Cycling of Dissolved and Particulate Organic Matter in the Open Ocean

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Radiocarbon ($\Delta^{14}C$), $\delta^{13}C$, bulk carbon and organic constituent concentration measurements are presented for dissolved and particulate carbon pools from the North Central Pacific Ocean (NCP) and the Sargasso Sea (SS). We operationally define three overlapping pools of dissolved organic carbon (DOC): (1) DOC that is oxidizable by UV radiation (DOC_{uv}); (2) "extra" DOC measured by Co/CoO flow-through high-temperature catalytic oxidation (DOC_{Ft-htc}), which also has low $\Delta^{14}C$ values like DOC_{uv} (Bauer et al., 1992a); and (3) a potential residual DOC fraction that is the difference between DOC measured by discrete-injection high-temperature catalytic oxidation (DOC_{htc}) and DOC_{Ft-htc}, and which has unknown $\Delta^{14}C$ signature. The distribution of a large fraction of DOC appears to be controlled by circulation of deep ocean waters between major oceans. The DOC in the SS is slightly younger than would be expected if circulation was the sole process controlling DOC cycling. We propose that there is more bomb ^{14}C in the deep SS DOC to account for this difference. The $\Delta^{14}C$ values of suspended, and to a lesser extent sinking particulate organic carbon (POC), decrease with depth, with the suspended POC displaying a much steeper gradient in the SS than in the NCP. These data reflect the incorporation of low-activity organic matter into the POC pool, possibly through incorporation of DOC by physical adsorption and/or biological heterotrophy.

1. INTRODUCTION

Dissolved organic matter (DOM) in seawater constitutes one of the largest exchangeable reservoirs of organic carbon on Earth ($\sim1.7 \times 10^{18}$ g C), though many questions concerning its origin and cycling remain unanswered. It is commonly believed that most dissolved organic carbon (DOC) in seawater originates directly and/or indirectly, from primary production in the euphotic zone. Evidence for a marine origin of DOC includes (1) its marine like $\delta^{13}C$ signatures [*Williams and Gordon*, 1970; *Williams and Druffel*, 1987]; (2) the low abundance or absence of terrestrially derived, lignin-oxidation products within the DOC pool [*Meyers-Schulte and Hedges*, 1986; this work]; and (3) the compositional dissimilarity between riverine-derived humic substances and those isolated from seawater [*Malcolm*, 1990; *Hedges et al.*, 1992]. The downward mixing and subsequent sequestering of surface-derived DOC into subsurface waters may be an important parameter controlling the residence time of photosynthetically fixed atmospheric CO_2 in the oceans prior to its oxidation and return to the atmosphere after several mixing cycles within the world ocean.

Dissolved plus colloidal organic carbon (DOC) and particulate organic carbon (POC) are operationally defined terms herein. POC is either the suspended organic carbon that is retained on 1-μm nominal pore diameter GF/C glass or on 0.8-μm Whatman quartz filters, or the sinking organic carbon collected in sediment traps. DOC is the organic carbon remaining in the water passing the filter. These pore diameters allow most bacteria, many microplankton, all viruses and small suspended particles [see *Koike et al.*, 1990] to pass the filter initially until the effective pore sizes are reduced by particle buildup and/or hydrophobic adsorption of DOC to filtered POC. The so-called DOC in the filtrate is composed of truly dissolved organic matter (<0.005 μm) plus some unknown percentage (probably less than 15% of the DOC below the euphotic zone) of colloidal organic matter (>0.001 to <0.2 μm), and small particle fractions (>0.2 μm to <1 μm).

Most values from recent studies show that DOC is more concentrated in seawater than POC, by 10 to 100 times in surface waters and by 100 to 1000 times at depth. This lack of definitive demarcation between particles, colloids, and DOM will result in an overlap of certain chemical, isotopic and biological properties between these various phases.

The recent DOC controversy and its implications for the oceanic carbon cycle [*Williams and Druffel*, 1988; *Toggweiler*, 1989; *Williams*, 1992] arise from reports of elevated DOC_{htc} concentrations in seawater, as measured using high-temperature combustion techniques (see *Williams* [1992] for summary). These elevated DOC_{htc} values can be up to twice those previously found using traditional wet chemical [*Menzel and Vaccaro*, 1964] and UV oxidation [*Armstrong et al.*, 1966] techniques. Theories as to why part of the DOC is not combusted by low-temperature techniques include possible chloride interference [*House*, 1962; *Skopintsev et al.*, 1976; *Bauer et al.*, 1992b], oxidation potentials that may exceed those of standard tested compounds [*Williams and Druffel*, 1988; Peyton, 1992], and production of refractory DOM during wet oxidations with UV, peroxodisulphuric acid, chromic acid or combinations thereof.

In our study we use bomb-produced ^{14}C as a tracer of organic carbon that is formed in the euphotic zone or upper water column (<1000 m). Bomb ^{14}C was produced in the stratosphere during the thermonuclear weapons testing of the late 1950s and early 1960s and has diffused into the upper ocean by gas exchange of CO_2. Thus all organic matter produced by photosynthesis, including that ingested by organisms, will be tagged by the bomb ^{14}C signal ($\Delta^{14}C$ > -50‰) and can be detected in subsurface organic carbon

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pools after vertical advection, particle sinking and sedimentation have occurred.

Radiocarbon measured in DOC_{uv} from a profile in the North Central Pacific (NCP) revealed the same general shape as that for dissolved inorganic carbon (DIC), though ^{14}C levels were much lower for DOC_{uv} [*Williams and Druffel*, 1987]. In sinking and suspended POC from the same site, $\Delta^{14}C$ values were all reflective of postbomb carbon, though they displayed a small, but significant decrease with depth [*Druffel and Williams*, 1990]. These data illustrated the recycled nature of the DOC_{uv} and the relatively young, primarily surface-derived source of the suspended and sinking POC.

In this paper we present new $\Delta^{14}C$ and $\delta^{13}C$ results from dissolved and particulate organic phases collected in the Sargasso Sea (SS) region of the western North Atlantic Ocean and compare these results with both previously published and new results from the NCP [*Williams and Druffel*, 1987; *Druffel and Williams*, 1990; *Bauer et al.*, 1992a]. Total molar concentrations of DOC_{uv}, DOC_{htc}, DOC_{Ft-htc} and suspended POC are also presented, as are concentrations of soluble "humic" substances and total (free plus combined) hydrolyzable amino acids (THAA) and carbohydrates (TCHO). Conclusions are drawn from the $\Delta^{14}C$ data, in light of important differences between the two oligotrophic ocean sites, namely, (1) sinking POC fluxes to the deep sea are about 2 times higher in the SS than in the NCP [*Smith*, 1987; *Deuser*, 1986]; (2) both dissolved oxygen and DIC $\Delta^{14}C$ values in the deep SS are higher due to local formation of North Atlantic Deep Water (NADW); and (3) the contribution of riverine organic matter to the Atlantic is about 2 times that found in the Pacific.

2. METHODS

2.1. Collection of Samples

The data reported here are from samples collected on two cruises to one station in the NCP (Alcyone-5 and Eve-1) and one cruise to the SS (Hydros-6) (summarized in Table 1). The cruises to the central NCP occupied a station 800 km north of Oahu, Hawaii. The SS station was located southeast of Bermuda, removed from the influence of organic inputs derived from Bermuda coastal water (W. Deuser, personal communication, 1991). This station is near Deuser's time series station and close to the Joint Global Ocean Flux Study (JGOFS) time series station (BATS) at $31°49'N$, $64°00'W$.

Stainless steel, 270-L Gerard barrels were used to collect seawater for isotopic and concentration measurements of the DIC, DOC, humic substances, and labile organic constituents. The barrels were scrupulously cleaned of organic matter prior to the cruises (see *Druffel et al.* [1989a]).

Water for total DOC analysis (by UV and high temperature combustion (htc) methods) and DOC $\Delta^{14}C$ measurements was filtered using a precombusted (500°C) GF/C glass fiber filter in a polyvinyl chloride (PVC) holder that attached directly onto the spigot at the bottom of the Gerard barrel. Selected 1-gal. samples from the Hydros-6 cruise were poisoned with 0.6 mL of a saturated $HgCl_2$ solution (to 10 ppm) and all samples were frozen at -20°C. Samples for total DOC analysis were flame sealed in precombusted, 20-mL glass ampoules which were immediately frozen in liquid nitrogen and stored at -20°C (Hydros-6) or sealed in ampules later after the gallon samples were thawed for DOC_{uv} ($\Delta^{14}C$) combustion (Alcyone-5, Eve-1).

Aliquots of the same filtered seawater were collected in precombusted (500°C) 125-mL amber glass bottles with teflon-lined caps for THAA, free amino acid (FAA) and TCHO analyses, and frozen at -20°C. One-liter samples from the upper 150 m were collected and immediately filtered for chlorophyll-a and phaeophytin analyses; the filter pads were frozen at -20°C in acidified acetone. Unfiltered 250-mL samples were also taken for total CO_2 and alkalinity and were preserved with 0.25 mL of saturated $HgCl_2$; they were run by A. Bradshaw using potentiometric titration techniques [*Bradshaw et al.*, 1981].

The remainder of the water from the Gerard barrel (~200 L) was pumped, unfiltered, into a 220-L plastic drum, where the water was acidified, heated to 50°C and purged of CO_2 with air using a recirculating pump. The purged CO_2 was absorbed into a solution of $SrCl_2$ and concentrated ammonium hydroxide, wherein strontium carbonate was precipitated [*Linick*, 1975].

Water for collection of humic materials was obtained from repetitive casts of the Gerard barrels to two depths (10 and 4200 m) on the Alcyone-5 cruise and to four depths (50, 850, 1500, 3200 m) on the Hydros-6 cruise. The humic substances were adsorbed onto macroporous, crosslinked polystyrene resins XAD-2 and XAD-4 (styrene-divinylbenzene copolymers of average pore diameters = 90 Å and 50 Å, respectively) and on XAD-8 (a styrene-polyacrylate copolymer of average pore diameter = 250 Å). The XAD-4 resin has been reported by *Aiken et al.* [1979] to have higher adsorption capacity for lower molecular weight compounds than either XAD-2 or XAD-8. These Amberlite[R] resins were all obtained in bulk quantities from Rohm & Haas Company (Philadelphia, Pennsylvania) and rigorously freed of fines and contaminants prior to use by extraction with 0.1 N NaOH, 0.1 N HCl, acetone, methanol and distilled water in various sequences [*Thurman and Malcolm*, 1981; *Ertel et al.*, 1986]. Humic substances were isolated from 270-L seawater samples passed directly from the Gerard barrels through precombusted (450°C), 142-mm diameter Gelman A/E glass fiber filters (1-μm nominal pore size). After acid-

TABLE 1. Site Information for the Three Cruises Discussed in This Paper

Cruise	Location	Latitude/Longitude	Cruise Dates	Days on Station	Bottom Depth, m
Alcyone-5	NCP	$31°00'N$, $159°00'W$	Oct. 5 to Nov. 9, 1985	25	5750 ± 50
Eve-1	NCP	$31°00'N$, $159°00'W$	June 3 to July 12, 1987	29	5750 ± 50
Hydros-6	SS	$31°50'N$, $63°30'W$	May 26 to June 25, 1991	24	4450 ± 50

ification, seawater was passed sequentially through XAD-2 then XAD-4, or through XAD-8 then XAD-4. The column sizes were 5 × 150 cm (or 3 L volume) and the flow rates about 1 L/min. The adsorbed humic substances were eluted with 5 L of 0.1 N NaOH, and, following acidification with 3 N HCl, readsorbed on 1.5 × 60-cm columns of the same resin at 25 mL/min throughput. This latter basic eluate (180 mL) was then passed through 100 mL of Dowex-50 W-8X ion exchange resin in H$^+$ form. The final, salt-free eluates were freeze dried at 30°–40°C in vacuo, redissolved in distilled water (leaving behind the bulk of the isolated lipids), relyophylized, and dried to constant weight at 25°C in vacuo. These resultant humic substances are predominantly fulvic acids with possibly small amounts of humic acids [Thurman, 1985]. Blanks for the XAD-2/Dowex-50 and XAD-4/Dowex-50 systems were determined by passing 5 L of UV-oxidized seawater through a scaled-down (50-fold lower volumes used) extraction sequence and product isolation scheme identical to the shipboard procedures. These extrapolated blanks were <1 mg per 270 L for both the XAD-2/Dowex-50 and XAD-4/Dowex-50 systems, and were supported by DOC$_{htc}$ analyses of the appropriate column eluates.

Suspended POC was collected using modified in situ pumps [Laird et al., 1967; Williams et al., 1980] deployed for 2-8 hours at 7 depths on Alcyone-5, 13 depths on Eve-1 and 15 depths on Hydros-6. During each deployment, 600–11,000 L of seawater, depending on depth and pump characteristics, were filtered through four 142-mm diameter precombusted (550°C) quartz fiber filters (Whatman ultra-pure QM-A 0.8-μm pore diameter) in PVC holders. The unrinsed filters were then frozen at -20°C. The filters from the Alcyone cruise were lost prior to ^{14}C analysis due to a failed freezer unit.

Sinking POC was collected at 600 m and 1600 m above the bottom (5165 and 4165-m depths) in the NCP during Alcyone-5 and Eve-1 using paired (0.25 m^2 each) Soutar traps [Bruland et al., 1981] deployed by K. Smith (Scripps Institution of Oceanography, SIO) for periods of 2 weeks. The SS sample was collected by W. Deuser from 3200 m depth at a site (31°50'N, 64°10'W) approximately 10 km from Station DW using a 0.5 m^2 single-cup PARFLUX cone trap [Deuser et al., 1988]. The trap was deployed from April 4 to June 5, 1989. Mercuric chloride was used as a preservative in the NCP traps, but no preservative was added to the SS trap. Sinking POC in the NCP samples was concentrated aboard ship by filtration onto precombusted 47-mm diameter quartz filters that were then frozen at -20°C. After thawing, large "swimmers" were picked from the filters and the filters were either cut into halves and quarters for carbon/hydrogen/nitrogen (CHN), combined amino acid and carbohydrate, and Δ^{14}C analyses (Alcyone-5, Eve-1) or left uncut for Δ^{14}C measurements alone (Hydros-6). Sinking POC in the SS trap was stored at 2°C in the dark, and the <38-μ size fraction was sieved and dried.

Samples for sedimentary organic carbon (SOC) analyses were obtained from a 75-mm-diameter lucite subcore of a Soutar box core [Soutar, 1979] sample collected on Alcyone-5 by C. Reimers (SIO) and from a 10-cm-diameter gravity core [Shaw, 1988] obtained on Hydros-6. Discrete sediment horizons were sectioned aboard ship with clean metal spatulas and thin polyethylene sheets and frozen at -20°C.

2.2. Radiochemical and Chemical Analyses

For the Δ^{14}C analyses of the DOC$_{uv}$, two 1-gal. samples were quickly thawed in warm water and 5 L introduced into a glass and quartz reactor, acidified to pH 2-3 with H$_3$PO$_4$, freed of DIC with N$_2$ and then saturated with oxygen. The DOC was oxidized with 1200 W UV radiation to CO$_2$ which was collected as described previously [Druffel et al., 1989a]. Blank values were $\leq$1.5 μM C. The dried humic materials extracted using XAD resins were combusted to CO$_2$ in double quartz tubes with CuO and silver at 850°C for at least 1 hour [Sofer, 1980]. For ^{14}C analysis of the DOC$_{Ft-htc}$, 100-mL seawater samples were acidified to pH 2-3 with 85% H$_3$PO$_4$, freed of DIC with O$_2$, and oxidized to CO$_2$ using a modified Dohrmann Model DC-90 total carbon analyzer [Bauer et al., 1992a]. Seawater was pumped through the analyzer at ~30 mL/h and DOC was oxidized to CO$_2$ with Co/CoO-alumina or Co/CoO-alumina plus 2% Pt-faujisite catalysts (provided by M. Occelli) at 900°C in an O$_2$ stream (150 mL min^{-1}). The resultant CO$_2$ was trapped on a molecular sieve at room temperature, desorbed at 450°C, and collected [Bauer et al., 1992b]. Blank values averaged 1.4 ± 2.5 μg C/h over all runs. The blanks were primarily due to passage of O$_2$ carrier gas through the system and secondarily to reactions of H$_2$O within the combustion tube.

The filters containing sinking and suspended POC were acidified with 1% H$_3$PO$_4$ for 24 hours at 20°C to remove the carbonates, dried under vacuum, and combusted to CO$_2$ in double quartz tubes as above. Aliquots of frozen sediment samples were acidified with 5% H$_3$PO$_4$, allowed to stand ~3 hours at 5°C to a constant pH of 2.5 to 3.0, and then dried at 60°C before combustion as above.

The CO$_2$ was split into samples for δ^{13}C and Δ^{14}C analyses. The CO$_2$ from the DOC$_{uv}$, humic substances, and the sinking and suspended POC was converted to graphite [Jull et al., 1986] whose ^{14}C content was measured using AMS (accelerator mass spectrometry) techniques at the University of Arizona TAMS Facility [Linick et al., 1986]. Errors of ±3 to ±19‰ were obtained and were dependent upon sample size and AMS system stability at the time of analysis. The CO$_2$ from the high-temperature flow-through combustions (DOC$_{Ft-htc}$) was converted to graphite [Vogel et al., 1987] and its ^{14}C content measured using the AMS facility at the Lawrence Livermore National Laboratories (LLNL) [Davis et al., 1991]. Errors of ±20 to ±59‰ were obtained, and again, were dependent upon sample size (70 to 150 μg C) and AMS system stability. All Δ^{14}C values were calculated using measured δ^{13}C values of CO$_2$ splits. The δ^{13}C measurements were performed on CO$_2$ obtained directly from the UV and htc oxidations of DOC in seawater using a VG Micromass 602E isotope ratio mass spectrometer in the laboratory of L. Keigwin at the Woods Hole Oceanographic Institution.

The strontium chloride/ammonium hydroxide solution was decanted from each DIC sample, then heated to dryness, leaving solid strontium carbonate. CO$_2$ was liberated using 4 N HCl and converted to acetylene gas according to Griffin and Druffel [1985]. The acetylene samples were counted for 5 to 6 2-day periods in quartz gas proportional beta counters at 90.0 cm Hg pressure and 21°C. Errors are determined from counting statistics and laboratory error. DIC δ^{13}C was measured as above on CO$_2$ from reburned acetylene gas samples.

DOC_{uv} concentration ($[DOC_{uv}]$) measurements (Tables 2-4) were obtained from the manometrically observed yield of CO_2 resulting from the UV oxidation of 5-L seawater samples as described above. DOC_{htc} concentrations ($[DOC_{htc}]$) in the NCP were measured by Y. Suzuki [Druffel et al., 1989b] and in the Atlantic by J. Bauer [Bauer et al., 1990] and Y. Suzuki (unpublished results, 1989). The former SS values are from 100-μL discrete seawater injections using the Dohrmann Model DC-90 analyzer in a single injection mode, and the latter from similar injections using a 3% Pt/alumina catalyst [Suzuki et al., 1992; Williams et al., 1992]. The two Atlantic [DOC_{htc}] profiles agree within 5% (Table 4). All values using the DC-90 system were corrected for injection blank values.

The concentrations of FAA and THAA were obtained using high performance liquid chromotography (HPLC) fluorimetric determination of the o-pthaldialdehyde derivatives [Lindroth and Mopper, 1979], following acid hydrolysis of the combined amino acids with 6 N HCl [Robertson et al., 1987]. These concentrations of THAA could be minimum values, since recent work by Keil and Kirchman [1991] using a vapor phase hydrolysis of seawater samples [Tsugita et al., 1987] indicated that the concentration of THAA in seawater may be 0.8 to 3.0 (average = 1.54 ± 0.43, n = 62) times that obtained by the standard 6 N HCl hydrolysis at 120°C.

The TCHO concentrations were measured spectrophotometrically on samples hydrolyzed with 0.1 N HCl using the procedure of Burney and Sieburth [1977] and are reported

TABLE 2. Isotopic and Concentration Measurements in Seawater Samples Collected on the Alcyone-5 Cruise

Depth, m	AA#	Event	Salinity, ‰	DOC htc-MRI	DOC UV	$\Delta^{14}C$ DOC_{uv}	±	$\delta^{13}C$ DOC_{uv}
3	2288	104	-	210	82	-163	18	-20.4
20	2392	161	35.286	218	77	-168	13	-20.6
20	2146	104	35.430		82*	-137	17	-20.8
50	2391	108	35.318	218	75	-145	14	-20.9
50		161	35.201					
100	2147	108	34.697		60*	-213	10	-20.9
100	2390	161	34.612	206	53	-254	19	-21.2
150	2369	108	34.514	184	49	-307	15	-20.8
200	2282	117	34.392	173	50	-323	13	-20.9
200		166	34.417					
300	2388	117	34.500	151	47	-363	14	-21.2
482		123	34.140	108	51*	Lost		-22.1
637	2283	117	34.001	96	42	-412	10	
757	2387	127	34.072	94	39	-447	12	-20.9
903	2143	127	34.231		39*	-447	9	-21.6
900	2291	166	34.252	90	37	-477	15	-20.8
903	2285	127	34.231		37	-478	13	-21.2
1152	2290	161	34.433		37	-508	13	-21.0
1152	2746	127	34.433		36	-513	4	-20.6
1308	2280	127	35.312	98	37	-489	11	-20.8
1769	2149	137	34.596		38*	-473	11	-22.3
1808	2292	166	34.583	106	34	-511	19	-20.7
2388	2281	137	34.638	108	35	-535	10	-21.1
3174	2284	145	34.665		35	-541	13	-21.0
3631	2144	145	34.661	110	40*	-441	8	
3631	2747	145	34.661		37	-519	4	-21.1
4227	2286	149	34.679	112	35	-527	10	-21.0
5227	2289	149	34.683	112	35	-529	13	-21.0
5670	2145	153	34.687	108	39*	-509	8	-21.3
5720	2287	153	34.691	110	35	-546	12	-21.2

AA# are the sample numbers for the DOC_{uv} $\Delta^{14}C$ analyses measured at the University of Arizona TAMS facility. Event numbers are consecutive sampling periods during the cruise that represent separate casts of Gerard barrels, Yentsch pumps, nets, etc. DOC_{htc}(Meteorological Research Institute—MRI) measurements were made by Y. Suzuki and reported previously [Druffel et al., 1989b]. DOC_{uv} values are 8% less than those reported earlier [Druffel et al., 1989a] due to a calibration correction. DOC_{uv} $\Delta^{14}C$ values are slightly less than those reported previously [Druffel et al., 1989a] due to the correction of $\Delta^{14}C$ using the actual $\delta^{13}C$ of CO_2 obtained from UV oxidation. DIC, alkalinity, FAA, THAA, TCHO, chlorophyll-a and phaeophytin concentrations, and DIC $\Delta^{14}C$ measurements were reported previously [Druffel et al., 1989a].
* Initial seven samples analyzed for DOC_{uv} $\Delta^{14}C$ that contained ~10% extra DOC than samples analyzed subsequently.

TABLE 3. Chemical and Isotopic Measurements in Seawater Samples Collected on the Eve-1 Cruise

Depth, m	WH#	AA#	Event	Salinity, ‰	DOC_{uv}, μM	DIC, μM	Alkalinity, μM	$\Delta^{14}C$, μM	±	$\delta^{13}C$ DOC_{uv}	$\Delta^{14}C$ DIC	±	AOU, μM	FAA, nM	THAA, nM	TCHO, μM
3		6005	156	-	72	2061	2292	-179	6	-20.6	131.7*		-15	18.0	354	2.08
20	829		145	34.609	65	2058	2323	-191	9	-21.2	113.6	3.1	-23	20.4	476	2.12
20	830		150	35.272	62	2024	2291	-218	5	-21.2	120.7	3.7	-23	20.2	324	1.97
50	834	6004	141	34.778	53	2028	2318	-264	4	-21.4	117.0	4.5	-15	12.6	277	1.73
100	836	3624	152	35.173		2046	2270				135.8	3.1	10	6.8	238	1.23
100	838		140	34.419							111.4	2.8	10	13.2	219	1.20
300	901	3625	138	34.296	53	2089	2280	-325	5	-21.1	77.1	3.1	50	3.5	134	0.96
450		6003	103	34.103	48	2142	-	-389	4	-21.3			98	4.2	164	0.93
598	904	3626	105	34.008	43	-	-	-405	5	-21.0	-77.8	2.6	220	0.9	165	0.83
757	954		106	34.096		-	-				-153.8	2.3	268	0.4	164	0.82
896	957		111	34.250	42	-	-	-532	3	-20.8	-183.9	2.3	297	0.8	153	0.78
900		5194	134	34.223	38	-	-	-470	4	-21.1			297	0.3	137	0.82
1148	912	4046	112	34.441	35	-	-	Lost		-20.8	-213.0	3.1	292	0.6	130	0.76
1293	962	5195	112	34.494	36	-	-	-533	4	-21.2	-224.2	2.5	283	0.5	159	0.72
1788	987	4039	133	34.589	35	-	-	-529	3	-21.2	-242.5	2.5	255	0.9	116	0.71
2398	983	3628	115	34.638	35	-	-	-528	3	-21.2	-248.9	2.5	235	0.2	109	0.68
2891	992	5172	113	34.662	35	-	-	-535	4	Lost	-242.9	2.5		0.2	110	
3586	993	4047	133	34.675	34	-	-	-528	4	-21.2	-239.0	2.5	193	0.5	126	0.60
4146	986	3629	120	34.682	36	-	-	-501	3	-21.2	-231.0	2.5	184	0.6	91	0.68
5150	957	3630	120	34.690	36	-	-	-502	3	-21.3	-216.3	2.5	177	0.4	100	0.63
5699		4045	125	34.684	34	-	-	-520	3	-21.4			157	0.6	95	0.64
5720	949	4044	125	34.690	34	-	-	-536	3	-21.1	-220.8	2.4	157	1.1	90	0.69

WH# are the sample numbers for the DIC $\Delta^{14}C$ analyses measured at the Woods Hole Oceanographic Institution Radiocarbon Laboratory. DIC and Alk are the total CO_2 and alkalinity measured in the seawater by A. Bradshaw. AOU values are calculated using oxygen concentrations measured in the same Gerard barrel samples. FAA, THAA and TCHO measurements are described in the text. Other quantities are described in Table 2 legend.
*DIC $\Delta^{14}C$ for the 3-m sample is an average of 16 analyses made for samples taken every other day throughout the cruise.

TABLE 4. Chemical and Isotopic Measurements in Seawater Samples Collected on the Hydros-6 Cruise

Depth, m	WH#	AA#	Event	Salinity, ‰	DOC htc SIO	DOC htc MRI	DOC Ft-htc SIO	DOC UV	DIC, µM	Alk, µM	$\Delta^{14}C$ DOC$_{uv}$	±	$\delta^{13}C$ DOC$_{uv}$	$\Delta^{14}C$ DIC	±	AOU, µM	TCHO, µM	Chla, µg/L	Phae, µg/L	±
250 µM		5180	118					580			-869	3	-28.4				2.62			
10 cm		5181	118					75			-280	8	-21.8				1.38			
3	930	5180	202	-	111	136		65			-238	9	-21.3				1.47	0.01	0.01	
20	943	5179	102	36.58	102	138		66	2076	2378	-210	6	-21.3	126.7	2.6	13	1.57	0.06	0.01	2.1
50	996		108	36.61	102	126	113	67	2088	2423				115.6	2.8	17	1.35	0.07	0.02	2.2
85	945	5177	109	36.60	96.6	131		58	2079	2410	-253	7	-21.2	119.0	2.6	4.5	0.99	0.41	0.23	2.1
85		5178	109 Hg	36.60				57	2088	2414	-252	5	-21.2	118.3	2.6	25				2.1
100	935	6006	110	36.60	95.2	124		59	2091	2404	-239	6	-21.0	97.1	3.0	29	0.85	0.34	0.26	
200	953	5184	113	36.57	119	120	101	54	2103	2402	-276	5	-20.9	111.8	2.6	37	0.64	0.00	0.01	2.4
400	942	5185	114	36.40	97.7	119		53	2128	2395	-260	6	-21.0	111.4	3.5	61	0.4			2.1
603	931	5186	116	35.85	91.1	113		45	2156	2364	-356	6	-21.0	50.9	2.8	92	0.31			2.8
852	965		117	35.16	90.4	96.4		40	2209	2333	Lost		-21.0	-55.5	2.5	146	0.24			2.2
852		5176	117	35.16				43			-375	5	-21.2							2.0
1099	940	5187	121	35.09	90.5	96.5		42	2197	2330	-412	10	-20.8	-67.1	2.8	122	0.24			
1310	994	5188	121	35.02	90.9	103		42	2184	2326	-377	5	-20.9	-45.1	2.8	92	0.41			2.2
1310	1011		140	35.02										-52.1	3.8	86				2.2
1510	926	5189	124	34.99	86.9	101	61	43	2182	2321	-378	5	-20.8	-32.3	2.5	71	0.42			3.0
1815	948	5174	124	34.98	91.4	108		44	2184	2324	-388	5	-20.2	-58.0	2.5	58	0.33			2.0
2216	939	5190	128	34.97	108	110		42	2172	2324	-395	5	-20.8	-78.7	2.6	78	0.36			2.0
2727	946	5190	128	34.95	95.5	108		41	2178	2328	-391	5	-20.9	-80.2	2.8	79	0.48			2.1
3220	947		140	34.91	93.6				2180	2333				-86.3	2.8	83	0.33			2.2
3237	995	5173	130	34.92	82.1	106	82	43	2191	2343	-414	5	-20.7	-84.2	2.6	83	0.34			2.2
3638	938	5192	130	34.90	93	108	66	44	2193	2344	Lost		-21.3	-84.9	2.4	86	0.36			2.1
3954	944	5175	137	34.88	99	110		44	2197	2341	-397	5	-20.8	-85.1	2.8	92	0.33			1.9
4454	934	5193	137	34.88	92.2	113		43	2205	2350	-391	5	-21.0	-94.3	2.8	150	0.38			2.2

DOC$_{htc}$(SIO), DOC$_{htc}$(MRI), and DOC$_{Ft-htc}$(SIO) are concentrations of DOC measured by discrete injection onto Co/CoO Dohrmann model DC-90 at SIO, that measured at MRI (by Y. Suzuki) and DOC measured by flow-through combustion on Co/CoO at SIO, respectively. Chl-a and phae are concentrations in µg/L of chlorophyll-a and phaeophytin of near-surface waters. Other quantities are described in Table 2 and Table 3 legends.

as glucose equivalents. These TCHO concentrations may also be minimum values, since *Pakulski and Benner* [1992] reported that hydrolysis with 12 M H_2SO_4 yields 2- to 4-fold more dissolved carbohydrate-containing compounds than are measured with HCl hydrolysis.

We assume a conversion factor for amino acids (nanomoles) to carbon equivalents of 4.4 times the amino acid concentration in nanomoles, and for the carbohydrates of 6 times the glucose equivalents in micromoles.

3. RESULTS AND COMPARISONS WITH EARLIER DATA

Measurements of $\Delta^{14}C$ in DOC, DIC and the concentrations of DOC_{uv}, THAA, FAA and TCHO from Alcyone-5 samples were published previously by *Williams and Druffel* [1987] and *Druffel et al.* [1989a]. $\Delta^{14}C$ measurements of suspended POC, DIC and DOC_{uv} from the Eve-1 cruise were reported graphically by *Druffel and Williams* [1990].

All of the data except that for humic substances and POC from the NCP (Alcyone-5 and Eve-1) cruises are summarized in Tables 2 and 3. (Some of Alcyone-5 data in Table 2 are corrected from those previously reported by *Druffel et al.* [1989a].) All data from the SS (Hydros-6) cruise, except the humic substances and POC, are listed in Table 4 and are described below. Data for the POC samples are in Table 5 and the humic substances in Table 6. In this section we discuss the SS $\Delta^{14}C$ data, compare it with that from the NCP, and then present the bulk carbon and organic constituent concentration measurements as they apply to the organic carbon cycle in the open ocean.

3.1. Sargasso Sea—$\Delta^{14}C$ Profiles

The $\Delta^{14}C$ values of DIC in the SS show the presence of bomb ^{14}C in the main thermocline (<850 m) and in the up-

TABLE 5. $\Delta^{14}C$ and $\delta^{13}C$ Measurements for Suspended POC (POC_{susp}) and Sinking POC (POC_{sink}) Collected During Our Three Cruises

Depth, m	Event-Filt. #	[POC], μM	AA#	$\Delta^{14}C$ POC_{sus}	±	$\delta^{13}C$	Sediment Trap Deployment Dates	AA#	$\Delta^{14}C$ POC_{sink}	±	$\delta^{13}C$
						Alcyone-5					
4120	118/154		2584				Oct. 11 to Nov. 6, 1985	2584	18	9	-22.0
5120	103/151		2583				Oct. 8 to Nov. 6, 1985	2583	-39	13	-24.1
						EVE-1					
20	188-B	2.610	3769	139	9	-22.6					
85	205-B	2.280	4715	140	8	-23.6					
100	188-B	1.300	3770	162	9	-25.0					
450	220-D	0.220	4714	129	11	-19.3					
900	160-C	0.129	3800	103	13	-21.7					
1800	160-B	0.091	3771	110	15	-21.8					
1800	160-C	0.094	3772	62	15	-22.2					
3000	183-A	0.057	3373	55	19	-22.4					
3400	199-B	0.059	4712	48	14	-21.8					
4200	173-C	0.050	3774	18	21	-22.6	June 21 to July 3, 1987	4792	99	12	-23.0
5120	162-B	0.049	3775	50	24		June 21 to July 3, 1987	4790	136	14	-22.5
5720	162-A	0.054	3801	43	28	-22.3					
						HYDROS-6					
20	135-B	0.260	4820	138	9	-20.5					
20	135-D	0.245	4022	124	11	-21.1					
48	179-D	3.170	5701	126	8	-20.4					
85	132-B	2.380	4821	124	13	-20.9					
85	132-D	2.170	4793	119	9	-20.9					
100	179-B	1.880	5691	118	10	-21.6					
600	111-D	0.105	5699	8	10	-20.4					
852	111-B	0.105	5692	34	10	-20.3					
1310	126-B	0.106	5693	40	11	-20.4					
1510	126-D	0.097	5700	16	12	-20.4	Apr.-May 1990	5770	179	8	
2700	123-D	0.063	5696	-11	14	-20.5					
3200	115-D	0.046	5702	-9	16	-20.4					
3200	138-B	0.053	4823	-55	15		Apr.-May 1990	5772	66	7	
3200	138-D	0.061	5703	19	15						
3600	165-D	0.040	5698	-26	16	-20.2					
4000	115-B	0.047	5697	-92	15	-20.3					
4450	165-B	0.072	5694	76	18	-20.5					

Concentrations of POC_{susp} in seawater (μM C) are determined from yields of CO_2 obtained from closed-tube combustions of quartz filters through which known volumes of seawater had passed.

TABLE 6. Chemical and Isotopic Data for Humic Materials Collected Using XAD Resins From the NCP (Alcyone-5) off Hawaii and SS (Hydros-6)

Depth, m	XAD Resin	Volume Extracted, L	Σmg Isolated	%C	%N	%H	C/N Atom	mgC/L	% DOC$_{uv}$	% DOC$_{htc}$	δ^{13}C ‰	Δ^{14}C ‰	±	AA# or TO#
Alcyone-5 (October 1985)														
10	2	400	47.8	48.52	1.21	4.89	47.2					-342	9	1726
10	2	400	36.5	46.16	1.17	4.81	45.9							
4200	2	415	47.5	49.88	1.34	5.19	43.5					196	6	1727
4200	2	425	33.7	49.66	1.22	5.25	47.3							
Hawaii 19°N (June 1985)														
183	8H	26500									-23.3	contam.		TO-792
183	2H	26500									-23.3	-310	6	TO-793
183	8F	26500									-22.6	-410	4	TO-789
183	2F	26500									-21.8	-400	4	TO-790
183	8-4HPA	26500									-20.4	-362	4	TO-791
Hydros-6 (July 1989) (JE)														
50	8	1080	240	53.92	1.13	5.76	55.9	0.12	16	7.7	-23.1	-329	5	5704
50	8-4	1080	233	48.72	3.01	5.27	18.9	0.11	14	6.7	-20.8	-374	6	5706
3200	8	1080	218	53.60	1.09	5.57	57.4	0.11	21	8.8	-22.9	-469	5	5705
3200	8-4	1080	206	48.57	2.95	5.14	19.3	0.09	18	7.5	-20.5	Lost		5707
Hydros-6 (July 1989) (PW)														
50	2	270	78	49.88	1.43	5.07	40.7	0.14	19	9.2	-22.1	-358	5	5086
50	2-4	270	21	45.32	2.22	4.25	23.8	0.04	4.7	2.3	-20.9	-402	9	5089
850	2	270	60	49.74	1.34	4.02	43.3	0.11	23	9.6	-21.9	-381	8	5107
850	2-4	270	12	45.60	2.46	3.94	21.6	0.02	4.2	1.8	-20.6	Lost		5090
1507	2	270	56	49.96	1.48	4.93	39.4	0.1	20	8.8	-22.0	-477	4	5087
1507	2-4	270	10	42.94	2.08	3.60	24.1	0.02	3.1	1.4	-20.9	-508	4	5091
3237	2	270	66	50.27	1.25	4.34	46.9	0.12	24	9.9	-22.0	-454	4	5088
3237	2-4	270	13	44.74	2.43	4.03	21.5	0.02	4.2	1.7	-20.8	-587	6	5092

NCP data by K. Meyers-Schulte, University of Washington, off Hawaii by R. Malcolm, USGS-Denver [see *Druffel et al.*, 1989b]. The Hydros-6 humics data were collected using two methods: JE = seawater run first through XAD-8, then through XAD-2; PW = seawater run first through XAD-4; then through XAD-2, then through XAD-4. The % DOC$_{uv}$ and % DOC$_{htc}$ values were obtained using [DOC$_{uv}$] and [DOC$_{htc}$(MRI)] values from Table 4. TO# are Toronto Isotrace AMS sample numbers.

per North Atlantic Deep Waters (NADW) (1300–1800 m) of the SS (Figure 1). Δ^{14}C values in 1989 at these two depth ranges are higher than those measured previously in the mid 1950s [Broecker et al., 1960], early 1970s during GEOSECS [Stuiver and Östlund, 1980] or early 1980s during the Transient Tracers in the Oceans cruises [Östlund, 1981] (Figure 1). Little, if any, bomb ^{14}C has penetrated to 800–850 m, the depth of the Antarctic Intermediate Water (AAIW) and the oxygen minimum.

The Δ^{14}C values for DOC$_{uv}$ (Table 4) range from an average of -238 ± 17‰ (SD) ($N = 5$) in the upper 100 m to an average of -394 ± 13‰ ($N = 9$) below 1000 m (Figure 2). There was no significant increase in Δ^{14}C in the 3, 20 and 85-m surface samples (Table 4) relative to the 100-m value. There may have been hydrocarbon contamination in the SS 3-m surface sample, judging from the Δ^{14}C and δ^{13}C values found for the surface microlayer (upper 250 μm) and 10-cm subsurface samples: -869 ± 3 and -280 ± 8‰, respectively (Table 4). This organic contamination was probably a result of exceptionally calm seas coupled with heavy shipping activities and/or the possible contribution of lubricating oil from a leak in the R/V Melville cycloid engine seals. Considerable amounts of floating debris (including a Sony television set) were also present during the entire cruise. It would only take 12% petroleum-derived carbon (Δ^{14}C = -1000‰) to lower the DOC Δ^{14}C value from -150 to -250‰, (x × (-150) + y × (-1000) = -250) or 7.8 μM based on a total DOC$_{uv}$ concentration of 65 μM. There was no indication of significant oil contamination in any of the samples below 3 m, judging from the absence of Δ^{14}C anomalies in the other samples and no visual "rainbow" light refraction patterns, diagnostic of oil films, on the Gerard barrels. In any case, the outside of the barrels were rinsed on deck prior to sampling and were not allowed to surface if oil slicks were evident.
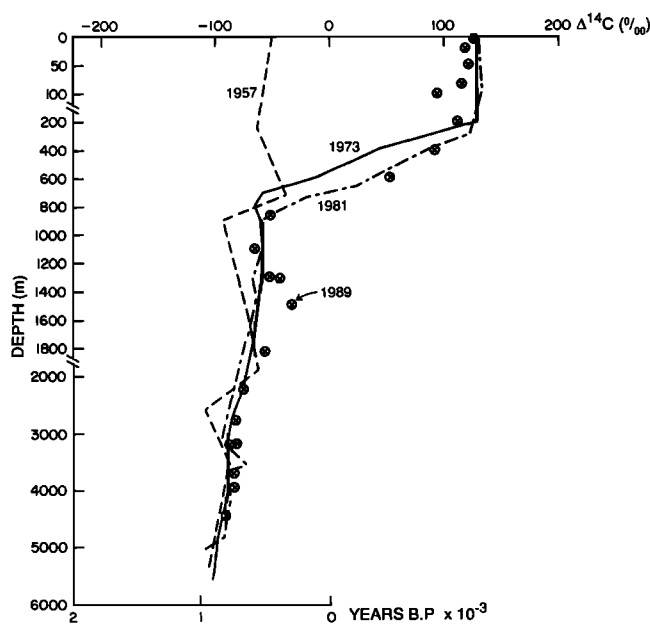
Fig. 1. DIC Δ^{14}C in the Sargasso Sea (SS) water column during different years, including our Hydros-6 cruise in June 1989. The 1957 data are from Broecker et al. [1960]; 1973 data from GEOSECS [Stuiver and Östlund, 1980]; and 1981 data are from TTO [Östlund, 1981]. Note changes in depth scale.
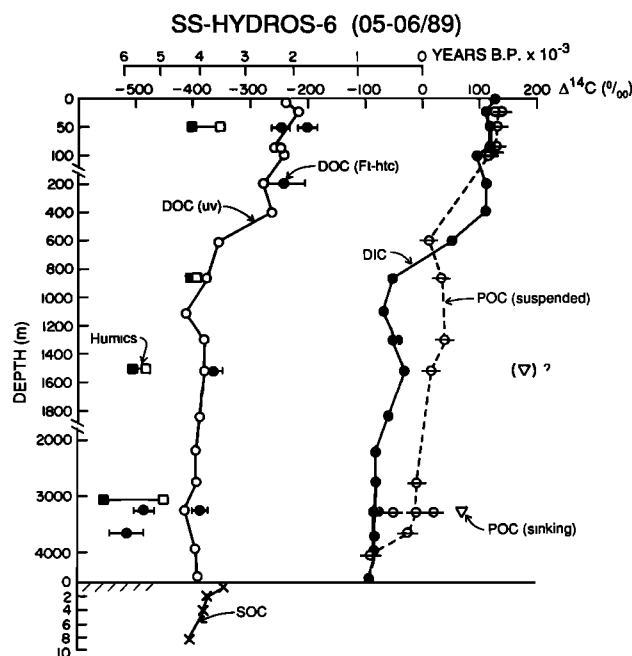
Fig. 2. Δ^{14}C measurements of DOC$_{uv}$, DOC$_{Ft-htc}$, humic materials, suspended POC, sinking POC, DIC and sedimentary organic carbon (SOC) from the Hydros-6 cruise in the SS. Solid squares are XAD-2 isolates and open squares are XAD-4 isolates. Bars on DOC$_{Ft-htc}$ represent errors of the Δ^{14}C measurements; the error of all other measurements are included in the size of the symbols.

The Δ^{14}C values of DOC$_{Ft-htc}$ for the SS [Bauer et al., 1992a] are listed in Table 4 and shown in Figure 2. There were no significant differences, within experimental error, between DOC$_{uv}$ Δ^{14}C and DOC$_{Ft-htc}$ Δ^{14}C values except at 852 and 3638 m, where the Δ^{14}C values for the DOC$_{Ft-htc}$ were approximately 100‰ lower than for the DOC$_{uv}$.

There is a consistent offset (300–350‰), between the DOC$_{uv}$ and DIC Δ^{14}C profiles (Figure 2). Even the general shapes of the profiles are similar. This parallelism suggests that a common process influences both carbon pools, the most obvious being circulation of the deep water masses. The lower Δ^{14}C values for the DOC$_{uv}$ pool imply that a major fraction of the DOC is recycled within the water column on much longer time scales than the DIC.

The humic substances separated from DOC in seawater by adsorption onto XAD-2, XAD-8 and XAD-4 resins all revealed Δ^{14}C values somewhat lower than the DOC$_{uv}$ at the same depths (Table 6, Figure 2). In most cases the Δ^{14}C value for the XAD-4 extractable humics at a given depth is higher than for the corresponding XAD-2 Δ^{14}C values, which reflects a somewhat "younger" apparent ^{14}C age for the XAD-4 isolates. The XAD-4 fractions also contain much higher nitrogen concentrations and more positive δ^{13}C values (average C/N by wt = 21.0 ± 2.4, $N = 7$; average δ^{13}C = -20.8 ± 0.2‰, $N = 6$) than those for the XAD-2 (C/N = 41.1 ± 3.3, $N = 5$; average δ^{13}C = -22.0 ± 0.1‰, $N = 4$) or the XAD-8 fractions (C/N = 57.0 ± 0.9, $N = 3$; δ^{13}C = -23.0 ± 0.1‰, $N = 2$) (Table 6). Thus the XAD-4 resin appears to be isolating a component of the DOC that is more hydrophilic, younger and contains a higher percentage of marine-derived material than that isolated with either the XAD-2 or XAD-8 resins.
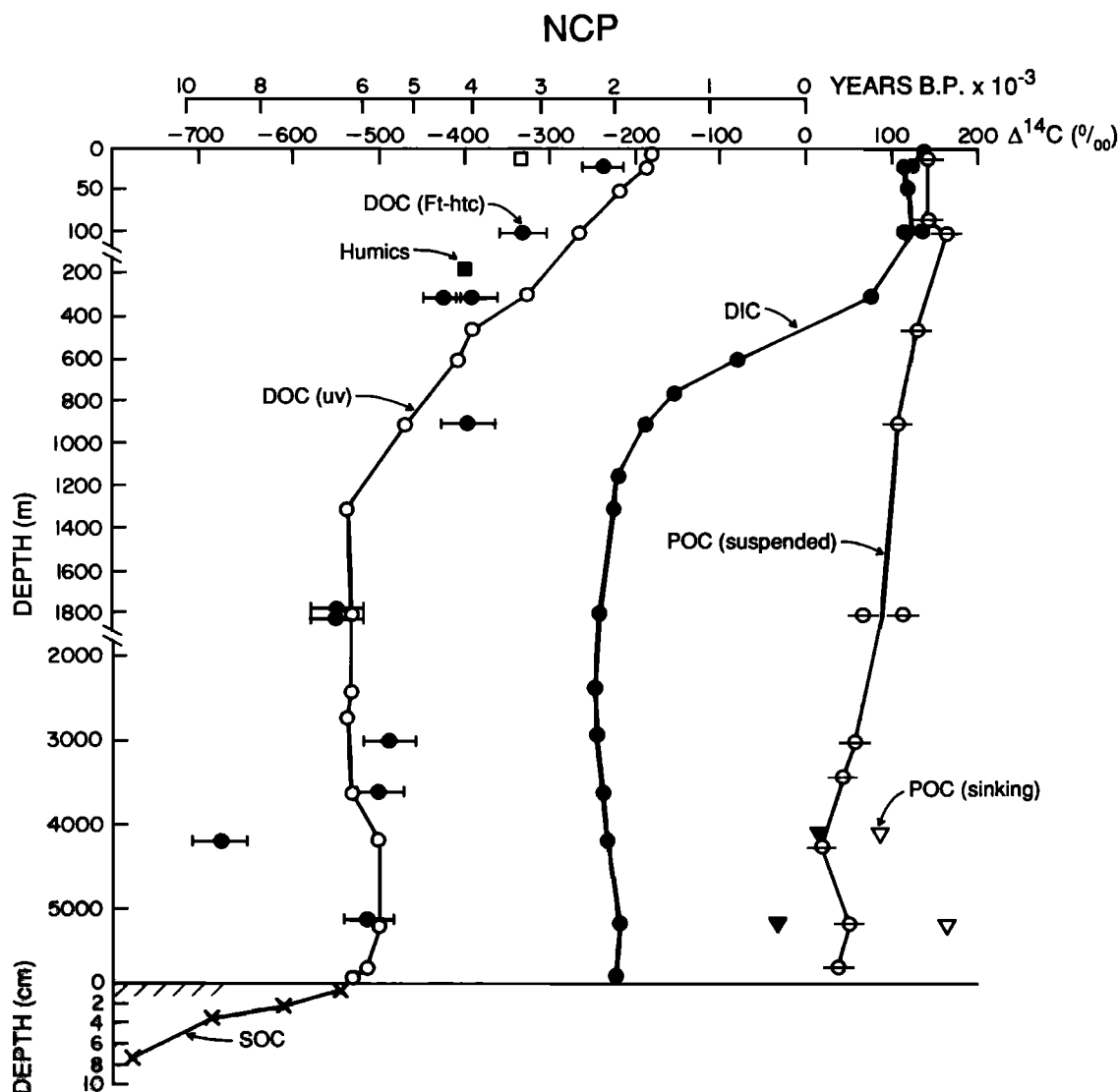
NCP

Fig. 3. Δ^{14}C measurements of DOC$_{uv}$, DOC$_{Ft-htc}$, humic materials (XAD-2), sinking POC, and DIC from the Alcyone-5 cruise in the North Central Pacific (NCP). The suspended POC and SOC Δ^{14}C measurements were from the Eve-1 cruise in the NCP. The Δ^{14}C of humic materials at 180 m were from XAD-2 and -8 isolates collected by Ron Malcolm at a site south of Oahu [*Druffel et al.*, 1989b]. POC(sinking) are represented as solid triangles = Alcyone-5 and open triangles = Eve-1.

In any event, humic substances isolated by adsorption on the XAD resins (2, 4 and 8) represent the more hydrophobic fractions of the DOC in seawater [*Thorn et al.*, 1987]. Polar compounds, e.g., proteins and carbohydrates per se, do not normally adsorb on these resins and hence the humic substances isolated in this work must contain more hydrophobic constituents and less ionizable, polar groups (such as carboxyl and hydroxyl) than would occur with the nonadsorbable DOC. In general, the percentage of humic acids reported for XAD isolates from seawater are <5% of the total humic material isolated, with most of the remainder being fulvic acids [*Thurman*, 1985].

Total yields of humic substances from the SS, their chemical and isotopic properties, and their percentages of the total DOC$_{uv}$ and DOC$_{htc}$ are given in Table 6. These data are derived from XAD-2 followed by XAD-4 isolates from 270-L seawater samples (50, 850, 1100 and 3200 m) and from XAD-8 followed by XAD-4 isolates from 1060-L seawater samples

(50 and 3200 m) samples. The high yields from XAD-4 following XAD-8 compared to XAD-4 following XAD-2 are perplexing. One explanation is material that was not adsorbed by XAD-8 but was collected on XAD-4 was actually adsorbed by the XAD-2 resin and subsequently eluted. This could explain why the two isolates are more N- and ^{13}C-rich than the XAD-8 isolates.

The Δ^{14}C of suspended POC in the SS ranges from values equal to those in surface DIC (118–129‰ in the upper 100 m, $N = 5$) to -92‰ at 4000 m depth (Figure 2, Table 6). All but one of these values are higher than prebomb surface DIC (Δ^{14}C = -50‰), which indicates the presence of bomb ^{14}C throughout the water column. That is, a significant fraction of the suspended POC in the deep SS had formed recently during photosynthetic fixation of DIC in the surface waters.

The Δ^{14}C of sinking POC (Table 5, Figure 2) obtained from a trap deployment at 3200 m was 66 ± 7‰, which is lower than the average Δ^{14}C value for suspended POC in
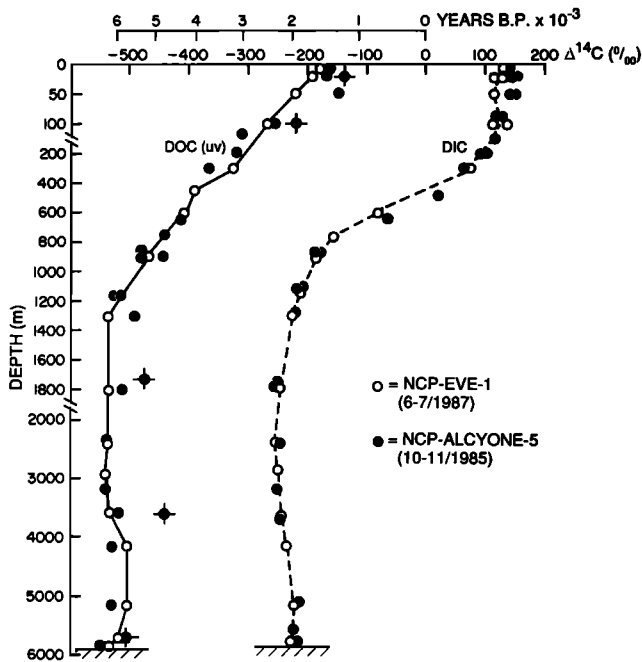
Fig. 4. A comparison of the $\Delta^{14}C$ measurements for DOC_{uv} and DIC from the two cruises (Alcyone-5 and Eve-1) to the same site in the NCP, collected 18 months apart.
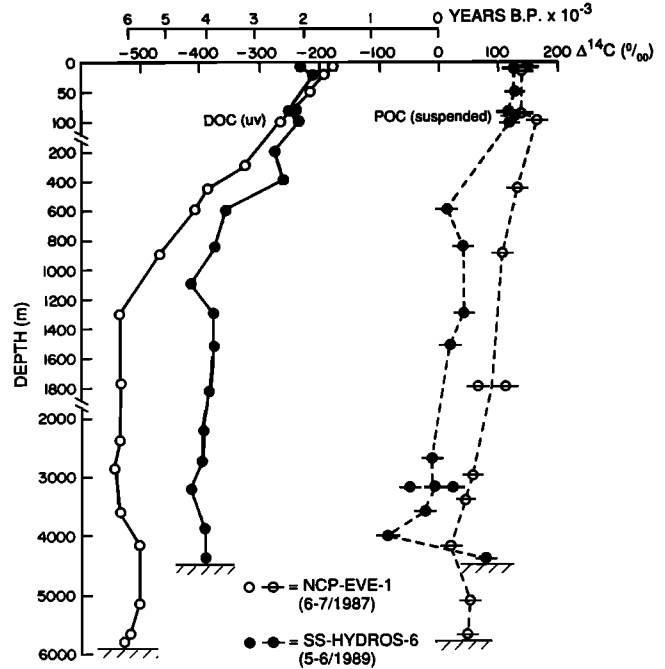

Fig. 6. A comparison of the $\Delta^{14}C$ measurements for DOC_{uv} and suspended POC from the North Atlantic (Hydros-6) and the NCP (Eve-1) sites.

the upper 100 m. POC from a second trap at 1500 m depth revealed a $\Delta^{14}C$ of 179 ± 8‰, which was higher than the surface values. This value may be the result of contamination with tracer levels of ^{14}C during sample collection (R/V *Weatherbird*) and/or subsequent workup.

Thus there must be some process(es) responsible for the incorporation of "old" organic carbon into the suspended, and to a lesser extent into the sinking, POC pools in the SS.

Fig. 5. A comparison of the $\Delta^{14}C$ measurements for DOC_{uv} and DIC from the North Atlantic (Hydros-6, SS) and the North Central Pacific (Eve-1, NCP) sites.

These results illustrate the extensive interactions between different pools of dissolved and particulate organic matter.

3.2. Comparison of SS and NCP $\Delta^{14}C$ Results

A 300‰ difference between DIC and DOC_{uv} $\Delta^{14}C$ values was found for both the NCP [*Williams and Druffel*, 1987] (Figures 3 and 4) and SS deep waters (Figure 5). In both oceans, the DOC_{uv} pool is consistently "older" than the DIC, indicating that DOC is recycled on a longer time scale than DIC. The similarity of the differences between the average deep DOC_{uv} $\Delta^{14}C$ and the average deep DIC $\Delta^{14}C$ values in the Atlantic and Pacific suggests that circulation is a major factor controlling the distribution of DOC in the deep sea. However, small differences in $\Delta^{14}C$ DOC_{uv} between the two oceans may reveal additional sources of young DOC to the Atlantic (see section 4).

The $\Delta^{14}C$ values of suspended POC are indistinguishable from DIC $\Delta^{14}C$ values in the upper 100 m from both the NCP (147 ± 13‰, $N = 3$) and SS (125 ± 7‰, $N = 6$) sites (Figures 2, 3, and 6). However, profiles of $\Delta^{14}C$ in the suspended POC decrease faster with depth in the SS than in the NCP (Figure 6). *Druffel and Williams* [1990] suggested that a source of "old" organic carbon, perhaps DOC, was incorporated into the suspended POC. Seasonal control on the $\Delta^{14}C$ profile of suspended POC is not known; studies are ongoing to determine the influence of flux rate on the $\Delta^{14}C$ values, and hence the degree to which the deep sinking POC is surface derived. It is possible that seasonal changes in the flux rates of sinking POC somehow influence the incorporation of "old" carbon into both the suspended and sinking POC pools.

The $\Delta^{14}C$ values of sinking POC at 4165-m and 5165-m depth at the NCP site during Eve-1 were 99‰ and 136‰, respectively, which are slightly lower than the average surface suspended POC $\Delta^{14}C$ value [*Druffel and Williams*,

1990] (Table 5). The same was true of the sinking POC Δ^{14}C at 3200 m in the SS. Δ^{14}C values for sinking POC collected on the Alcyone-5 cruise during the low flux period (18‰ and -39‰) were significantly lower than those obtained during Eve-1, the high flux period, suggesting that a higher fraction of "old" organic carbon was contained within the sinking POC during periods of low flux.

Δ^{14}C values of the total sedimentary organic carbon (SOC, particle plus porewater fractions) in a gravity core taken at Station DW in the SS (bottom depth = 4460 m) were -346 ± 6‰ (0-0.5 cm), -372 ± 8‰ (1.2-2 cm), -380 ± 5‰ (3-4 cm) and -411 ± 5‰ (7-8 cm) (Figure 2), compared to NCP (Alcyone-5, bottom depth = 5710 m) values of -538 ± 4 (0-1 cm), -607 ± 4‰ (1-2 cm), -686 ± 3 (2-3 cm) and -787 ± 4 (5-7 cm) (Figure 3). The Δ^{14}C values for the DOC_{uv} 50 m above the bottom at these two sites were -391 ± 5‰ (SS) and -546 ± 12‰ (NCP). These close similarities between the Δ^{14}C of surficial SOC and that in the bottom water $DO^{14}C_{uv}$ values, if not fortuitous, suggest that the SOC is either a source or a sink for the bottom water DOC_{uv} or that the seawater-pore water exchange of DOC_{uv} masks other organic ^{14}C signals in the upper sedimentary column.

3.3. Comparison of SS and NCP $\delta^{13}C$ Results

The δ^{13}C profiles for DOC_{uv} from the SS and NCP (Figure 7) are similar, averaging -20.9 ± 0.3‰ ($N = 16$, Hydros-6, surface film and 10-cm results excluded) and -21.2 ± 0.2 ‰ ($N = 11$, Eve-1). The Alcyone-5 values (not illustrated) averaged -21.0 ± 0.3‰ ($N = 24$).

The δ^{13}C values for suspended POC are significantly higher in the SS (by about 1.6‰) than those in the NCP. These data are contraindicative of a larger river contribution to North Atlantic POC, as river-derived material has a much lower δ^{13}C signature (-26 to -28‰) than marine plankton. However, there is an enrichment of about 0.5‰ in DIC δ^{13}C in SS surface waters over those in the NCP
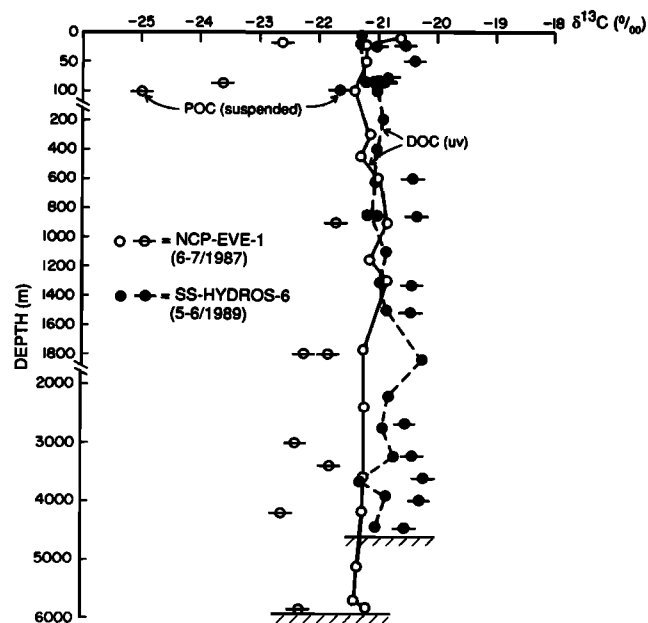

Fig. 7. A comparison of the δ^{13}C measurements for DOC_{uv} and suspended POC from the North Atlantic (Hydros-6) and the NCP (Eve-1) site.

[*Kroopnick*, 1985]. Also, we expect a higher δ^{13}C of plankton formed in the SS surface waters, based on lower equilibrium $CO_{2(aq)}$ concentrations calculated according to the relationship of *Rau et al.* [1991]. It is these fundamental differences, reflected in fixed carbon, that likely impart the difference in the suspended POC δ^{13}C profiles between the two oceans.

A decrease in δ^{13}C of POC observed at the base of the euphotic zone in the NCP was ascribed by *Jeffrey et al.* [1983] as being due to increased remineralization rates, and hence preferential oxidation of the more labile, ^{13}C-enriched organic compounds at the bottom of the pycnocline (~100 m). Since the pycnocline was not well defined below the upper 5- to 10-m isothermal layer at the SS site, the δ^{13}C values did not display a significant minimum in δ^{13}C values.

The suspended POC δ^{13}C data permit limits to be placed on the types of processes that could control the incorporation of old organic matter onto surface POC. Using a mass balance calculation for deep POC δ^{13}C, less than 5% of the suspended POC could have originated via chemosynthetic pathways (e.g., those suggested by *Karl et al.* [1984]), assuming a starting value equal to surface DIC δ^{13}C (0‰) and a fractionation factor in producing organic matter chemosynthetically from DIC of -33‰. The δ^{13}C results support the idea that DOC adsorption/incorporation onto POC is an important process for reducing the Δ^{14}C values with depth due to the similarity of DOC and POC δ^{13}C signatures.

3.4. $[DOC]_{uv}$ and $[DOC]_{htc}$ Results—NCP and SS

Some interesting trends are revealed in the profiles of total DOC concentrations as measured by UV oxidation ($[DOC_{uv}]$) and discrete-injection high-temperature combustion ($[DOC_{htc}]$) (Tables 2 and 4; Figure 8). First, $[DOC_{uv}]$ and $[DOC_{htc}]$ in SS surface waters (66 and 135 μM, respectively) are significantly lower than those concentrations in NCP surface waters (80 and 210 μM). Second, deep SS waters contain higher $[DOC_{uv}]$ (43 ± 1 μM) than those in the deep NCP (36 ± 1 μM, Alcyone-5; 35 ± 1 μM, Eve-1). Third, the average $[DOC_{htc}]$ in the deep waters at both sites is the same (109 ± 2 μM) and is remarkably constant below 1800-m depth. This assumes that these average $[DOC_{htc}]$ values are valid. Thus the fraction of DOC_{htc} that is UV oxidizable is higher in the SS at nearly all depths of the water column (except from 300-700 m) than those in the NCP. These inherent differences suggest that there might be source(s) of DOC to the SS deep water.

The relationship between apparent oxygen utilization (AOU), as determined from in situ measured O_2 subtracted from the corresponding in situ saturated values, and $[DOC_{htc}]$ and $[DOC_{uv}]$ are shown in Figure 9 for each of our sites. Least squares fits of the $[DOC_{uv}]$ versus AOU and $[DOC_{htc}]$ (using Co/CoO) versus AOU for the SS reveal slopes ($d[DOC]/d[AOU]$) of -0.29 and -0.48, respectively [*Bauer et al.*, 1990]. If we assume a Redfield ratio of -0.78 for organic carbon and oxygen utilization (C/-O_2 = 106/136) in the water column [*Redfield et al.*, 1963], then it appears that there is far more oxygen consumption than can be accounted for by DOC utilization throughout the entire water column at the SS site. A similar conclusion is reached with the NCP data, which displayed slopes of 0 and -0.21 at depths greater than 482 m for $d[DOC_{uv}]/d[AOU]$ and $d[DOC_{htc}]/d[AOU]$, respectively [*Druffel et al.*, 1989b].
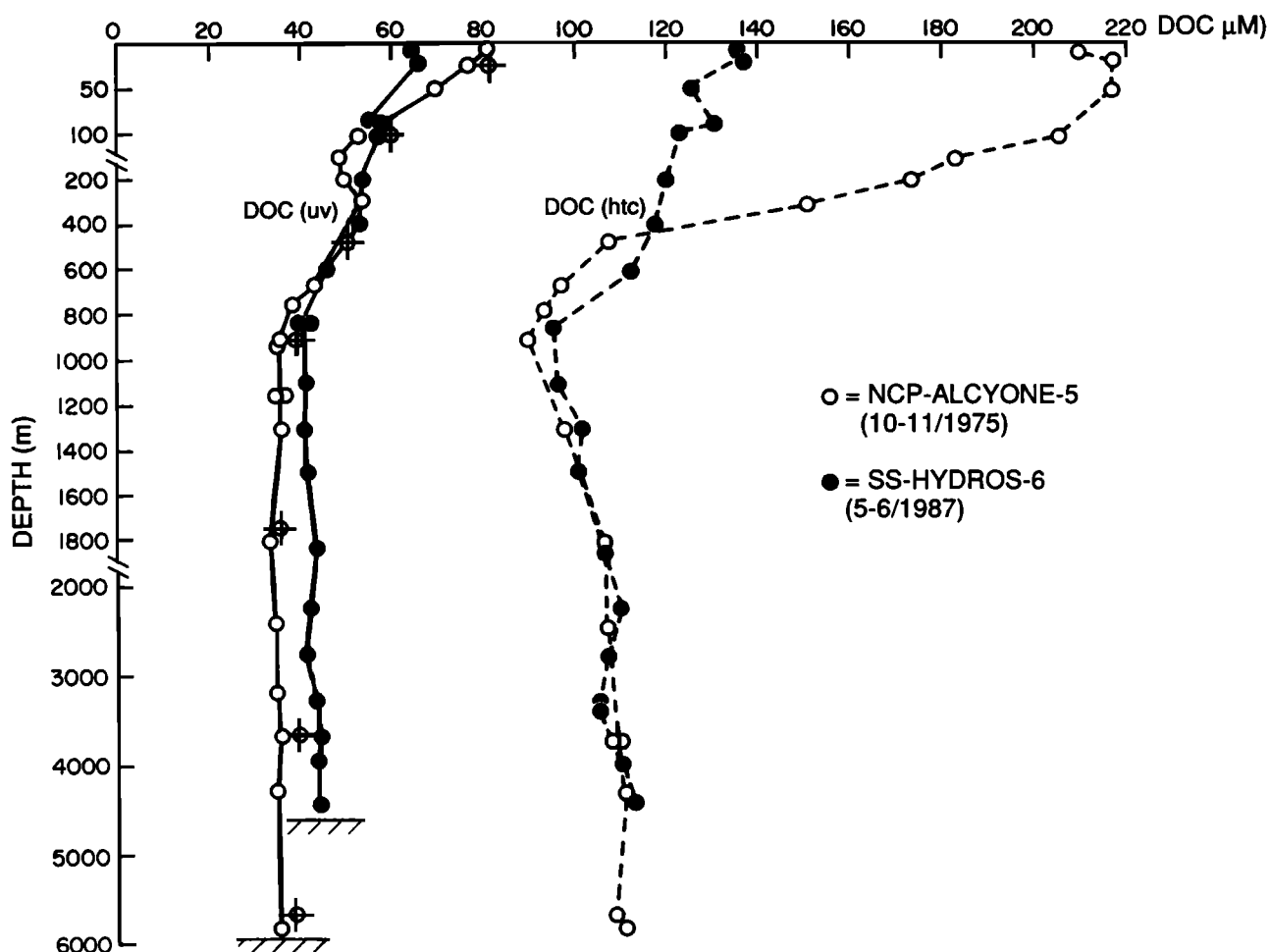
Fig. 8. Concentrations of DOC$_{uv}$ and DOC$_{htc}$ in the SS (Hydros-6) and the NCP (Alcyone-5) water column.

3.5. Organic Constituent Results—NCP and SS

Total (free plus combined) hydrolyzable sugars (TCHO) and amino acids (THAA) (Tables 2-4) measured in NCP and SS waters are plotted in Figure 10. TCHO values in the SS are approximately half those in the NCP. TCHO constitutes about 12 μM of the total 80 μM DOC$_{uv}$ (or 200 μM DOC$_{htc}$) in the NCP surface waters (0-100 m), whereas they comprise only about 6 μM of the total 65 μM DOC$_{uv}$ (or 130 μM DOC$_{htc}$) in the surface SS (0-100 m). In the deep waters, the TCHO values are remarkably constant with depth, constituting about 2.1 μM (4.9% of [DOC$_{uv}$] or 1.9% of [DOC$_{htc}$]) in the SS and about 4.0 μM (11% of [DOC$_{uv}$] of 3.7% of [DOC$_{htc}$]) in the NCP.

The lower TCHO values in the Atlantic are perplexing. Analytical error was unlikely based on repeat analyses of selected NCP samples using the same reagents as used for the SS measurements. Intuitively, one would expect biochemical oxidation of TCHO during the 1500-year transit of deep waters from the Atlantic to the Pacific, a transit which is reflected in lower soluble O$_2$ and higher PO$_4^{3-}$ and NO$_3^-$ concentrations in the Pacific. One explanation is that dissolution of particles occurs with time, slowly increasing [TCHO] as water ages on its way to the Pacific. This presumes that this TCHO fraction is not readily utilized by heterotrophic organisms. Another possibility is that there are more polysaccharides of recent origin in the SS water column that resist hydrolysis and are only slowly hydrolyzed at

depth to the more reactive oligomeric or monomeric material or HCl-hydrolyzable derivatives (J. D. Pakulski and R. Benner, personal communication, 1991). This slow conversion of polymeric to monomeric carbohydrates would result in the higher concentrations of TCHO measured in the "older" NCP deep water.

The profiles of THAA and FAA in the NCP (Figures 10b and 10c) have the same general features as TCHO, with the scatter in the FAA values probably due to the extremely low concentrations measured here in deep water. The DOC equivalent of the THAA in the NCP is 1.8 μM C in the surface waters (0-100) and 0.44 μM C at depth. Thus the sum of the acid-hydrolyzable TCHO plus THAA in the surface and deep waters of the NCP represents 17% and 12% of the DOC$_{uv}$ and 7% and 4% of the DOC$_{htc}$, respectively.

The contribution of TCHO plus THAA in the NCP and TCHO in the SS (THAA analyses for the SS were suspect) to the various DOC pools is best seen in Figure 12, keeping in mind that both TCHO and THAA values may be minimum concentrations.

4. THE CYCLING OF ORGANIC MATTER IN THE WATER COLUMN

4.1. Other Sources of Organic Carbon

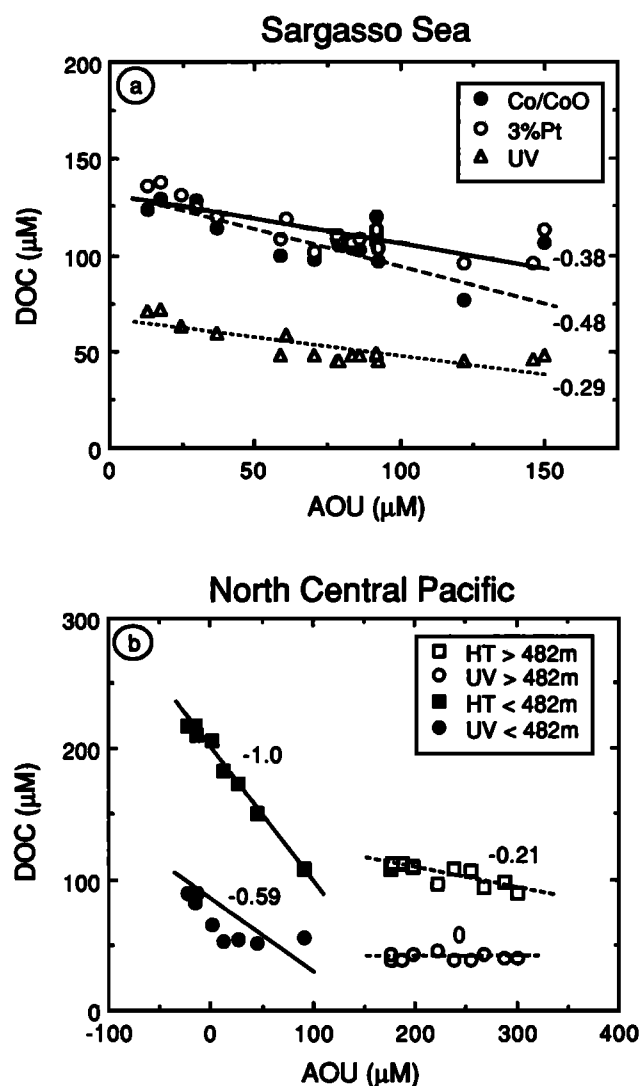In the following discussion we assume that the major source of organic carbon to the water column is directly

Sargasso Sea

North Central Pacific

Fig. 9. AOU (micromoles) versus DOC_{htc} and DOC_{uv} (micromoles) in the (a) SS and (b) NCP. Negative numbers are the slopes of the best fit lines obtained from least squares regressions of the data.

and/or indirectly from primary production of organic matter by photoautotrophs in the euphotic zone. This assumption is subject to an unknown degree of uncertainty, as some of the possible sources of organic carbon are not well quantified. For instance, atmospheric deposition could be a significant contributor of organic carbon to the ocean, yet measurements are scarce. An estimate of annual organic carbon flux derived from wet and dry deposition measurements reported by Zafiriou et al. [1985] for Enewetak was 0.63 g $C/m^2/yr$. This value is of the same order as the flux of organic carbon to the deep sea (4200- to 5200-m depth) in the NCP (0.3-0.6 g $C/m^2/yr$) [Smith, 1987]. From samples of atmospheric particle matter collected at Enewetak and the North Atlantic, Chesselet et al. [1981] concluded that about 80% of the POC was found on the smallest particles (radius <0.5 μm), and that the $\delta^{13}C$ of this fraction was -26 ± 2‰, representative of terrestrially derived material. These studies indicate that the contribution of terrestrial carbon to the deep-sea flux could be significant and could alter the perception that carbon in the oceanic water column is entirely of marine origin.

Estimates of DOC input via rivers to the global ocean span a factor of 10 [Duce and Duursma, 1977; Richey, 1981; Meybeck, 1982]. An estimate of the importance of this source to the oceanic organic carbon pool can be made by calculating the flux of organic carbon needed to maintain the present oceanic DOC reservoir. DOC derived from riverine sources is apparently postbomb, or, for example, $\Delta^{14}C = 100\text{-}200‰$ from the Amazon [Hedges et al., 1986]; the average seawater DOC_{htc} $\Delta^{14}C$ value (mean of Atlantic and Pacific results) is -450‰, or has an apparent ^{14}C age of 4800 years B.P. If we assume that the oceanic DOC reservoir size is 1.7×10^{18} g C (assuming the DOC_{htc} values are valid), a riverine flux of 3.5×10^{14} g C/yr ($1.7 \times 10^{18}/4800$) into the ocean would be required solely to maintain the oceanic DOC reservoir. This estimate is about twice the average of global river DOC input estimates made by a number of authors [Duce and Duursma, 1977; Williams, 1975; Mopper and Degens, 1978; Meybeck, 1982]. The low magnitude of this flux, coupled with the marine like $\delta^{13}C$ values reported for DOC [Williams and Gordon, 1970; Williams and Druffel, 1987; Bauer et al., 1991] and the low or unmeasurable amounts of lignin oxidation products found in humic extracts in the Pacific [Meyers-Schulte and Hedges, 1986] and Atlantic (J. Ertel, unpublished data from Hydros-6 isolates, 1989), suggest that the bulk of organic matter in the ocean is derived from marine sources. We have assumed that lignin phenols are a conservative tracer for riverine DOC, although the lignin signal can be lost in surface water by photochemical reactions [Ertel, 1990].

The degree to which sediments and associated pore waters contribute to organic matter in the water column is largely unknown. Maxima in porewater DOC_{htc} profiles have been observed near the sediment-water interface in cores from the slope [Martin and McCorkle, 1990] and from abyssal depths for DOC measured by persulfate oxidation [Heggie et al., 1987] and by high-temperature catalytic oxidation (J. Bauer et al., manuscript in preparation, 1992), indicative of a net flux of DOC into bottom waters from the sediment. However, the dearth of data makes it impossible to quantitatively assess the contribution of sediment-derived DOC to the oceanic water column on a global basis.

Mopper et al. [1991, 1992] find that fluorescence measurements and amino acid enantiomeric ratios in sediment pore water are similar to those same fingerprints in deep-sea humic substances, suggesting a SOC source for the DOC, assuming it is not the DOC fingerprinting the SOC. There are also some measurements of DOC_{htc}, THAA and TCHO from 48-hour deployments of benthic chambers [Jahnke, 1990] in the Santa Monica Basin (P. M. Williams, unpublished results, 1988). No significant increases in DOC_{htc}, THAA or TCHO were found in filtered (GF/F) aliquots sampled approximately every 10 hours using automated syringes. It is risky, however, to extrapolate these basin results to open-ocean sedimentary regimes.

Other potentially important sources of carbon to the water column include carbon advected laterally from locations remote to the sampling sites, such as continental slopes [Walsh, 1991], the Antarctic Convergence, and hydrothermal vents and seeps. At this time, sparse data ($[DOC_{uv}]$ or $[DOC_{htc}]$) from these areas make an assessment of the magnitude of these contributions impossible. Thus we are restricted in our view of the cycling of organic matter to an ocean that mixes in one dimension.
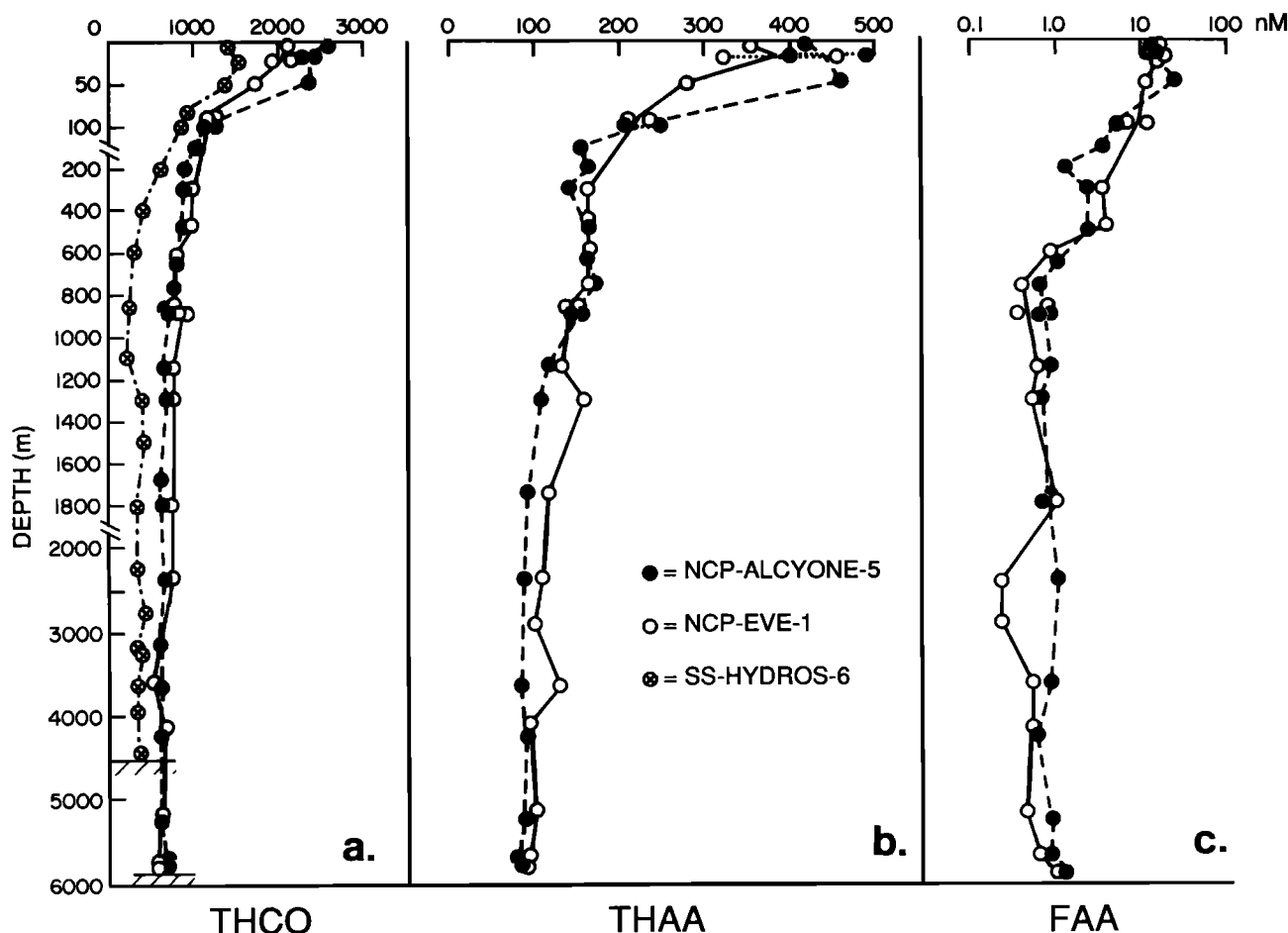
Fig. 10. Concentrations (in nanomoles) of (a) TCHO, (b) THAA, and (c) FAA in samples from the SS and NCP sites. The conversion factor for amino acids to carbon equivalents is 4.4 times the FAA and THAA concentrations, and for the carbohydrates, this factor is 6 times the glucose equivalents.

4.2. Sources of Old Carbon to the POC Pool

Though suspended POC is 10–30 times lower in concentration than DOC in the surface ocean (Figure 11), it must be an important precursor for the high ^{14}C activity DOC in the water column. The much higher Δ^{14}C values found for POC than for DOC (Figure 6) reflect the predominence of bomb ^{14}C in the suspended POC pool and indicates a much shorter turnover time.

However, decreases of suspended and, to a lesser extent, sinking POC Δ^{14}C with depth observed in both the SS and NCP are not commensurate with commonly held dogma about particle cycling. If POC is derived from the surface ocean (and hence is imparted with surface DIC Δ^{14}C signatures), and has turnover times of 5–10 years (or less) for the suspended POC fraction [Bacon and Anderson, 1982], and weeks to months turnover times for the corresponding sinking POC fraction [Deuser et al., 1988; Honjo, 1984; Alldredge and Silver, 1988], we would expect the Δ^{14}C of both suspended and sinking POC to have post-1970 values (> +120‰) [Druffel, 1987, 1989] throughout the water column.

Instead, we observe gradients in suspended POC Δ^{14}C from surface to 50 m above bottom of 220‰ in the SS and 100‰ in the NCP (Figure 6). These trends indicate that there is a source of "old," or low-Δ^{14}C, organic carbon into

the POC pools of both oceans. It appears that "old" organic matter is incorporated to a greater extent into the deep suspended POC of the SS. A likely source of "old" carbon is the incorporation of "old" DOC onto POC by heterotrophic bacterial uptake on particles and/or by physical adsorption. Secondary processes which could result in lowered ^{14}C activities in the suspended POC pool may include heterotrophic uptake of in situ, low-activity DIC by bacteria [Paerl, 1978] and/or by anapleurotic carboxylations or chemoautotrophic fixation [Karl et al., 1984; Rau et al., 1986, 1991], and resuspension of "old" sedimentary organic carbon.

The fact that the deep carbon flux of organic carbon to the SS [Deuser, 1986] is higher than that in the NCP [Smith, 1987] could affect the suspended Δ^{14}C POC profiles in the two oceans in the following way. If an increased carbon flux supported a more active bacterial population, then this might result in a higher utilization of the more labile, supposedly ^{14}C-enriched fraction of the sinking and suspended POC.

However, we do not know how dependent the deep POC (suspended or sinking) Δ^{14}C values are on flux rate, which varies according to season at both the SS and NCP sites. It appears possible from our few NCP trap data that predominantly surface-derived material (with high Δ^{14}C) falls to the deep sea during high flux, and that relatively more deep-derived "older" material falls during periods of low
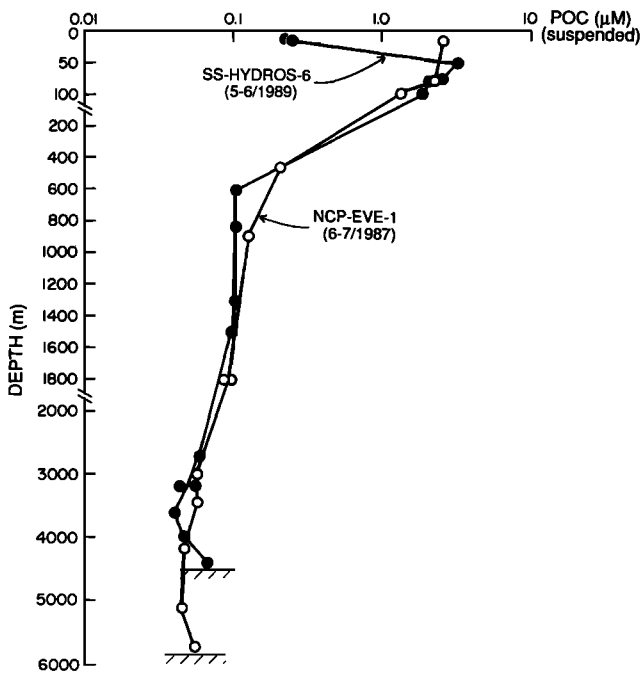
Fig. 11. Concentrations of suspended POC (micromoles) (on a log scale) in samples obtained by in situ filtration aboard the Eve-1 and Hydros-6 cruises.

flux. This was observed with ^{228}Th fluxes as reported by *Murname et al.* [1990]. Biological processes at mid depths presumably change according to flux rates and it is likely that some of the processes responsible for recycling of POC are also dependent on flux rate.

4.3. Mass Balance Calculations

The amounts of humic substances isolated from seawater (from the XAD-2 plus XAD-4 or XAD-8 plus XAD-4 resins) represent a nearly constant percentage of the DOC throughout the SS water column (Table 6), constituting an average of 25% of the DOC_{uv} and 11% of the DOC_{htc} (or 35 and 16% for the XAD-8 plus XAD-4 isolates). This consistency gives important insight into the origin of these humic substances in SS surface waters when considering their $\Delta^{14}C$ values and the contribution of the identifiable constituents (TCHO, THAA). If the deep-water humic substances at a concentration of 10 μM are recycled and are present in this concentration in surface waters, then there must be a source of 5 μM additional humic substances in the surface waters to account for their constant percentage of the DOC.

Viewing this as a simple, two-component system, we can imagine a background concentration (10 μM) of old humic material with a $\Delta^{14}C$ of -490‰ throughout the SS water column. In order to obtain an average $\Delta^{14}C$ of -380‰ for humics at 50-m depth, a mass balance calculation reveals that the additional 5-μM humics present in the surface waters would have an average $\Delta^{14}C = -160‰$. This additional humics pool would be considerably younger than the bulk humics, and would contain a fraction of newer carbon which presumably originates in the surface ocean from a combination of recycled DOC_{uv} plus recently synthesized DOC.

Extending this simple model to calculate the $\Delta^{14}C$ of the total DOC_{uv} in the surface ocean, we assume that DOC_{uv} is composed of recycled DOC_{uv} from the deep-water and

post bomb DOC resulting from recent primary production in the euphotic zone during the past 35 years. If the background DOC_{uv} has a concentration of 43 μM in the SS and a $\Delta^{14}C$ of -390‰(the deep-water value), and the surface DIC has a $\Delta^{14}C$ of +116‰, then the total DOC_{uv} (66 μM) in the surface water would have a calculated $\Delta^{14}C$ value of -214‰(= $\frac{43}{66}(-390) + \frac{23}{66}(116)$). This agrees well with the observed value of -210‰. For the Alcyone NCP cruise, if the background DOC_{uv} has a concentration of 36 μM and a $\Delta^{14}C$ of -525‰, and the surface DIC has a $\Delta^{14}C$ of 147‰, then the total DOC_{uv} (80 μM) in the surface ocean would have a calculated $\Delta^{14}C$ value of -155‰ (= $\frac{36}{80}(-525) + \frac{44}{80}(147)$). Again, this agrees well with the observed value of -153‰. The agreement between the calculated $\Delta^{14}C$ of DOC_{uv} (-237‰) and the observed value (-191‰) is not as close for the Eve-1 cruise to the NCP. The fact that the $\Delta^{14}C$ values for the NCP surface water DOC_{uv} is higher than DOC_{uv} in the SS may be due to higher concentrations of "modern" DOC_{uv} in the Pacific during the sampling periods, coupled with greater mixing downward of surface waters in the SS.

The agreement between calculated and measured DOC_{uv} $\Delta^{14}C$ results is supporting evidence for the theory that the $\Delta^{14}C$ signature of DOC_{uv} in surface waters can be explained by simple mixing of DOC recently produced in the surface waters with DOC recycled from the deep water. The presence of low ^{14}C activity DOC in surface waters supports the theory that DOC_{uv} is being recycled numerous times in the ocean.

We operationally define three pools of DOC in the ocean based on the assumption that total DOC_{htc} concentrations measured by the discrete injection technique are accurate: (1) DOC_{uv} that is present as 32-43% of total DOC_{htc} in deep water, and 26-49% of DOC_{htc} above 1000 m; this fraction most likely includes the THAA plus TCHO and the humic materials; (2) The "extra" DOC measured by Co/CoO flow-through high-temperature catalytic oxidation, which is also old like DOC_{uv} and accounts for an additional 18-44% of total DOC_{htc} in deep waters and 8-46% in surface waters; (3) A residual DOC_{htc} fraction of unknown $\Delta^{14}C$ signature that in the NCP deep water varies from 8% at 900 m (O_2 minimum) to 24% at 5200 m, and in SS deep water varies from 38% at 1510 m to 20% at 3237 m. More variable results were obtained in surface waters. These various pools are illustrated in Figure 12, where the total UV-oxidizable fraction, including TCHO and THAA, the humic fractions and the "unknown" fractions are plotted within the total DOC_{htc} envelope.

4.4. Cycling of DOC in the Deep Oceans

It appears from the great age observed for deep DOC and its relatively constant concentration in the deep SS and NCP that the major processes controlling the cycling of DOC in the oceans are (1) recycling of DOC within the surface and deep ocean and (2) deep-water mass circulation, starting with NADW in the North Atlantic, transiting south through the Antarctic Circumpolar Current, and flowing north into the NCP. Following the calculation made by *Broecker* [1974], we calculate the transit time of DIC between the deep SS ($\Delta^{14}C = -83 \pm 5‰$, apparent ^{14}C age 700 years) and the deep NCP ($\Delta^{14}C = -239 \pm 5‰$, apparent ^{14}C age 2200 years) to have been around 1500 years, assuming a closed
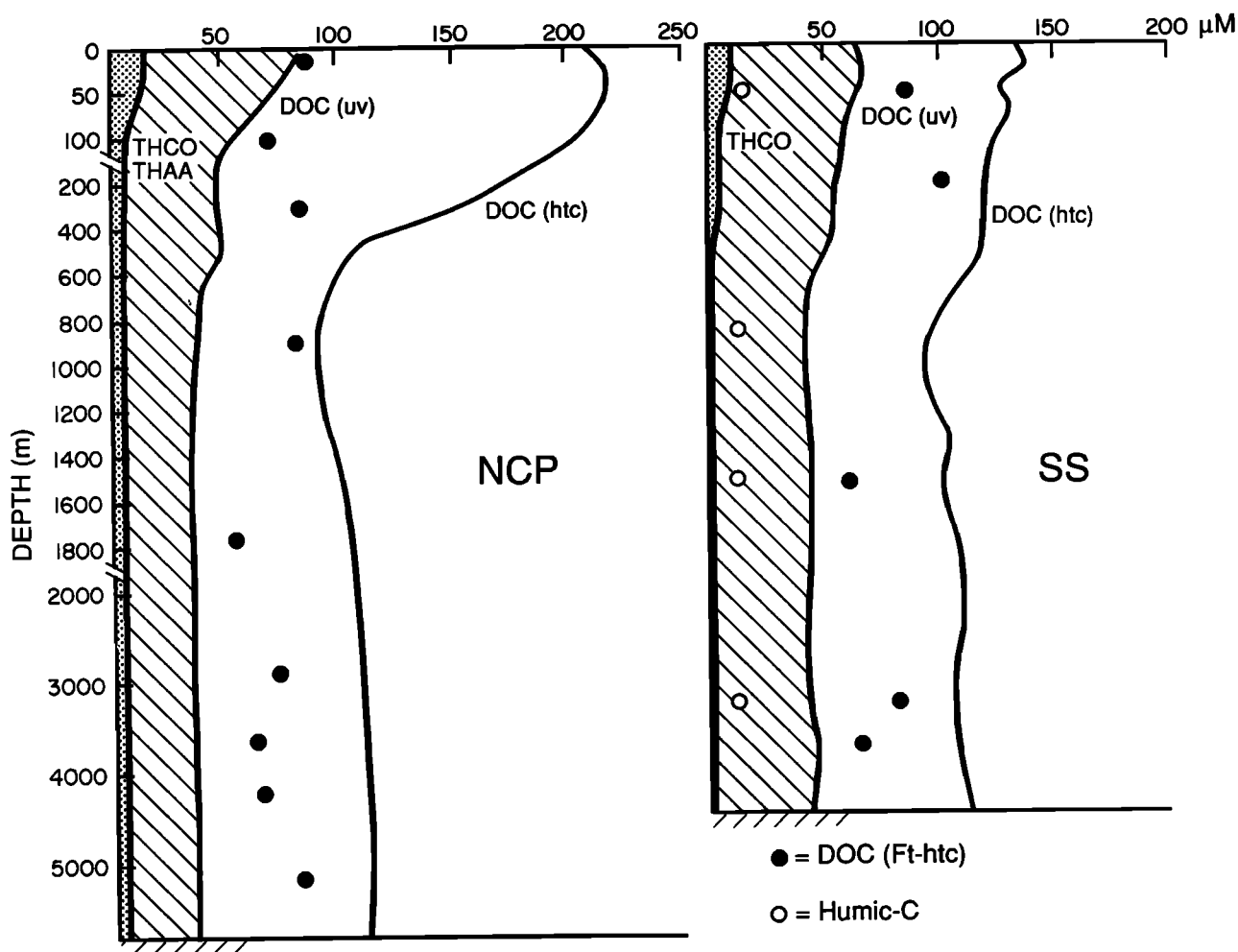
Fig. 12. Concentrations of THAA plus THCO and humic substances (as carbon equivalents), DOC_{uv}, and DOC_{htc} (a) in the NCP (Alcyone-5), and (b) in the SS.

system unaffected by common water formation in the southern ocean [*Stuiver et al.*, 1983; *Broecker*, 1991].

If the DOC_{uv} pool follows the same transport pathway as for the DIC pool, with no DOC_{uv} sources or sinks enroute, then we would expect to see a similar apparent age difference between the two deep DOC_{uv} pools. The actual apparent age difference between the deep SS DOC_{uv} ($\Delta^{14}C = -390 \pm 10\%_o$, 3970 years) and the deep NCP DOC_{uv} ($\Delta^{14}C = -525 \pm 20\%_o$, 5980 years) is 2000 years. This value is close to the apparent age difference between the DIC in both oceans, which indicates that most of the DOC_{uv} is transported with the deep waters of the oceans. Also, its great apparent ^{14}C age is consistent with the idea that a large fraction of the DOC is recycled (over many thousands of years) between surface and deep waters, before being oxidized to CO_2 or otherwise removed from circulation.

To estimate the fraction of DOC that is recycled during each mixing cycle of the world's deep ocean (approximately 1500 years), we use the following $\Delta^{14}C$ balances for the NCP and SS, respectively:

$$\Delta^{14}C_{deep \ NCP} = a \cdot \Delta^{14}C_{NCP \ Recycled} + y \cdot \Delta^{14}C_{NCP \ New} \qquad (1)$$

$$\Delta^{14}C_{deep \ SS} = b \cdot \Delta^{14}C_{SS \ Recycled} + z \cdot \Delta^{14}C_{SS \ New} \qquad (2)$$

$\Delta^{14}C_{deep \ NCP}$ and $\Delta^{14}C_{deep \ SS}$ are the average $\Delta^{14}C$ values in the deep NCP and SS ($-525\%_o$ and $-390\%_o$), a and b are the fractions of recycled DOC in the NCP and SS, y and z are the fractions of new DOC in the NCP and SS (where $a + y = b + z = 1$), $\Delta^{14}C_{NCP \ New}$ and $\Delta^{14}C_{SS \ New}$ are the prebomb $\Delta^{14}C$ values of the new DOC added to the NCP and SS deep waters (assumed to be $-200\%_o$ and $-50\%_o$), and $\Delta^{14}C_{NCP \ Recycled}$ and $\Delta^{14}C_{SS \ Recycled}$ are the $\Delta^{14}C$ values of deep DOC after one mixing time of the deep oceans (1500 years) ($-602\%_o$ and $-490\%_o$), respectively. We assume a steady state for the processes controlling the $\Delta^{14}C$ signature over the mixing time of the oceans. Solving for a and b gives values of 0.81 and 0.77 for the NCP and SS, respectively. This means that approximately 80% of the DOC in each deep-water mass is recycled during each complete circulation cycle, assuming a closed system.

Superimposed on this large-scale cyclical nature of the DOC pools are local processes within each ocean which may impart small but significant differences to the $\Delta^{14}C$ signatures and concentrations of these various pools. For example, mixing processes between surface and deep waters in the SS are much more intense than those in the NCP. The

transit time of NADW, from its formation in the Norweigan and Greenland Seas to $32°N$ latitude in the SS, is of the order of 30 years [*Ostlund and Rooth*, 1990], as illustrated by the presence of bomb ^{14}C in the deep SS by 1989 (Figure 1). Hence there should be a relatively greater amount of higher activity (bomb ^{14}C-tagged) organic matter present in the deep SS than there is in the deep NCP. The end result would be a higher overall $\Delta^{14}C$ value due to the presence of bomb ^{14}C in the deep SS DOC pool.

There are alternative, less satisfactory explanations for introducing high $\Delta^{14}C$ organic matter to the SS that are suggested by the extra DOC_{uv} in the deep SS and by the higher flux rates of sinking POC observed in the deep SS [*Deuser*, 1986; *Smith*, 1987]. The additional 7-μM DOC_{uv} observed in the deep SS may include some "younger" (higher $\Delta^{14}C$) fraction, which would impart a lower age to the DOC pool. The input of DOC from rivers to the Atlantic is 4 times that to the NCP on a per volume basis [*Meybeck*, 1982]. This accounts for an addition of 3.5 μM in 100 years, suggesting the rivers might provide the requisite amount of young DOC (assuming prebomb $\Delta^{14}C = 0‰$) to account for the younger activity of DOC in the deep SS. However, a riverine source is contraindicated by heavier DOC $\delta^{13}C$ ratios in the SS than in the NCP and the lack of chemical or spectroscopic evidence for the presence of appreciable quantities of riverine organic matter in the deep DOC pools.

Another possible source of high $\Delta^{14}C$ organic matter to the SS is indirectly related to the higher fluxes of organic matter from the euphotic zone to the deep sea in the SS as compared to the NCP. The inference is that there is less utilization, relative to the amounts produced, of recently fixed, and hence young, organic matter in the surface waters of the Atlantic as compared to the Pacific. This means that relatively larger quantities of high ^{14}C activity surface-derived organic matter may enter the deep organic matter pool in the SS.

The DOC concentration measurements support the theory of simple DOC cycling between oceans. There is close correspondence between the DOC_{htc}(MRI—Meteorological Research Institute) concentrations in the deep water (>1800 m) of the SS (109 ± 2 μM) and central NCP (109 ± 2 μM) (Tables 2 and 4, Figure 8). Assuming that these similar high concentrations prove to be valid, this suggests that the additional 7 μM DOC_{uv} in the SS may be altered enroute to the NCP, and replaced with an equal amount of DOC oxidized only by high-temperature catalytic oxidation methods. Oxidation of the extra 7-μM DOC_{uv} in transit to the Pacific could result in increased concentrations of carboxylic acid-type compounds that are known to be among the most resistant to free radical attack such as occurs with UV and persulphate wet combustions [*Peyton*, 1992].

All fractions of DOC that we have measured, including DOC_{uv}, humic material and a portion of the DOC_{htc}, have mean ages essentially identical to each other. Therefore we conclude that a large part of each of these fractions are old and have a similar origin, and that they compose, in effect, a very old background of organic matter which resists in situ oxidation, chemical or biochemical. Superimposed on this old fraction may be a more reactive, younger DOC component, particularly in the upper 500 m of the water column, which recycles on faster time scales than we measure here. It is this fraction which may correlate with AOU. Nevertheless, it is obvious that the bulk of the DOC does not control AOU directly at these two oligotrophic ocean sites.

4.5. Deep-Sea DOC and Photosynthetically Fixed Carbon

Assuming a steady state concentration of DOC and no terrestrial, riverine or atmospheric inputs, the amount of photosynthetically fixed carbon that enters the deep sea as DOC and is concurrently oxidized completely to CO_2 can be estimated from the mean apparent age of the DOC pools in the NCP and SS. At 40 μM of DOC_{uv} or 110 μM of DOC_{htc}, the total reservoirs of DOC_{uv} and DOC_{htc} in the deep sea (vol = 1.3×10^{21} L for 300–4100 m depth) [*Sverdrup et al.*, 1942] are about 6×10^{17} and 17×10^{17} g, respectively. Taking the apparent age (B.P.) of these DOC pools as 5000 years (mean of 6000 years for the NCP and 4000 years for the SS), gives DOC replenishment rates of $\sim 1.2 \times 10^{14}$ g yr^{-1} for DOC_{uv} and $\sim 3.4 \times 10^{14}$ g yr^{-1} for DOC_{htc}. If we then assume a total global primary production (PP_t) rate of 100×10^{15} g yr^{-1} (estimates range from $\sim 30 \times 10^{15}$ to $>150 \times 10^{15}$ g yr^{-1}) [e.g., *Berger et al.*, 1987; *Martin et al.*, 1987; *Jenkins*, 1982; *Laws et al.*, 1989], and that new production (PP_n) is of the order of 20% of PP_t (6–30%) [*Eppley and Peterson*, 1979; *Martin et al.*, 1987; *Pace et al.*, 1987; *Laws et al.*, 1989], or 20×10^{15} g C/yr^{-1}, then the steady state input of DOC represents 0.12% of PP_t and 0.6% of PP_n for DOC_{uv}, and 0.34% of PP_t and 1.7% of PP_n for DOC_{htc}.

For comparison, these inputs are about 2 to 10 times lower than the average amount of primary production (as organic carbon) that sinks to the seafloor annually (0.5 to 3%) [*Berger et al.*, 1987; *Deuser and Ross*, 1980; *Martin et al.*, 1987; *Smith*, 1992] and probably correspond more closely to the organic carbon permanently buried in marine sediments (of the order of 0.1% of the PP_t) [*Hinga et al.*, 1979; *Smith*, 1992].

Dissolution and solubilization of sinking POC as it falls through the deep-water column in the NCP (1000–5800 m) and SS (1000–4500 m) oligotrophic gyres could supply the requisite DOC to replace that oxidized during the 6000- and 4000-year residence times of DOC in the NCP and SS, respectively. For the NCP, a m^2-section from 1000 to 5800 m contains 2.1×10^3 g of DOC_{uv} (at 36 μmoles L^{-1}) and 6.3×10^3 g of DOC_{htc} (at 110 μmoles L^{-1}). The corresponding DOC replenishment rates for a 6000-year residence time are 0.35 g C/yr^{-1} (~ 1 mg C d^{-1} for DOC_{uv}), and 1.1 g C/yr^{-1} (~ 3 mg C d^{-1}) for DOC_{htc}. At a sinking rate of 50 m d^{-1} for POC (estimates vary from 30 to >150 m d^{-1}) [*Smith*, 1987; *McCave*, 1975; *Karl et al.*, 1988; *Deuser et al.*, 1981], it would take 96 days for sinking particles to fall from 1000 to 5800 m, and thus the differences in POC fluxes between 1000 and 5800 m needed to replenish the DOC (in mg C m^{-2} d^{-1}) would be 26% ($\frac{96}{365}$) of the experimentally measured values. In effect, to supply 1 mg C d^{-1} (DOC_{uv}) or 3 mg C d^{-1} (DOC_{htc}) would require flux differences of 0.26 mg C m^{-2} d^{-1} and 0.78 mg C m^{-2} d^{-1}, respectively.

These are realistic flux gradients based on extrapolations of *Martin et al.* [1987] for flux measurements in the upper 2000 m of the NCP. There are, however, no data for organic carbon flux measurements taken concurrently at ~ 1000 m and ~ 5800 m. The fact that the requisite DOC inputs can be attributed to flux differences does not take into consideration other DOC sources to the deep-water DOC pool, namely, mixing or advection of surface water DOC into the deep ocean, diffusion of DOC from the sediments into the overlying water, and solubilization of suspended POC.

The corresponding flux gradients required for the SS (assuming $DOC_{uv} = 43$ μmoles L^{-1}, $DOC_{htc} = 110$ μmoles

L^{-1}, apparent age of DOC = 4000 years B.P., depth range = 1000–4500 m), assuming a sinking rate of 50 m d^{-1}, are essentially the same as those calculated for the NCP. It would require flux differences of 0.23 mg C m^{-2} d^{-1} to replenish the DOC_{uv} that is completely oxidized each year (0.45 g) and 0.58 mg C m^{-2} d^{-1} to replenish the DOC_{htc} oxidized each year (1.1 g). As in the NCP, there are no data for flux measurements made concurrently at ~1000 m and ~4500 m. There is also the problem of horizontal transport of particles through the water column near the SS site as described by *Deuser et al.* [1991].

5. CONCLUSIONS

In our study of the organic matter in the oligotrophic NCP and SS, we have determined that most of the deep DOC has an average apparent ^{14}C age of 4000 (SS) to 6000 (NCP) years B.P. This reflects a recycling of about 80% of the deep DOC during each deep ocean mixing cycle assuming a closed system. The apparent ages of the fractions (DOC_{uv}, DOC_{Ft-htc}, humic materials) within an oceanic water column appear to reveal the same general values. There appears to be a significant amount of bomb ^{14}C in the deep SS DOC pool, since the values there are slightly higher than those expected from deep circulation only. Most of the DOC in the oceans at our two sites shows little correspondence with AOU, but this does not negate the possibility that a more reactive, younger fraction of DOC exists that is oxidizable only by discrete injection high-temperature catalytic oxidation and recycles on shorter time scales than in the DOC pools measured here.

To learn more about the origin and cycling of DOC in the oceanic water column, the following information is imperative: (1) characterization on a molecular level of the remaining 80–90% of DOC in seawater, including their isotopic signatures where possible, and (2) seasonal studies of suspended and sinking POC (including marine snow), to determine the origin of particles (whether surface or deep) in the water column.

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