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RADIOCARBON IN DISSOLVED ORGANIC AND INORGANIC CARBON FROM THE CENTRAL NORTH PACIFIC

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ABSTRACT. Radiocarbon measurements are reported for dissolved organic carbon (DOC) and inorganic carbon (DIC) from seawater samples collected from the Alcyone-5 cruise in the central North Pacific Ocean in 1985. Differences between the UV-radiation techniques used here and those reported by Williams, Oeschger and Kinney (1969) to oxidize and recover the DOC from sea water are presented. UV unoxidizable DOC in these samples is discussed in a separate publication (Druffel, Williams & Suzuki, 1989). We briefly discuss the penetration of the bomb ^{14}C signal into the DOC and DIC pools. The temporal variability of $\Delta^{14}\text{C}$ in DIC in surface samples taken every 2-3 days is presented. Concentrations of total dissolved free (FAA) plus combined (hydrolyzable) amino acids (THAA) and total dissolved carbohydrates (TCHO) measured in the same water samples are also reported. Our main aim is to present the chemical and isotopic data from samples collected during the Alcyone-5 cruise. Detailed interpretation is published elsewhere.

INTRODUCTION

The origin of DOC in ocean water has long been the subject of debate. We have some basic knowledge of the sources and sinks of the carbon to the DOC pool. Inputs of DOC to sea water include intra- and extra-cellular solubles produced by phytoplankton and from sloppy feeding by zooplankton, dissolution of fecal material, plus DOC derived from atmospheric and riverine inputs. Less is known about the source of DOC from subsurface vents, sediments and living bacteria. Sinks for DOC include microbial utilization, coalescence to form particles and adsorption onto existing particles. Quantitative assessments of the importance of each of these processes are not fully evaluated. Overall, it appears that DOC is derived primarily from marine sources, considering the similarity of the $\delta^{13}\text{C}$ in DOC and in marine organisms (Williams & Gordon, 1970) and the low concentration of lignin present in sea water (Meyers-Schulte & Hedges, 1986).

^{14}C was measured nearly two decades ago in DOC from the northeast Pacific to determine its turnover time in the ocean. Williams, Oeschger and Kinney (1969) reported $\Delta^{14}\text{C}$ values of $-351 \pm 27\%$ at 1880m and $-341 \pm 23\%$ at 1920m collected in 1968 and 1969, respectively, from 30°N , 120°W . Two years later, four samples from 30°N , 140°W were measured (-88 ± 20 , -11 ± 18 , -176 ± 14 , $-274 \pm 13\%$ from 10m, 200m, 500m and 2000m, respectively) (Arhelger *et al*, 1974; Williams *et al*, 1978). These ^{14}C analyses were performed on CO_2 resulting from UV-oxidation of acidified sea water. L Jeffries (unpub data) used adsorption onto activated charcoal as a means for separating the DOC from sea water. Her measurements on Gulf of Mexico water were -485% at 690m, and -560% at 2290m (Bada & Lee, 1977). Gas proportional counting techniques were used to measure ^{14}C in these samples, thus, 500 - 1000L of sea water were needed to make an analysis. Based on these early studies, deep-sea DOC has been assigned an apparent age of 3400 yr BP.

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A recent study by Williams and Druffel (1987) reveals that the $\Delta^{14}\text{C}$ of UV-oxidizable DOC in the deep Pacific is much lower than previously reported. We present these measurements and concentrations of FAA, THAA and TCHO in dissolved organic matter from a detailed profile in the central North Pacific. From a near high-precision $\Delta^{14}\text{C}$ profile measured in DIC ($\Delta^{14}\text{C}_{\text{DIC}}$), we examine the penetration of the bomb ^{14}C transient into the main thermocline since the GEOSECS survey of 1973. In addition, $\Delta^{14}\text{C}_{\text{DIC}}$ was measured in surface water samples collected every 2–3 days during the Alcyone-5 cruise to study short-term variability at a single open ocean site. The effect of a high wind storm on this short-term variability was also observed.

METHODS

Collection of Samples

The data presented here are from samples collected aboard the *R/V Melville* during the Alcyone-5 cruise to the central North Pacific Ocean in October and early November 1985. One location was occupied (20km², 31°N, 159°W) 800km north of Oahu, Hawaii in the predominantly eastward flowing North Pacific Current.

Gerard barrels, constructed of stainless steel with a volume of 270L, were used to obtain sufficient carbon for near high-precision $\Delta^{14}\text{C}$ analyses of the DIC fraction. The barrels were scrubbed and rinsed clean with dilute HCl, xylene, acetone, methanol and distilled water to remove all traces of oil and other organic matter, as well as inorganic carbon. Partial disassembly of the barrels was required so that o-ring grooves could be cleaned and viton o-rings installed. The plastic parts on the barrels were replaced with similar items constructed of brass (*ie*, water spigot). Barrels were mounted on the trawl wire and lowered to the desired depths. For near surface samples, a minimum of 20 min elapsed before the messenger was sent to close the lids to allow for adequate flushing at the desired depth. Drains and other tanks aboard ship were flushed out away from the immediate collection site. For the deeper samples, reversing thermometers were used to provide depth corrections, and salinity and silicate measurements from piggy-backed 5L Niskin bottles were compared with those from the barrels to check for pre-tripping or partial closure of the barrels.

Water for DOC concentration and ^{14}C analysis was filtered using a pre-fired (500°C) GFC glass fiber filter in a PVC holder that attached directly onto the spigot at the bottom of the Gerard barrel. One-gal glass bottles, which were previously cleaned with hot chromic acid, rinsed with double distilled water and protected from the atmosphere, were then rinsed three times with the sample water and filled. They were then sealed with teflon-lined caps and frozen at -20°C. Four bottles were collected from depths below 450m and two bottles were taken from shallower depths.

Aliquots of the same filtered sea water were collected in cleaned bottles for FAA, THAA and TCHO analyses, and frozen at -20°C. One-L samples from the upper 150m were collected and immediately filtered for chlorophyll-a and phaeophyton analyses. Samples were taken for total CO₂ ([DIC]) and alkalinity (250ml).

The remainder of the water was pumped (using a Jabsco pump), unfiltered, into a plastic 220L plastic drum. The water was acidified, heated (50°C) and purged of CO_2 using a peristaltic pump. The purged CO_2 was absorbed into a solution of SrCl_2 and concentrated ammonium hydroxide, wherein strontium carbonate was precipitated (Linick, 1975).

Radiochemical and Chemical Analyses

For the dissolved organic ^{14}C (DO^{14}C) analyses, 1gal samples were quickly defrosted in warm water and 5L introduced into an all-glass reactor (Fig 1), acidified to $\text{pH } 2.5 \pm 0.2$ with 50% H_3PO_4 , and sparged-free of DIC with nitrogen gas (organic and inorganic carbon-free) at 425ml min^{-1} for 3 hr. The sea water was then saturated with clean oxygen gas and the reactor vessel closed using 85% H_3PO_4 to lubricate and seal the glass ball joints. The sample was oxidized for 6 hr using a 1200 watt Hanovia Hg-arc lamp at $70\text{--}75^\circ\text{C}$. The resultant CO_2 derived from DOC was passed through the KI trap to collect chlorine gas, and water frozen out in the first Horibe trap cooled with dry-ice isopropanol. The sample was then collected in the second Horibe trap (Fig 1) using liquid N_2 . This collection was done by sparging the reactor with nitrogen gas at 235ml min^{-1} for 2 hr at atmospheric pressure. The trapped CO_2 was then pumped free of condensed air using the rough vacuum, and transferred successively from the Horibe trap to the U-tube, then to the cold finger below the Pirani gauge. After measuring the CO_2 pressure, the CO_2 was split into samples for ^{13}C and ^{14}C analyses.

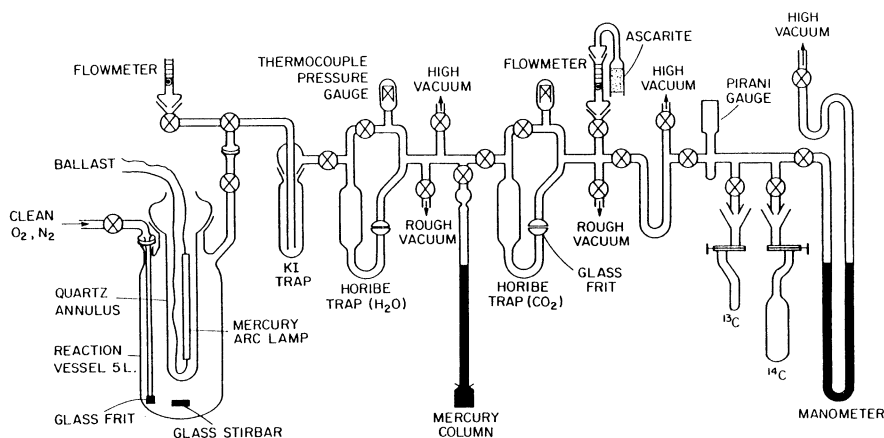


Fig 1. Schematic diagram of the vacuum line used for oxidation and extraction of DOC from sea water. See text for detail.

The CO₂ from the DOC was converted to graphite at the University of Arizona (Jull *et al*, 1986). ¹⁴C was measured using AMS techniques at the University of Arizona TAMS Facility (Linick *et al*, 1986). Errors of ±4–15‰ were obtained, and were dependent upon sample size and AMS system stability at the time of analysis. Δ¹⁴C was calculated assuming a δ¹³C of –21‰ for the graphite targets. δ¹³C-DOC measurements reported in Table 1 were performed on CO₂ obtained directly from the UV oxidation of DOC in sea water.

For the DI¹⁴C analyses, the strontium chloride and ammonium hydroxide solution was decanted off, then heated to dryness, leaving solid strontium carbonate. CO₂ was liberated using 4 N HCl, and converted to acetylene gas (Griffin & Druffel, 1985). The acetylene samples were counted for 4–6 2-day periods in quartz gas proportional beta counters at 90.0cm Hg and 21°C. Errors ranged from ±2.4 – 3.6‰ as determined from counting statistics. δ¹³C_{DIC} was measured on CO₂ from reburned acetylene gas samples.

The FAA and THAA analyses were done using HPLC fluorimetric determination of the o-phthalialdehyde derivatives (Lindroth & Mopper, 1979), after acid hydrolysis of the combined amino acids (Robertson, Williams & Bada, 1987). The TCHO was measured spectrophotometrically on hydrolyzed samples using a modification of the procedure of Burney and Sieburth (1977) and are reported as glucose equivalents. The conversion factor for amino acids (nM) to carbon is 4.4 times amino acid concentration, and for the carbohydrates (μM), this factor is 6 times the glucose equivalents.

RESULTS AND INTERPRETATION

The Δ¹⁴C_{DOC} and Δ¹⁴C_{DIC} data and results of chemical analyses are listed in Table 1. Figure 2 shows the Δ¹⁴C_{DOC} and Δ¹⁴C_{DIC} results. An initial discussion and a graphic representation of all but two of the Δ¹⁴C_{DOC} results were presented by Williams and Druffel (1987).

The Δ¹⁴C_{DOC} values in the upper 2000m of the water column are 60–220‰ lower than those from the same depths observed in the earlier studies (Williams, Oeschger & Kinney, 1969; Arhelger *et al*, 1974, Williams *et al*, 1978). Though the earlier results were obtained from 1300–2600km east, the differences in Δ¹⁴C_{DOC} are probably not due to location. We believe that the earlier results are due to incomplete oxidation of the lower activity (older) fraction of DOC as the original yields were only of the order of 70% of the total UV-oxidizable fraction.

The Δ¹⁴C_{DIC} results are plotted *vs* those reported by Östlund and Stuiver (1980) for the GEOSECS Station 212 (30°N, 160°W) in September 1973 (Fig 2b). These data show that bomb ¹⁴C has penetrated an additional 150m in 12yr, from ca 850–1000m. The prebomb Δ¹⁴C_{DIC} profile in the upper ocean is shown for comparison.

Δ¹⁴C_{DOC} values are 300‰ lower than the Δ¹⁴C_{DIC} values at all depths of the water column (Fig 2c). The similarity in the shape of the two profiles

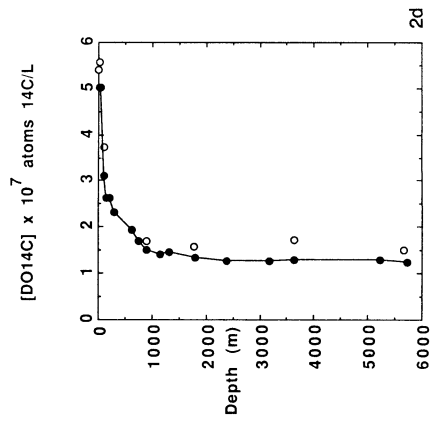
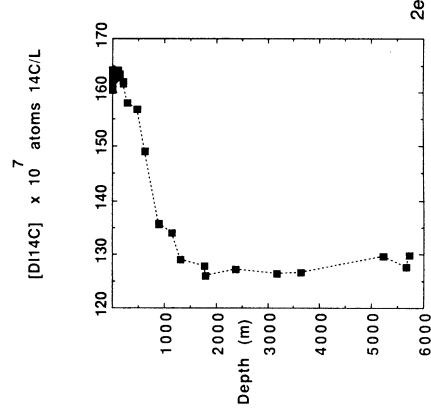
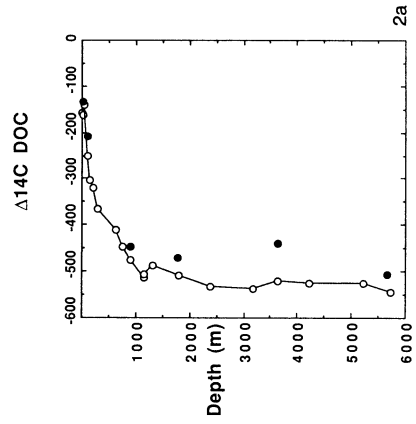
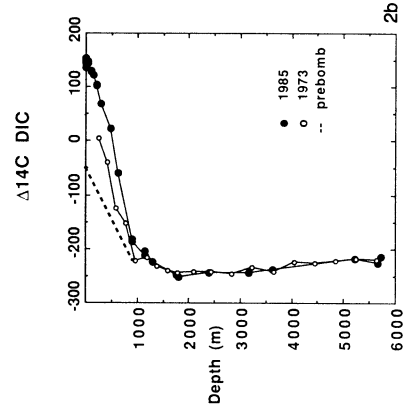
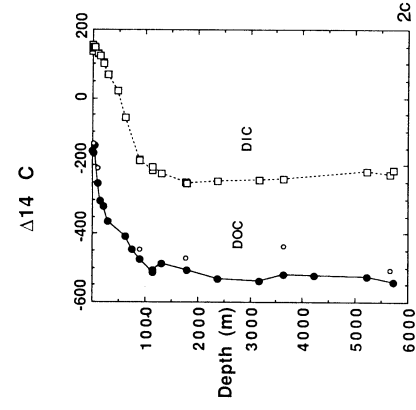


Fig 2 a. $\Delta^{14}\text{C}_{\text{DOC}}$ vs depth at 31°N , 159°W . Off-curve $\Delta^{14}\text{C}_{\text{DOC}}$ values (\bullet) are of samples oxidized using the initial Hg arc lamp. b. $\Delta^{14}\text{C}_{\text{DIC}}$ at 31°N , 159°W (\bullet), $\Delta^{14}\text{C}_{\text{DIC}}$ in seawater samples taken from GEOSECS station 212 (30°N , 160°W) in Sept 1973 (Östlund & Stuiver, 1980) (\circ), and prebomb depth distribution of $\Delta^{14}\text{C}_{\text{DIC}}$ (---) approximated from earlier seawater measurements from North Pacific sea water (Bien, Rakestraw & Suess, 1965). c. $\Delta^{14}\text{C}_{\text{DOC}}$ and $\Delta^{14}\text{C}_{\text{DIC}}$ vs depth at 31°N , 159°W . d. Concentrations of DO^{14}C (\circ , \bullet). e. DI^{14}C (\bullet) (in atoms $^{14}\text{C}/\text{L} \times 10^7$) vs depth at 31°N , 159°W

suggests that bomb ^{14}C has penetrated into the DOC pool to at least the same depth as in the DIC pool, that is ca 1000m. The shift toward lower numbers indicates that a major component of the DOC pool is 'old' with respect to ^{14}C , and is recycled on very long time scales (10^3 – 10^4 yr or longer).

In order to observe changes in the concentration of ^{14}C in each of these carbon pools, $[\text{DO}^{14}\text{C}]$ and $[\text{DI}^{14}\text{C}]$ values are calculated using the following equations:

$$[\text{DO}^{14}\text{C}] = [\delta^{14}\text{C}/1000 + 1] * f * [\text{DOC}] * A \quad (1)$$

$$[\text{DI}^{14}\text{C}] = [\delta^{14}\text{C}/1000 + 1] * f * [\text{DIC}] * A \quad (2)$$

where $\delta^{14}\text{C}$ is defined by Stuiver and Polach (1977), f is the $^{14}\text{C}/\text{C}$ ratio in 95% NBS oxalic acid-1 standard (1.176×10^{-12} ; Stuiver, 1980), A is Avogadro's number, and $[\text{DOC}]$ and $[\text{DIC}]$ are in moles/L. Figure 2d shows that the surface $[\text{DO}^{14}\text{C}]$ is four times greater than that in the deep-sea, whereas surface $[\text{DI}^{14}\text{C}]$ is only 1.3 times that in the deep-sea. The large DO^{14}C concentration gradient illustrates that large amounts of DOC are recycled within the upper few hundred meters of the water column by (1) remineralization of organic matter fixed in the euphotic zone, and (2) remineralization of organic matter in the upper 1000m of the water column due to microbial and other degradative processes.

Results of vertical profiles of FAA, THAA, TCHO and DOC are listed in Table 1 and shown in Fig 3. The FAA results (Fig 3a) are very low below 450m depth; they indicate that there is little if any contamination by labile carbon of the Gerard barrel samples during collection. The low results also illustrate rapid bacterial utilization of FAA in deep waters. The THAA results (Fig 3b) were ca 100 times higher than FAA and show variations with depth. The increase in THAA from 400–800m may be caused by partial conversion of the surface-derived particulate organic carbon rain to DOC or *in-situ* production of organic matter (Cindy Lee, pers commun, 1988). The TCHO values are about seven times higher than the THAA values, and are essentially invariant with depth below 900m. The sum of THAA and TCHO carbon is ca 11% of the total DOC below 1000m and comprises 19% of the DOC at the surface (Fig 3c).

The seven DOC values denoted by open circles in Figure 3c are 6–14% higher than the other DOC values. Likewise, the $\Delta^{14}\text{C}_{\text{DOC}}$ of 6 of these 7 samples were higher than the other values (Fig 2a). We suspect that the higher DOC values were the result of a 'younger' fraction of DOC that was oxidized only in the first seven samples processed using the initial "more potent" Hg-arc UV lamp (for discussion, see Druffel, Williams & Suzuki, 1989).

^{14}C measured in 11 surface water samples collected over the course of the 33-day cruise are listed in Table 1. Pre-storm $\Delta^{14}\text{C}_{\text{DIC}}$ results are relatively constant, with an average of 151.3 ± 0.8 (SD) ‰ ($n=3$) through day-8 of the cruise. Post-storm results, however, were more variable and averaged 146.6 ± 6.2 (SD) ‰ ($n=8$). In order to observe changes in DI^{14}C concentration with time $[\text{DI}^{14}\text{C}]$ values in the surface seawater samples are calculated using Eq 2 and shown in Figure 4a. $[\text{DI}^{14}\text{C}]$ was also more variable during the post-storm period. An increase was observed in $[\text{DI}^{14}\text{C}]$ in the

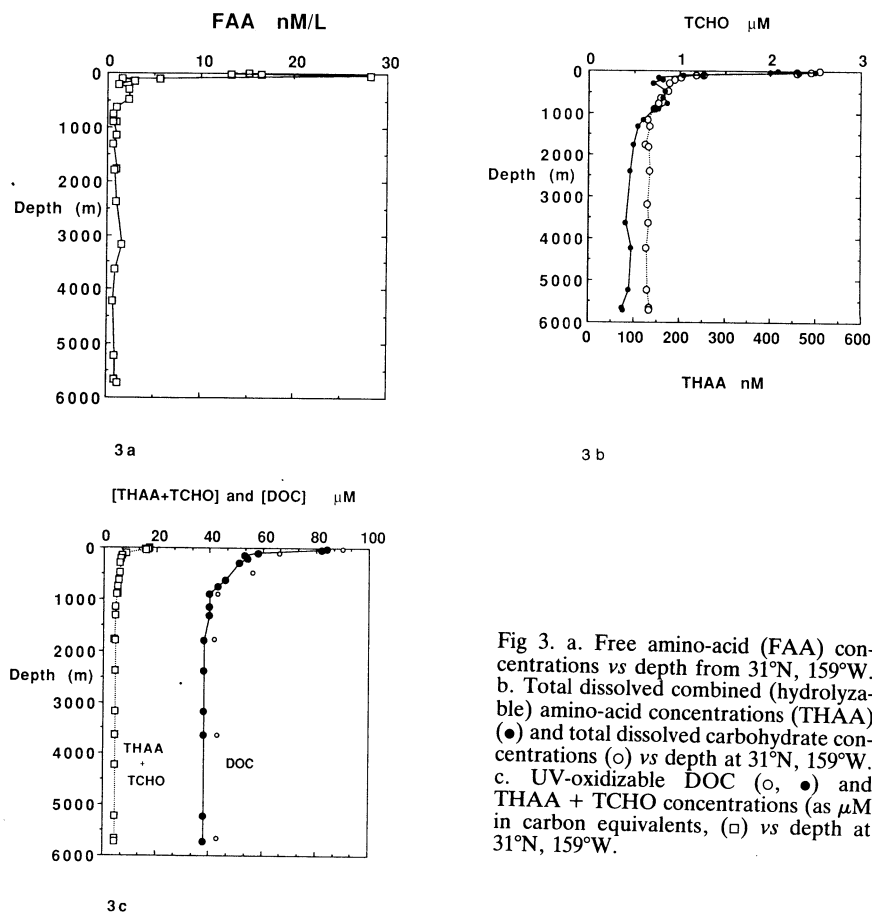


Fig 3. a. Free amino-acid (FAA) concentrations vs depth from 31°N, 159°W. b. Total dissolved combined (hydrolyzable) amino-acid concentrations (THAA) (●) and total dissolved carbohydrate concentrations (○) vs depth at 31°N, 159°W. c. UV-oxidizable DOC (○, ●) and THAA + TCHO concentrations (as μM in carbon equivalents, (□) vs depth at 31°N, 159°W.

upper 200m during the post-storm period (see Fig 4b), due primarily to the higher total CO_2 values. Whether the higher values were due to entrainment of atmospheric CO_2 into the mixed layer, or to spatial variability induced by storm activity, cannot be determined from the existing data set.

CONCLUSIONS

The study of ^{14}C in DOC in the central North Pacific has revealed that a major portion of the DOC is recycled within the water column on time scales of 10^3 to 10^4 yr or longer. Bomb ^{14}C is present to a depth of at least 1000m in the DOC pool, and is probably present in small amounts in the deep sea. Labile constituents of DOC (THAA and TCHO) are present in minor amounts in sea water (11–19% of DOC).

The $^{14}\text{C}_{\text{DIC}}$ profile reveals that the bomb ^{14}C transient has penetrated an additional 150–200m since the GEOSECS survey of 1973. These data have important implications for determining the ventilation rate of the main thermocline with respect to excess CO_2 .

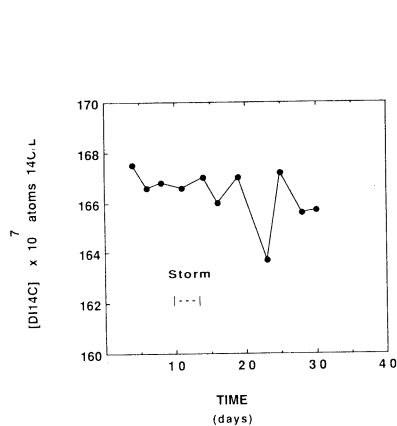


Fig 4 a. $[\text{DI}^{14}\text{C}]$ in surface sea water vs time during the Alcyone-5 cruise at 31°N , 159°W .

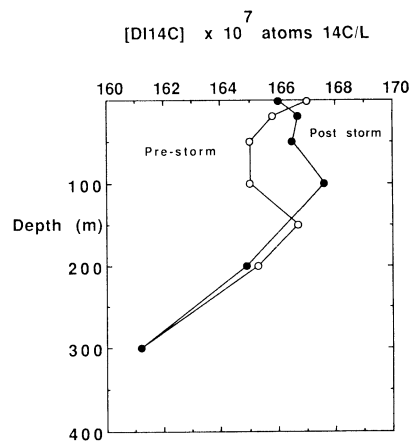


Fig 4 b. $[\text{DI}^{14}\text{C}]$ vs depth for the pre-storm and post-storm sampling periods.

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