change in scale at 1,000 m.

	HTC		Ultraviolet		HTC Discrete injection§	
Depth (m)*	DOC$_{htc}$ (μM)†	Δ^{14}C (‰)‡	DOC$_{uv}$ (μM)†	Δ^{14}C (‰)‡	Depth (m)	DOC (μM)
North-central Pacific						
20	82	−236 ± 39	65	−195 ± 6	20	218 ± 6
100	71‖	−331 ± 41‖	53	−264 ± 4	100	206 ± 4
300	85 ± 16	−409 ± 43¶	53	−325 ± 5	300	151 ± 3
896	83	−395 ± 41	42	−532 ± 3	900	90 ± 3
1,788	57 ± 2	−551 ± 44¶	35	−529 ± 3	1,769	n.d.
2,891	76	−486 ± 41	35	−535 ± 4	3,174	n.d.
3,586	63‖	−503 ± 40‖	34	−528 ± 4	3,631	110 ± 3
4,146	67	−675 ± 38	36	−501 ± 3	4,227	112 ± 3
5,150	85	−516 ± 45	36	−502 ± 3	5,227	112 ± 3
Sargasso Sea						
50	87 ± 11	−224 ± 36¶	62	lost	50	130 ± 12
200	101‖	−245 ± 41‖	54	−276 ± 5	200	114 ± 3
1,510	61	−370 ± 20	43	−378 ± 5	1,510	98 ± 6
3,237	82 ± 6	−438 ± 59¶	43	−414 ± 5	3,237	103 ± 2
3,638	66‖	−514 ± 44‖	44	lost	3,638	102 ± 2

* Depths listed are those at which both continuous-injection HTC and ultraviolet oxidations were done.

† Concentrations determined by collection, vacuum-line purification and quantification of CO_2 derived from either continuous-injection HTC or standard ultraviolet oxidations. For samples oxidized by continuous-injection HTC oxidation, we used a Co/CoO-on-alumina catalyst, except for those designated by (‖), for which we used 2% Pt-on-zeolite catalyst. Measurement error (±1σ) for concentration determinations was ±1 μM. Errors associated with DOC concentrations are ±1σ of the mean of duplicate oxidations.

‡ Δ^{14}C errors are ±1σ resulting from counting statistics, sample δ^{13}C and blank Δ^{14}C corrections; ¶ indicates average ±1σ of replicate oxidations. For samples oxidized by continuous-injection HTC we used a Co/CoO-on-alumina catalyst, except for those designated by (‖), for which we used 2% Pt-on-zeolite catalyst.

§ Discrete-injection DOC measurements made using either 3% Pt-on-alumina (north-central Pacific samples)[12] or Co/CoO-on-alumina (Sargasso Sea samples) catalysts[23]. Values for the north-central Pacific were previously reported[12] for the Alcyone-5 cruise to the same site, resulting in slight depth differences. Values for the Sargasso Sea were calculated from standard CO_2 and glucose calibration curves which were corrected by appropriate standard water (ultra-high-purity double-distilled) blank values. Errors associated with DOC concentration values are ±1σ of the mean of 3-5 replicate injections. n.d., not determined.

representative of the 'total' DOC and treating the solutions to the same procedure as natural seawater samples. Recoveries of the humic substances were all 100 ± 2% of the known amounts added, and Δ^{14}C values were identical to those determined by sealed-tube combustion of the solid humics (−374 ± 21‰ by HTC and −387 ± 26‰ by STC for 50 m; −509 ± 30‰ by HTC and −495 ± 30‰ by STC for 3,200 m).

We investigated the possibility that the Δ^{14}C of DOC$_{uv}$ is biased because of selective oxidation of organic matter. First, serial ultraviolet oxidations of samples from 20 and 1,800 m in the north-central Pacific showed no consistent differences in Δ^{14}C values of the material that was oxidized over each interval. Secondly, high-energy ultraviolet irradiation, which oxidized 4-18% more DOC than the standard ultraviolet irradiation, gave Δ^{14}C values similar to those obtained by the standard ultraviolet irradiation (Fig. 1a and b). Both results indicate that little fractionation of ^{14}C of DOC$_{uv}$ occurs as a function of DOC$_{uv}$ recovery.

The Δ^{14}C of DOC$_{htc}$ strongly resembled the more extensive profiles for DOC$_{uv}$ in both the north-central Pacific and Sargasso Sea (Fig. 1a and b). The Δ^{14}C of DOC$_{uv}$ from the north-central Pacific (Fig. 1a) ranged from −179‰ at 3 m to −535‰ at 2,900 m, similar to values obtained for sea water collected at this site in

1985 (ref. 1). The range of Δ^{14}C values for DOC$_{htc}$ (excluding the value at 4,146 m) was −236‰ at 20 m to −551‰ at 1,800 m. Nearly all of the change in Δ^{14}C of the DOC fractions occurred in the upper 1,000 m. The range in Δ^{14}C values from 3 m to 900 m was 353‰; from 900 m to 5,700 m it was only 34‰. The significantly greater Δ^{14}C value of the sample from 900 m (O_2 minimum zone) measured by HTC oxidation may be indicative of a biologically refractory fraction having a younger apparent age, whereas the low Δ^{14}C value at 4,146 m seems to be anomalous. For all samples shallower than 300 m, the DOC$_{htc}$ had slightly lower Δ^{14}C values (>1σ but <2σ) than the DOC$_{uv}$ (Fig. 1a).

The Δ^{14}C values of DOC$_{htc}$ for Sargasso Sea water were also, with one exception (3,640 m, Pt-zeolite catalyst), similar to the DOC$_{uv}$ Δ^{14}C values (Fig. 1b). The Δ^{14}C profiles of DOC$_{uv}$ from the Sargasso Sea were notably different from those for the north-central Pacific. At 20 m, the Δ^{14}C value was 15‰ lower in the Sargasso Sea because of smaller amounts of recently fixed DOC in the surface waters. At all depths greater than 20 m, however, Δ^{14}C values of DOC$_{uv}$ were significantly greater in the Sargasso Sea. The magnitude of the offset between Atlantic and Pacific Ocean waters averaged −41‰ from 50 m to 600 m and −139‰ from 900 m to ~3,400 m. As in the north-central Pacific, nearly the entire gradient in DOC Δ^{14}C values occurred in the top 1,000 m and can be attributed to the presence of recently fixed carbon ultimately derived from planktonic production in surface waters.

The recoveries of DOC using continuous-injection HTC oxidation were consistently greater than, and varied relative to, the standard ultraviolet oxidations (Table 1). For both sites, continuous-injection HTC oxidation recovered 25-40% more DOC from shallow waters (20-100 m) and 83 ± 28% ($N = 11$) more from deep waters (>100 m) than did ultraviolet oxidation. The recoveries by continuous-injection HTC relative to discrete-injection HTC could be due to several factors including incomplete oxidation, loss of DOC during freezing and storage, or adsorption of hydrophobic components of the DOC in near-surface samples. The similarity of Δ^{14}C values for DOC$_{htc}$ and DOC$_{uv}$ spanning this range of recoveries suggests that these fractions are characteristic of the mean Δ^{14}C values for the average bulk DOC pool, especially in the deep sea.

The δ^{13}C values of representative DOC$_{htc}$ samples from 200 and 3,600 m in the Saragasso Sea were −22.5 ± 0.4‰ ($N = 3$) and −21.5 ± 0.4‰ ($N = 3$), respectively, indicating that DOC$_{htc}$ is marine in nature and that no significant isotope fractionation occurred during HTC oxidation. For Sargasso Sea samples, the mean δ^{13}C value of DOC$_{uv}$ was −20.9 ± 0.3‰ ($N = 18$) and the average value over all depths for the north-central Pacific was −21.2 ± 0.5‰ ($N = 17$), identical to previously reported values for this location[1]. This indicates that the DOC$_{uv}$ fraction in both oceans is the same with respect to δ^{13}C and is also of marine origin.

The Δ^{14}C values of humic material from north-central Pacific sea water (Fig. 1a) were previously found to be −342‰ (20 m) and −400‰ (180 m), respectively[12] (K. Meyers-Schulte and J. Hedges, personal communication). In the Sargasso Sea, the Δ^{14}C values of humic isolates were significantly lower than DOC$_{uv}$ (Fig. 1b) except at 850 m (O_2 minimum), where Δ^{14}C values of the XAD-2 and XAD-4 isolates (XAD-4 is a lower-molecular-weight, more-hydrophilic fraction than that isolated on XAD-2) and DOC$_{uv}$ were identical, indicating that these fractions of the DOC all cycle on similar timescales at this depth.

In both sites, total concentrations of DOC measured by continuous-injection HTC and ultraviolet oxidations, both of which use direct collection and quantification of CO_2, were less than those measured by discrete-injection HTC using infrared analysis of CO_2 (Table 1). Assuming that a portion (~30%) of the nonhumic DOC pool was not combusted and was unfractionated with respect to ^{14}C by continuous-injection HTC oxidation (a contention supported by the data), we may calculate the Δ^{14}C

values of a hypothetical 'total' DOC pool, assuming that the discrete-injection DOC_{htc} values are accurate. (Currently this accuracy is an open question[28].) We further assume that this additional fraction is younger and has a post-bomb $\Delta^{14}C$ value of +120‰, similar to that of the dissolved inorganic carbon (DIC) in the mixed layer[13]. The calculated $\Delta^{14}C$ values of this 'total' DOC pool for the shallowest and deepest samples measured using Co/CoO HTC are -129‰ (20 m) and -325‰ (5,150 m) in the north-central Pacific and -121‰ (50 m) and -271‰ (3240 m) in the Sargasso Sea. If recoveries of DOC in the shallow samples were only 50% of the DOC measured by discrete injection (Table 1), then the $\Delta^{14}C$ value of the total shallow-water DOC pool would increase to -60‰ (apparent age 500 yr BP) in the north-central Pacific and -52‰ (apparent age 430 yr BP) in the Sargasso Sea. However, this poses two paradoxes: first, that the hypothetical extra, 'modern' DOC is impervious to either ultraviolet or continuous-injection HTC oxidation, and second, that ~30% of the 'total' DOC in the deep ocean is uniformly modern.

As the DOC ages are mean values, it can be calculated from a two-age component model[14] that 40% of the DOC in the deep Pacific and 55% in the deep Atlantic could have a post-bomb radiocarbon signature ($\Delta^{14}C = +120‰$), provided that the remainder of the DOC is 'dead' ($\Delta^{14}C = -1,000‰$). Discussions have thus far implied that $\Delta^{14}C$ values associated with oper-ationally defined fractions represent discrete groups or types of DOC. Although this possibility cannot be unequivocally ruled out, DOC in ocean waters may be more realistically described as a continuum of material of all apparent ages ranging from modern to fossil. Therefore, we cannot preclude the input to the deep ocean of a significant proportion of DOC derived from incorporation of pre-bomb ($\Delta^{14}C = -50‰$) to post-bomb ($\Delta^{14}C = +120‰$) DIC into the DOC pool via carbon fixation in surface waters. In fact, in both sites the presence of a DOC component of higher $\Delta^{14}C$ than average bulk DOC oxidized by ultraviolet or HTC can be deduced by simple mass balance of this bulk DOC and the DOC represented by the humic isolates, which are completely oxidized by both methods (Fig. 1a and b). A better understanding of the chemical make-up of deep-ocean DOC, its heterotrophic utilization, and the $\Delta^{14}C$ distribu-tions of refractory and biologically usable DOC, as well as further direct collections of CO_2 from DOC oxidation, will help resolve these apparent discrepancies.

The combined DOC_{htc} and DOC_{uv} $\Delta^{14}C$ data sets indicate average minimum apparent ages for DOC in north-central Pacific and Sargasso Sea near-surface sea water (roughly 0–900 m) of at least 3,100 and 2,500 yr BP, respectively. If we account for the certain presence of post-bomb carbon in the DOC, these ages are greater still. The average apparent ages of DOC in the deep ocean below 900 m (5,900 and 4,100 yr BP in the north-central Pacific and Sargasso Sea, respectively) are also minimum estimates given the likely presence of ≤10% post-bomb DOC ($\Delta^{14}C \approx +120‰$) in the deep sea. This old DOC fraction must therefore represent biologically and chemically resistant background material in oligotrophic regions and may account for previous observations of extremely low rates of heterotrophic respiration and DOC utilization in the deep ocean[15-17]. The fact that the apparent ^{14}C age of DOC in the deep Sargasso Sea is ~2,000 yr younger than that in the north-central Pacific suggests that a high proportion of the total DOC is transported along with deep waters in the world ocean, which have transit times of ~1,400 yr from the North Atlantic to the North Pacific[18,19,29].

The ultimate sinks of organic carbon produced in the euphotic zone, including both dissolved and particulate forms, are removal to the sediments[20,21] and heterotrophic respiration[22]. Processes that bypass these sinks will result in a net recycling of organic carbon and an increase in its residence time. Both the extent of recycling and the residence time of DOC will be directly proportional to its efficiency of conversion to biomass

and inversely proportional to its mineralization rate, neither of which is well understood in the deep ocean. Even at relatively high conversion efficiencies (say, ~70%), a diminishing propor-tion of organic carbon will be recycled, especially at rapid rates of utilization (years to decades). With respect to the ~30% of the 'total' DOC from deep ocean waters that might not be oxidized by continuous-injection HTC oxidation, there is no evidence that this fraction is modern and heterotrophically labile. The great apparent ages of the DOC fractions seen here confirm that most of the DOC in the deep ocean is remineralized extremely slowly. □

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Rapid coupling of sinking particle fluxes between surface and deep ocean waters

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SETTLING particles are thought to be responsible for much of the transport of mass and energy from the upper ocean to the sea floor. Photosynthetic production by phytoplankton is a major source of these particles, either as phytoplankton biomass sinks directly[1] or as it is transformed into rapidly sinking forms such as aggregates[2,3] and zooplankton faeces[4]. Because a variety of processes may act on sinking matter, however, it is not known to what extent fluxes of organic matter to the deep sea are coupled to processes at the ocean surface. Some studies have provided evidence for direct coupling[2,5-7], but transformation processes and advection exist which have the potential to modify the transmission of surface signals to the deep sea[8-11]. If these mechanisms over-whelm surface production signals, seasonal and annual variations