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CONCENTRATIONS AND RADIOCARBON SIGNATURES OF DISSOLVED ORGANIC MATTER IN THE PACIFIC OCEAN

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Abstract. We present evidence suggesting that only a portion of the dissolved organic carbon (DOC) in the seawater analyzed previously by Williams and Druffel (1987) was oxidized by the UV-radiation method. High temperature catalytic (HTC) methods (Sugimura and Suzuki, 1988) used to reoxidize the central North Pacific gyre water samples reveal that the total DOC (DOC_{HTC}) is about twice that of the UV-oxidizable DOC (DOC_{UV}). Indications from the original study suggest that this additional DOC contains higher concentrations of radiocarbon than in the DOC_{UV} (Williams and Druffel, 1987). This evidence implies that DOC_{UV} is older and thus more refractory with respect to biological utilization, yet is more chemically reactive with respect to photooxidation, than the fraction resistant to UV (DOC_{res}).

We report accelerator mass spectrometry (AMS) $\Delta^{14}C$ measurements of humic, fulvic and hydrophilic acid fractions isolated from water collected at 180 m in the North Pacific (19°N, 158°W) using XAD macroporous resins. $\Delta^{14}C$ values of the humic material are less than those of DOC_{UV} from a similar depth 1200 km further north (Williams and Druffel, 1987) indicating that these humic substances are part of the 'old' recycled DOC_{UV} in the ocean.

Introduction

For the past twenty years, measurements of DOC in seawater have been commonly achieved by two methods: photooxidation by UV-radiation from a Hg-arc lamp (Armstrong et al., 1966) and by wet oxidation using peroxodisulfuric acid (Menzel and Vaccaro, 1964). Plunkett and Rakestraw (1955) obtained high DOC results using wet oxidation with chromic acid after removal of most of the chloride ion (Krogh, 1934). Higher, but erratic, DOC values were also reported earlier using a variety of high temperature techniques (see references in Williams and Druffel, 1988).

Recently, Sugimura and Suzuki (1988) measured non-volatile DOC using direct injection of acidified seawater onto a high temperature platinum-on-alumina catalyst. They found DOC concentrations up to 3 times higher than those measured using wet oxidation techniques. Oxidation of chloride ion by the aforementioned wet oxidation techniques may lower the oxidation potential in these systems below the threshold value necessary to combust the more resistant DOC. Sugimura and Suzuki's (1988) data, not yet rigorously confirmed, imply that virtually all of the AOU (apparent oxygen utilization) in the western North Pacific can be accounted for by the oxidation of DOC and dissolved organic nitrogen (DON).

We report measurements of DOC using the HTC method on the same seawater samples from the central North Pacific (31°N, 159°W) by Williams

and Druffel (1987). This HTC method suggests that there are 2 to 3 times more DOC in our seawater samples than previously measured. If correct, correlations between DOC and AOU indicate that DOC is responsible for the major amount of oxygen utilization in the upper few hundred meters of the water column only.

Methods

Concentrations of DOC were measured in filtered (1.0 μ GFC glass fibre) water samples collected from 31°N, 159°W during the Alcyone-5 cruise aboard the R/V Melville (October 1985). Frozen and thawed aliquots of both UV-oxidized (DOC_{UV}) and unoxidized (DOC_{HTC}) water samples were analyzed from sealed ampoules shipped to Japan. Small samples (200 μ l) of acidified CO_2 -free seawater were injected into an oxygen stream onto a 3% Pt-on-alumina catalyst at 680°C (Sugimura and Suzuki, 1988), with subsequent detection of the resultant CO_2 by infrared absorption. The error of DOC_{HTC} and DOC_{res} measurements is estimated from replicate analyses of the same water samples to be $\pm 3 \mu M$.

The humic materials were separated by Ronald Malcolm (USGS) from filtered seawater collected from the North Pacific (60 km SW of Oahu, HI) by sorption onto XAD macroporous resins. XAD-2 and XAD-8 were used to isolate humic and fulvic acids (Thurman and Malcolm, 1981) and the effluent from XAD-8 was passed through XAD-4 to collect the hydrophilic acids (lower molecular weight, more hydrophilic compounds) (R. Malcolm, personal communication). Radiocarbon in the individual fractions was measured using AMS techniques at the University of Toronto Isotrace Facility.

Results

Residual DOC (DOC_{res}) was detected in all of the 19 UV-oxidized seawater samples analyzed, with values ranging from 46-144 μM (Table 1). The subtraction of the original DOC_{UV} values from DOC_{HTC} measured in the corresponding 19 unoxidized samples are remarkably close to the DOC_{res} values (Table 1).

If these results are a true representation of DOC concentration, then the DOC pool in the central North Pacific Ocean is about twice as large as had previously been believed (Figure 1). It also means that there is indeed variation in the DOC depth profile, where UV- and wet-oxidation techniques had indicated an invariant DOC profile at depths > 1000 m.

Figure 2 shows DOC_{HTC} (in μM) plotted versus AOU (in μM), which was calculated from oxygen, salinity and potential temperature measured during the Eve-1 cruise at the same location (31°N, 159°W) in June 1987. The plot of results from the upper part of the water column (3-482 m) shows a slope of 1.0 ($d[AOU]/d[DOC_{HTC}]$), which is close to the value of 1.3 obtained by Redfield et al., (1963) for organic carbon and oxygen utilization in the water column. The similarity to Redfield ratios imply that DOC is responsible for most of

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Table 1. DOC in original seawater measured by UV ($2\sigma = \pm 1.5 \mu\text{M}$) and HTC ($1\sigma = \pm 3.0 \mu\text{M}$) oxidation, and DOC remaining (DOC_{res}) in the UV-oxidized samples measured by HTC oxidation. All samples were collected from $31^\circ\text{N}, 159^\circ\text{W}$ in October 1985 (Williams & Druffel, 1987).

Depth (m)	DOC_{UV} (μM)	DOC_{HTC} (μM)	DOC_{res} (μM)	$\text{DOC}_{\text{HTC}} - \text{DOC}_{\text{UV}}$ (μM)	AOU (μM)
3	90	210	144	120	-15
20	84	218	120	134	-23
20	90*				
50	82	218	130	136	-15
100	58	206	144	148	10
100	66*				
150	53	184	132	131	28
200	54	173	110	119	38
300	51	151	96	100	50
482	56*	108	48	52	98
637	46	96	48	50	220
757	43	94	48	51	268
900	40	90	46	50	297
900	40				
903	43*				
1152	40				292
1152	39**				
1308	40	98	52	58	283
1769	42*				
1808	38	106	66	68	255
2388	38	108	69	70	235
3174	38				
3631	38**				
3631	43	110	68	67	193
4227	38	112	72	74	184
5227	38	112	72	74	177
5670	43*	108	65	65	157
5720	38	110	70	72	157

* One of the seven initial samples oxidized by UV. The 482 m ^{14}C sample was lost (Williams and Druffel, 1987).

** Result not reported in original study (Williams and Druffel, 1987).

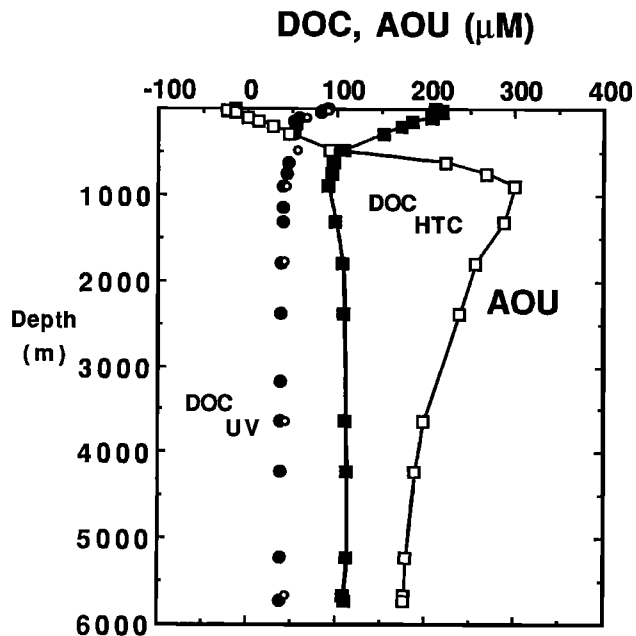


Fig. 1. DOC_{UV} (\circ, \bullet) (Williams and Druffel, 1987) and DOC_{HTC} (\blacksquare) measured in seawater collected from the North Pacific gyre ($31^\circ\text{N}, 159^\circ\text{W}$) during the Alcyone-5 cruise in October 1985. Apparent oxygen utilization values (\square) were calculated from a detailed oxygen profile measured on a subsequent cruise to the same site in June-July 1987.

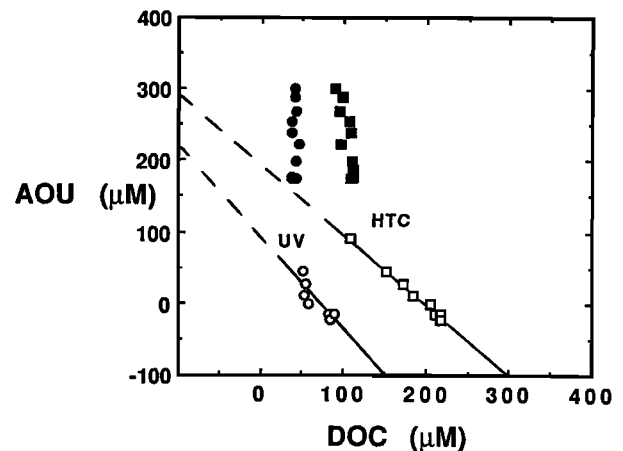


Fig. 2. DOC_{HTC} (\square, \blacksquare) and DOC_{UV} (\circ, \bullet) versus AOU. Open symbols represent near surface samples (HTC: 3-482, uv: 3-300 m) and closed symbols represent all deeper samples.

the AOU in the upper ocean. The deeper results (637-5720 m) reveal a slope for $d(\text{AOU})/d(\text{DOC}_{\text{HTC}})$ of 4.8, which indicates that there is far more oxygen being utilized than DOC can account for in the deep sea. In contrast, Suzuki and Sugimura (1988) found a single, linear relationship with a slope of 0.9 for samples from 1-4000 m depth from three western North Pacific sites, indicating that DOC is responsible for most of the AOU throughout the entire water column.

The differences between our results and those of Sugimura and Suzuki (1988) indicate that one or more of the following may be taking place at our site: 1) Other species are being oxidized, especially in the deep sea (i.e., DON, particulate organic carbon and nitrogen); 2) There is a possible additional process for oxygen utilization in the deep sea, i.e., lateral advection and subsequent oxidation of DOC-rich water from continental margins which may not be present at the western North Pacific sites; or 3) DOC was lost prior to the HTC analyses during slow freezing (24 hours) and/or thawing of our unpoisoned seawater samples, especially in the upper several hundred meters. However, higher DOC_{HTC} values were measured at the oxygen minimum at $31^\circ\text{N}, 159^\circ\text{W}$ ($90 \mu\text{M}$) than at the oxygen minima in the western North Pacific ($40 \mu\text{M}$, Sugimura and Suzuki, 1988), suggesting that more of the chemically resistant DOC was present in the NCP intermediate waters. The plot of AOU vs. DOC_{UV} (Figure 2) reveals a slightly higher slope for the shallow samples (1.3, 0-300 m), which may indicate the presence of another oxidizable substrate (i.e., DOC_{res}) or differing AOU values for the July 1987 samples from those DOC samples measured in 1985 (oxygen was not measured on the October 1985 cruise). The slope of infinity for the deep samples (482-5720 m) indicates that DOC_{UV} in the deep sea is not oxidizable on the timescale of oxygen utilization, an assertion which is supported by the low $\Delta^{14}\text{C}$ results (-520‰) for DOC_{UV} in the deep sea (Williams and Druffel, 1987). Further measurements may determine which of the above factors control the change of $d(\text{AOU})/d(\text{DOC}_{\text{HTC}})$ in the deep sea.

In order to understand the source(s) of DOC_{res} , we must determine the ^{14}C signature and composition of this pool of organic matter. There was evidence in the DOC_{UV} concentrations and in the $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measurements from the original study (Williams and Druffel, 1987) of the nature of the DOC_{res} . First, the initial seven of 26 seawater samples oxidized by UV yielded 7-14% higher DOC values than succeeding samples from the same Gerard barrel (20, 100, 903, 3631 m) or samples from similar depths (482, 1769, 5670 m) (Table 1,

Figure 1). It is improbable that these higher results were due to contamination, as no further CO₂ was liberated upon reoxidation of the same samples, nor was there any difference in percent recovery (100 ± 2%) of the n-acetyl-D-glucosamine standard run before and after these samples. We speculate that the Hg-arc lamp was more efficient, that is, the amount of effective energy emitted in the 180–220 nm wavelength range was higher during the initial stages of this particular lamp's lifetime as discussed in Williams and Druffel (1987). This could produce a higher concentration of hydroxyl radicals in solution early in the reaction, enabling a fraction of the more resistant, "chemically inert" organic matter to be oxidized. This incremental increase was not observed during the initial use of two new lamps during the last 14 oxidations.

Second, the $\Delta^{14}\text{C}$ values of the DOC oxidized in six (the 482 m sample was lost) of the anomalous samples were significantly higher (by 20–100‰, 3–14 σ) than values from succeeding samples from the same Gerard barrel or those from similar depths (Figure 3). Assuming that these higher $\Delta^{14}\text{C}$ results reflect the added DOC, the $\Delta^{14}\text{C}$ values of the additional DOC, $\Delta^{14}\text{C}_a$, are calculated using the mass balance relationship:

$$\Delta^{14}\text{C}_a = [\Delta^{14}\text{C}_h - \Delta^{14}\text{C}_l * f_l] / f_a \quad (1)$$

where $\Delta^{14}\text{C}_h$ represents values in the 6 anomalously high samples, $\Delta^{14}\text{C}_l$ in subsequent analyses (low) from the same depths, and f_l and f_a are the fractions of DOC in each of the two pools of DOC. The calculated values of $\Delta^{14}\text{C}_a$ decrease with depth, from +270 ± 40‰ at 20 m to -350 ± 30‰ at 5670 m (see ■ in Figure 3). These high values (young ages) for $\Delta^{14}\text{C}_a$ are counter intuitive, as previous conjectures held that the chemical as well as biological stability of organic matter is proportional to radiocarbon age.

These new results suggest the presence of bomb ¹⁴C in the deep sea DOC pool, which most likely has its source from sinking particulate matter produced in the euphotic zone and subsequent dissolution at depth. As these are the only estimates available of DOC_{res}, it is tempting to extend this approach one step further and assume that all of the DOC (listed in Table 1) has the higher $\Delta^{14}\text{C}$ values we calculated for the additional DOC (Figure 3). The range for the $\Delta^{14}\text{C}$ of total DOC (DOC_{HTC}) can thus be calculated and is shown in Figure 3 (3631 m point excluded). This assumption is an oversimplification of the actual case, as DOC_{res} more likely contains a variety of $\Delta^{14}\text{C}$ values, which decrease with depth. This indicates that the average turnover time of DOC_{HTC} in the deep sea may be much shorter ($\Delta^{14}\text{C} = -310$ ‰, apparent ¹⁴C age 3,000 yrs B.P.) than previously reported (-520‰, 5,900 yrs B.P.; Williams and Druffel, 1987).

The $\delta^{13}\text{C}$ results of the 3 anomalous deep (>1000 m) samples averaged -21.3 ± .2‰, 0.4‰ lower than the average value for normal samples of -20.9 ± 0.3‰ (SD) (Williams and Druffel, 1987). Additional $\delta^{13}\text{C}$ analyses of DOC_{res} are needed before conclusions can be drawn.

In an effort to date individual fractions of the DOC_{UV}, humic substances (fulvic, humic and hydrophilic acids) were isolated from filtered seawater collected at 180 m in the North Pacific by sorption onto XAD macroreticular resins (Ronald Malcolm, personal communication). We assume that humic materials are completely oxidized by UV-radiation based on the complete recovery of humic substances added to UV-oxidized seawater (P.W. Williams, unpublished results). Precise percentage yields of the humic substances isolated by R. Malcolm were not determined. However, humic plus fulvic acids isolated from seawater onto XAD resins constitute about 5 to 20% of the DOC_{UV} in deep and surface waters (Harvey et al., 1983; Meyers-Schulte and Hedges, 1986). Humic acids, however, were much less abundant than either the fulvic or hydrophilic acids (Table 2), and we will

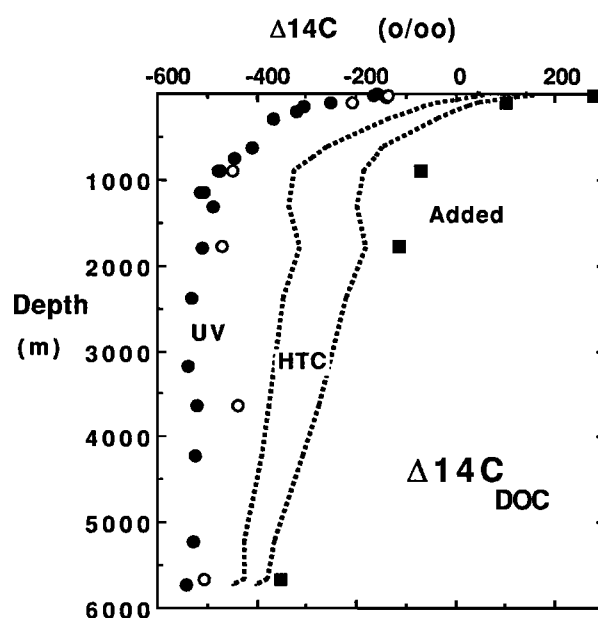


Fig. 3. $\Delta^{14}\text{C}_h$ (○) and $\Delta^{14}\text{C}_l$ (●) (Williams and Druffel, 1987), $\Delta^{14}\text{C}$ calculated for additional DOC oxidized in 6 of the first 7 samples oxidized (■), and calculated $\Delta^{14}\text{C}$ for DOC_{HTC} (without the 3631 m value). See text for discussion.

assume that 20% of the DOC_{UV} was collected on the XAD-2, -8 and -4 resins.

The $\Delta^{14}\text{C}$ values (Table 2) were -410 and -400‰ for the fulvic acids (XAD-8 and -2, respectively) and -310‰ for the humic acids (XAD-2). An intermediate value (-362‰) was obtained for the hydrophilic acid fraction (XAD-8, -4). For comparison, $\Delta^{14}\text{C}$ of DOC_{UV} at 200 m at 31°N, 159°W was -314‰ (Williams^{UV} and Druffel, 1987). The average $\Delta^{14}\text{C}$ values are higher and $\delta^{13}\text{C}$ are lower in the humic acid fraction (-310‰, -23.30‰) than those in the fulvic (-405‰, -21.75 to -22.63‰) or hydrophilic (-362‰, -20.37‰) acid fractions. These data suggest that there are significant differences in the sources to and/or degradative processes acting on these various classes of humic substances.

Table 2. $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values measured in various fractions of DOC separated using XAD resins. The $\Delta^{14}\text{C}$ results are the average of those from two machine-ready targets measured on different dates and are corrected for natural, preparation and sputtering fractionation to a $\delta^{13}\text{C}$ of -25‰. Ages are uncalibrated radiocarbon years using the Libby ¹⁴C half-life of 5568 years.

No.	Sample Desc.	XAD Resin Used	$\Delta^{14}\text{C}$ (±1 σ ‰)	$\delta^{13}\text{C}$ (‰)	Apparent ¹⁴ C age (yrs B.P.)
0-2HA	Humic A.	8	**	-23.27	
TO-792					
0-4HA	Humic A.	2	-310±6	-23.32	2,980±70
TO-793					
0-1FA	Fulvic A.	8	-410±4	-22.63	4,240±50
TO-789					
0-3FA	Fulvic A.	2	-400±4	-21.75	4,100±50
TO-790					
HPI-A	Hydro. A.	8,4	-362±4	-20.37	3,610±50
TO-791					

** Contaminated with modern carbon subsequent to elution from XAD-8 column.

Assessment of the problem

First, the labile compounds (total [free plus combined] dissolved amino acids and carbohydrates, THAA and TCHO) measured in the same samples used for the DOC analyses makeup approximately 19% and 11% of the DOC_{uv} contained within the surface and deep water carbon pools, respectively (Williams and Druffel, 1987; Druffel et al., 1989). We assume that both of these components are completely oxidized by UV-radiation based on the complete recovery of two representative compounds (N-acetyl glucosamine and serum albumin) added to UV-oxidized seawater (Williams and Druffel, 1987). Due to the lability of these compounds with respect to utilization by bacteria (Liebezeit et al., 1980; Carlucci et al., 1986) and their probable surface water origin, we suspect that the $\Delta^{14}\text{C}$ signature of this small portion of the DOC pool is post-bomb ($\sim +100\%$) (Druffel, 1987).

Second, the range of $\Delta^{14}\text{C}$ values in the abundant classes of humic substances (fulvic and hydrophilic acids) from 180 m depth (-410 to -362%) is less than the average value for bulk DOC_{uv} at 200 m (-314%), indicating that this fraction (<20% of DOC_{uv}) is part of the refractory, recycled DOC in seawater.

If we assume that the DOC_{uv} at 200 m ($\Delta^{14}\text{C} = -314\%$) is composed of 10% labile carbon (THAA + TCHO; $\Delta^{14}\text{C} = 100\%$) and 20% humic carbon (fulvic, humic and hydrophilic acids, weighted $\Delta^{14}\text{C} = -386\%$), then the mean $\Delta^{14}\text{C}$ value of the remaining 70% carbon in the DOC_{uv} will be -353% , a value similar to that resulting from DOC_{uv} composed solely of 10% labile carbon and 90% humic substances (-337%). This implies that the "missing" fraction of the DOC_{uv} also appears "humic" in its ^{14}C signature and, perhaps, its origin and history.

Third, the ^{14}C signature of DOC not oxidized by UV (DOC_{res}) is as yet unknown. Evidence shows that this organic matter is high in nitrogen (C/N atom ratio = 5-7) (Suzuki et al., 1985; Sugimura and Suzuki, 1988), and possibly younger with respect to radiocarbon age than the UV-oxidizable DOC. In a relative sense, DOC_{res} is chemically inert with respect to UV-radiation and more labile with respect to biological utilization, as attested to by its co-variance with AOU. Carlucci et al. (1986) demonstrated that low-nutrient requiring, heterotrophic bacteria isolated from seawater grow in UV-irradiated seawater, which illustrates the presence of significant amounts of biologically utilizable DOC in this media. It would be consistent with the chemical stability of DOC_{res} if it were not soluble, but instead existed in colloidal (.005-.05 μm diameter) and/or small particle (.05-1.0 μm diameter) form.

The results reported here are an attempt to further our limited knowledge of the age and identity of DOC in the ocean. These results must be augmented by 1) confirmation of the HTC technique using other methods (i.e., combustion of dried seawater), and 2) direct isotopic ($\Delta^{14}\text{C}$, $\delta^{13}\text{C}$) measurements of DOC_{HTC} using the gas produced by HTC methods. It is imperative that characterization of DOC_{res} and DOC_{uv} be pursued. Not until this is achieved will we understand the sources, sinks and transformations of DOC, perhaps the largest actively-exchanging reservoir of carbon on earth.

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