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Radiocarbon in dissolved organic matter in the central North Pacific Ocean

Permalink

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Journal

Nature, 330(6145)

ISSN

0028-0836

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Publication Date

1987

DOI

10.1038/330246a0

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Although there is no single measure that accounts for all extracellular biomass, many of these polymers include a polysaccharide component¹⁸. By agitating sediment samples, centrifuging to exclude cells and detritus, and analysing the supernatant (phenol-sulphuric acid hydrolysis), we have previously found elevated levels of 'colloid' carbohydrates corresponding to bacterial and microalgal mats^{5,6}. In this study, colloid concentrations (138–319 µg glucose equivalents per g sediment) were an order of magnitude greater than most values determined for a benthic diatom mat^{5,6}. At Pinellas Point, the carbohydrate index of extracellular material ($n=21$) was significantly correlated with Bchl *a* ($r=0.46$, $p=0.025$) and Chl *a* ($r=0.73$, $p=0.001$) as well as u_{*crit} ($r=0.77$, $p<0.001$). These relations suggest that, in our experiments, pigment biomass indicators were related to the mass of extracellular material (carbohydrates). More direct assays of mat extracellular material are desirable, but are not readily available and may be too complex for practical engineering purposes. However, where bacterial mats are dominated by obvious groups of specific photoautotrophs, as commonly occurs with purple sulphur bacteria and cyanobacteria^{8,17}, pigment measures may provide useful predictors of u_{*crit} . In mats where non-photosynthetic bacteria dominate (for example *Beggiatoa*), indicators such as sulphur content¹⁹ or colloid carbohydrate could be related to erosion criteria. We conclude that there are a variety of biological parameters that may form the basis of a predictive relation with critical erosion thresholds. This approach will provide more realistic threshold values for natural sediments of a given grain size than values obtained from criteria developed for abiotic sediments (for example Shields' curve; see Miller *et al.*¹).

To predict the stability and transport of natural sediments, determination of u_{*crit} must be supplemented by information on the transport rates of eroded sediment. The extracellular material of well-developed mats had an armouring effect⁴, such that erosion occurred by a 'blow-out' phenomenon for $u_* > u_{*crit}$, and the mat surface rapidly broke up into pieces that were transported as large aggregates. Even with less developed bacterial mats (clear cores), small aggregates of sand and mucus rather than individual grains were transported as bed-load. The flow eroded the underlying sediment, now exposed, until reaching laminae with a higher u_{*crit} (for example cyanobacteria below clear sediment: Table 1). In these cases standard bed-load equations do not apply.

We obtained preliminary results on microbial binding and sediment transport rate from the mass of sediment collected in miniature traps (flush-mounted scintillation vials) downstream of cores. Bed-load transport from a control core with sterile sand ($u_* = 1.24 \text{ cm s}^{-1} > u_{*crit}$) occurred at a rate of $3 \times 10^{-3} \text{ g cm}^{-1} \text{ s}^{-1}$. In contrast, three natural cores with clear surface sand were eroded at rates of $3\text{--}8 \times 10^{-4} \text{ g cm}^{-1} \text{ s}^{-1}$ at $1.20 < u_* < 1.65 \text{ cm s}^{-1}$. These initial experiments indicate that despite low mat development, sediment transport rate can be reduced by an order of magnitude compared with sterile sand transport at a similar or even smaller u_* . Detailed studies of organismal effects on transport rates are lacking, and the reader is cautioned that adjusting u_{*crit} is only the initial step in accounting for biotic factors in models of natural sediment transport.

The laminated microbial community we have studied (Fig. 1F; 'Farbstreifensandwatt' or 'versicoloured sandy tidal flat'¹⁷) is common in shallow tropical and temperate sandy sediments⁸. Extensive mats of sulphur bacteria are also known from continental shelves and the deep sea^{8,20}. The effects reported here on the erosion and transport of biotically stabilized sediments will be widespread, with major implications for sedimentology, seabed engineering and disposal, nutrient flux¹⁹ and numerous other studies.

We thank Kelly Walker for assistance with field and laboratory experiments, Walter Bowles for grain-size analysis, John Paul for advice on microscopy, Bob Byrne for the use of scanning spectrophotometers, Ferenc Stefani for help with the photo-

graphic plate, and Craig Emerson and Jim Novitsky for valuable comments on the manuscript. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Received 29 April; accepted 6 September 1987.

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Radiocarbon in dissolved organic matter in the central North Pacific Ocean

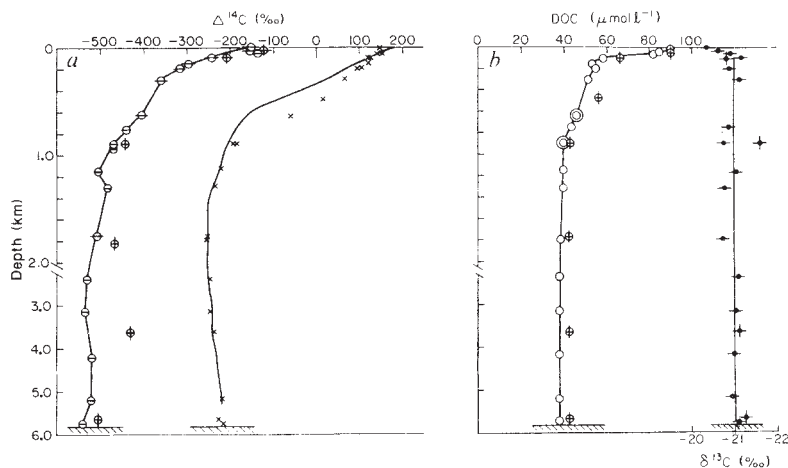
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The origin of dissolved organic carbon (DOC) in the ocean has been long debated. Whereas Mantoura and Woodward¹ have used the conservative nature of DOC in a British estuary to conclude that $\geq 50\%$ of DOC in the oceans could be river-derived, recent lignin results in the equatorial Pacific² have indicated that $\leq 10\%$ of the DOC is potentially of terrestrial origin. In addition, the $\delta^{13}\text{C}$ signature (relative to the PDB standard) of DOC ranges from -20 to -24% (refs 3, 4), indicating that the primary source of DOC is from marine-derived organic carbon. Here we present the first detailed profile of radiocarbon measured in DOC and dissolved inorganic carbon (DIC) in the oligotrophic gyre of the central North Pacific. $\Delta^{14}\text{C}$ (per mil deviation from the activity of 19th-century wood) of DOC ranged from -150% (1,310 yr BP) in surface waters to -540% (6,240 yr BP) at 5,710 m, 40 m off the bottom, where these 'apparent ages' or 'residence times' are mean values for the combined constituents of the DOC. The surprising similarity in the shapes of the profiles of $\Delta^{14}\text{C}$ in the DOC and DIC pools suggests that similar processes are controlling the radiocarbon distribution in each of the two reservoirs and that bomb-produced radiocarbon has penetrated the DOC + DIC pools to a depth of ~ 900 m. The depletion of the $\Delta^{14}\text{C}_{\text{DOC}}$ values by 300% with respect to the $\Delta^{14}\text{C}_{\text{DIC}}$ values suggests that a certain fraction of the DOC is recycled within the ocean on longer time-scales than DIC.

Radiocarbon in DOC and DIC was measured in 25 water samples collected from the central North Pacific Ocean (31°N , 159°W), one sample from each of 21 depths, with duplicate casts at 20, 100, 900 and 1,800 m. The water for DOC oxidation was filtered on board ship directly from 270-l stainless steel Gerard barrels through 1.0-µm pore-diameter, pre-combusted glass-fibre filters into cleaned glass bottles and frozen at -20°C . A 5-l sample was then thawed, acidified to pH 2.5 with H_3PO_4 , purged of DIC with pure N_2 gas, saturated with O_2 , and the DOC converted to CO_2 by photo-oxidation for 6 h

Fig. 1 *a*, $\Delta^{14}\text{C}_{\text{DOC}}$ (\ominus , \oplus) and $\Delta^{14}\text{C}_{\text{DIC}}$ (\times) values versus depth at 31°N , 159°W . The $\Delta^{14}\text{C}_{\text{DOC}}$ values were measured using TAMS techniques and are corrected to a $\delta^{13}\text{C}$ of -25% and are not yet corrected using the actual $\delta^{13}\text{C}$ values of the graphite. The error from counting statistics plus assumed graphite- $\delta^{13}\text{C}$ assignments and $\delta^{13}\text{C}$ values of the DOC samples range from ± 8 to $\pm 19\%$ and are indicated by horizontal error bars. Off-curve $\Delta^{14}\text{C}_{\text{DOC}}$ values (\oplus) are discussed in the text. The $\Delta^{14}\text{C}_{\text{DIC}}$ values, measured using conventional gas proportional counting techniques, are reported in the usual manner³⁰. The surface (3 m) value is the average of 12 surface $\Delta^{14}\text{C}_{\text{DIC}}$ values taken during the 35-day cruise in October 1985. The error from counting statistics is ± 2.9 to $\pm 3.3\%$. The smoothed curve represents $\Delta^{14}\text{C}_{\text{DIC}}$ results from GEOSECS Station 204, September 1973, located at $31^\circ 22' \text{N}$, $150^\circ 02' \text{W}$ (ref. 8). *b*, Total DOC concentrations (\circ , \oplus) and $\delta^{13}\text{C}_{\text{DOC}}$ values (\bullet , \blacklozenge) versus depth at 31°N , 159°W . DOC values are from manometric measurements of the CO_2 resulting from the photo-oxidation of DOC. The experimental error is $\pm 1.5 \mu\text{mol C l}^{-1}$. Double circles denote replicate samples from the same depth. Off-curve total DOC values (\oplus) are discussed in the text. $\delta^{13}\text{C}$ values were measured separately at the Woods Hole Oceanographic Institution. The experimental error, $\pm 0.15\%$, is given by the horizontal bars, where the vertical bars indicate values corresponding to the off-curve $\Delta^{14}\text{C}_{\text{DOC}}$ values. The vertical line is the mean value of all 20 points.



at 75°C in an all-glass reactor, according to published techniques^{3,5}. DIC was absorbed in $\text{SrCl}_2\text{-NH}_4\text{OH}$ on board ship from 200-l, unfiltered, acidified seawater samples⁶ for subsequent proportional counting at the Woods Hole Oceanographic Institution Radiocarbon Laboratory.

The $\Delta^{14}\text{C}_{\text{DOC}}$ measurements were made by A. J. T. Jull *et al.*⁷ by tandem accelerator mass spectrometry (TAMS). Profiles of 25 $\Delta^{14}\text{C}_{\text{DOC}}$ and 24 $\Delta^{14}\text{C}_{\text{DIC}}$ results are shown in Fig. 1*a*, along with $\Delta^{14}\text{C}_{\text{DIC}}$ values measured in 1973 during the GEOSECS Pacific expedition⁸. Profiles of total DOC concentrations and their corresponding $\delta^{13}\text{C}$ values are given in Fig. 1*b*. $\Delta^{14}\text{C}_{\text{DOC}}$ values range from -150% at 3 m to -540% at 5,710 m. These $\Delta^{14}\text{C}$ values are 100–200% lower than earlier results^{5,9} measured in the northeastern Pacific. We believe this discrepancy is a result of incomplete oxidation (recoveries were $\sim 70\%$) of DOC in the 500-l samples processed earlier.

The difference between $\Delta^{14}\text{C}_{\text{DOC}}$ in surface and deep waters (390%) is exactly the same as that observed between surface (150%) and deep (-240%) $\Delta^{14}\text{C}_{\text{DIC}}$ from the same water samples, although the DOC values are 300% more negative (Fig. 1*a*). The very old apparent ages of DOC, coupled with constant $\delta^{13}\text{C}_{\text{DOC}}$ values (Fig. 1*b*), indicate that there is a recycled component of DOC which is resistant to oxidation. This is supported by the invariant concentration of DOC in deep waters of the North Pacific and Atlantic oceans (L. I. Gordon, personal communication and ref. 10), as shown in Fig. 1*b* for the central North Pacific, and its resistance to rapid bacterial utilization^{11,12}.

At present, it is possible to characterize only 20–30% of the organic matter in DOC. The sum of the total (free plus hydrolysable) soluble amino acids (measured fluorometrically¹³) and carbohydrates (measured spectrophotometrically¹⁴) at 31°N , 159°W is equivalent to $\sim 6\%$ of the total DOC below 1,000 m and 16% at the surface, and this may be considered the most labile (modern) fraction of the DOC. The higher $\delta^{13}\text{C}$ values in the upper 20 m (Fig. 1*b*) probably reflect the greater content of labile, modern constituents in surface waters. Humic material (fulvic and humic acids), which can be isolated by absorption onto XAD macroporous resins, constitutes 5–20% of the DOC in deep and surface waters of the open ocean^{2,15,16}, while lipids account for 2–5% of the DOC^{17,18}. The remaining 60–80% of the DOC has not yet been characterized, primarily due to the difficulties inherent in isolating polar organic material from dilute saline solutions.

The fact that the $\Delta^{14}\text{C}_{\text{DOC}}$ and $\Delta^{14}\text{C}_{\text{DIC}}$ curves (Fig. 1*a*) are almost identical in shape suggests that similar processes are controlling the radiocarbon distributions in each of these two reservoirs. It is commonly believed that the decrease in $\Delta^{14}\text{C}_{\text{DIC}}$

observed in North Pacific Deep Water represents the transit time of North Atlantic Deep Water from its origin in the North Atlantic to the North Pacific¹⁹, with consideration of the short circuit introduced by common water formation in the Antarctic²⁰. The similarity strongly suggests that a fraction of the DOC within the deep-water circulation is cycled in much the same way as DIC.

There are seven samples whose DOC concentrations (denoted by crossed circles, Fig. 1*b*) are 6–14% higher than the other corresponding DOC values. These higher concentrations were observed only in the first seven samples photo-oxidized. This cannot be due to increased oxidation of more refractory, older DOC as the $\Delta^{14}\text{C}$ values of six of these seven samples (Fig. 1*a*, crossed circles) were equal to or greater than the $\Delta^{14}\text{C}_{\text{DOC}}$ trend of the remaining samples and reoxidation of several of these surface and deep-water counterparts for an additional 6 h yielded 1% or less additional CO_2 . We suspect the higher DOC concentrations and $\Delta^{14}\text{C}$ values of these seven samples were due to modern, post-bomb organic matter ($\Delta^{14}\text{C} = 100\text{--}200\%$) that was photo-oxidized only in samples processed using the initial UV lamp. Subsequent oxidations with this same lamp or new lamps did not duplicate the earlier results. However, known compounds (for example, *N*-acetylglucosamine and serum albumin) were 100% oxidized with all lamps, regardless of their histories.

Intriguing deviations from the smooth curve are apparent in the $\Delta^{14}\text{C}_{\text{DOC}}$ results (Fig. 1*a*). There is a suggestion of a minimum in $\Delta^{14}\text{C}$ at 1,150 m, coincident with the lower portion of the oxygen minimum (950 m). The deepest sample, 40 m off the bottom, was significantly lower in $\Delta^{14}\text{C}$ than the other deep-water samples, suggesting that old DOC derived from low ^{14}C -activity sedimentary organic matter^{9,21} may be exchanging with DOC in the water column. The increase in $\Delta^{14}\text{C}_{\text{DOC}}$ of 100% at 3,600 m, if valid, may reflect increased sea-floor mineralization of modern particulate organic matter at this depth, as postulated by Jahnke and Jackson²². These deviations from the smooth $\Delta^{14}\text{C}_{\text{DOC}}$ trend are being verified by further measurements.

The average of four $\Delta^{14}\text{C}_{\text{DOC}}$ values in the upper mixed layer (~ 40 m) was -146% . This could result from a mixture of 44% old, deep-water DOC (average $\Delta^{14}\text{C} = -525\%$) and 56% post-bomb, surface DOC derived during the past 30 yr from planktonic biocarbon (average $\Delta^{14}\text{C} = 150\%$). In this model, of the $87 \mu\text{mol C l}^{-1}$ (average concentration of DOC in the surface mixed layer, Fig. 1*b*), $38 \mu\text{mol C l}^{-1}$ represents the recycled fraction of deep-water DOC resistant to rapid bacterial utilization, and $49 \mu\text{mol C l}^{-1}$ is the labile fraction continuously

utilized by microplankton and heterotrophic bacteria. The fact that the DOC content of oceanic surface waters is never less than $\sim 35 \mu\text{mol C l}^{-1}$ (ref. 23) can be attributed to the presence of this recycled, refractory DOC component.

The $\Delta^{14}\text{C}_{\text{DIC}}$ results agree well with a previous profile made during the GEOSECS study⁸ 12 years previously (Fig. 1a). Our data show a deeper penetration of the bomb radiocarbon transient to 900 m, ~ 100 – 200 m deeper than that measured in 1973. However, there is essentially no difference between our $\Delta^{14}\text{C}$ values deeper than 1,100 m and comparable GEOSECS measurements. Similarity of the $\Delta^{14}\text{C}_{\text{DIC}}$ and $\Delta^{14}\text{C}_{\text{DOC}}$ curves strongly suggest that bomb radiocarbon has also penetrated the DOC pool to 900 m depth, most likely by advective and diffusive transport along isopycnal surfaces. An increase in $\Delta^{14}\text{C}_{\text{DIC}}$ at 3,600 m in concert with that observed in the $\Delta^{14}\text{C}_{\text{DOC}}$ profile is not expected, as the concentration of DIC is 50 times that of DOC in the deep sea, and thus much less susceptible to small changes.

Assuming a steady-state concentration and no terrestrial input of DOC, the apparent age of 6,000 yr for the DOC is also an indication of the amount of photosynthetically fixed carbon which enters the deep sea as DOC and is concurrently combusted to CO_2 . The average amount of carbon fixed photosynthetically in the world's open oceans (excluding adjacent seas) has been estimated at between $130 \text{ g C m}^{-2} \text{ yr}^{-1}$ (ref. 24) and $500 \text{ g C m}^{-2} \text{ yr}^{-1}$ (ref. 25), amounting to a global production of approximately 40 – $150 \times 10^{15} \text{ g yr}^{-1}$. At $40 \mu\text{mol l}^{-1}$ of DOC, the total reservoir of DOC in the deep sea (vol. = $1.3 \times 10^{21} \text{ l}$ for 300–4,100 m depth²⁶) is about $6 \times 10^{17} \text{ g}$, and thus the steady-state input of DOC is $0.1 \times 10^{15} \text{ g C yr}^{-1}$ ($6 \times 10^{17} \text{ g C}$ per 6,000 yr) or about 0.067–0.25% of the photosynthetically fixed carbon. This input of DOC is 0.5–3% of the amount of particulate organic carbon falling out of the upper 300 m into the deep ocean^{24,25,27} (new production), assuming the above global carbon production rates.

If 50% of the DOC in the deep sea were derived from global riverine sources¹, then it would require $\sim 1,500$ yr to fill the ocean with respect to terrestrial DOC at a riverine flux of $2 \times 10^{14} \text{ g C yr}^{-1}$ (ref. 28), assuming that riverine DOC entering the ocean is retained as DOC and that it is in steady-state concentration. The average $\Delta^{14}\text{C}$ value for soluble humic and fulvic acids collected between 1982 and 1984 from the Amazon River system²⁹ is 270‰, indicating that terrestrially-derived DOC is modern in age. Thus a potential terrestrial DOC component, even during the pre-bomb period when $\Delta^{14}\text{C}$ was supposedly 0‰, would have to be recycled at least as many times as marine-derived DOC in the world oceans to give the resultant low $\Delta^{14}\text{C}_{\text{DOC}}$ values in the deep sea. We believe that the absence of significant amounts of lignin in open-ocean humic substances² coupled with the constraints imposed by marine $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values, precludes a terrestrially derived DOC component exceeding 10% of the total DOC.

In summary, we speculate that a substantial fraction of DOC, regardless of its origin, may be common to all oceanic deep waters and undergoes multiple recycling, similar to the recycling of salt in the ocean. The apparent mean ages or residence times of about 6,000 yr BP could result from mixing 51% dead DOC ($\Delta^{14}\text{C} = -1,000$ ‰) with 49% pre-bomb DOC (-40 ‰), neglecting any recent input of bomb radiocarbon. However, the striking similarity between the $\Delta^{14}\text{C}_{\text{DIC}}$ and $\Delta^{14}\text{C}_{\text{DOC}}$ curves suggests that there is indeed bomb radiocarbon in the DOC pool, at least in the upper 900 m of the central North Pacific Ocean. Our reoccupation of this site in June 1987 will help resolve this question, as further penetration of the bomb radiocarbon signal into the DOC pool is anticipated 18 months later.

We thank Drs A. Jull, D. Donahue and T. Linick for analysing DOC samples at the University of Arizona TAMS facility, S. Griffin and J. Frankenthal for measuring $\Delta^{14}\text{C}_{\text{DIC}}$, K. Robertson for analysing amino acids and carbohydrates, John Hedges and Rick Jahnke for helpful comments and R. Paddock, K. Smith

and the crew of the R V *Melville* for help with sample collection and ship logistics. Financial support was provided by the NSF. Woods Hole Oceanographic Institution Contribution No. 6593.

Received 12 June; accepted 11 September 1987.

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Is the periodicity of extinctions a taxonomic artefact?

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The evidence that extinctions since the mid-Permian show periodicity of ~ 26 million years rests primarily on the stratigraphic ranges of marine families. We have checked the echinoderm and fish families which together make up about 20% of the data. Only 25% of these fish and echinoderm extinctions are real (disappearance of a monophyletic group). The remaining 75% is noise, chiefly 'extinctions' of non-monophyletic groups, mistaken dating, and 'families' containing one species only. The signal-to-noise ratio is very similar in echinoderms (27:73) and fishes (23:77). Periodicity in our sample is a feature of the noise component, not of the signal.

Periodicity of extinctions has received much attention recently, both as concerns the phenomenon^{1–18} and possible explanations for it^{12–26}. Raup and Sepkoski¹ initially analysed a subset culled from Sepkoski's *Compendium of Fossil Marine Families*²⁷ covering the last 250 million years (Myr) (late Permian to mid-Miocene). They omitted all extant families, all whose last occurrences were not known to stage, and all with questionable taxonomic or stratigraphic designation. In their opinion¹, this culling 'removed much of the noise that characterizes data sets of this kind'. The 567 families analysed comprised roughly 35% cephalopods, 11% vertebrates, 10% echinoderms, and 6–8% each bivalves, brachiopods, bryozoans, sponges and gastropods. All extinctions were treated as occurring at the end of the stage in which each taxon is last recorded. Twelve extinction peaks were found, and when fitted to the Harland *et al.*²⁸ timescale, a 26 Myr cycle centred on the end-Cretaceous extinction coincided with seven of the 11 other peaks. Statistical testing showed that this is highly significant.