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Isotopic signatures $(^{14}C, ^{13}C, ^{15}N)$ as tracers of sources and cycling **of soluble and particulate organic matter in the Santa Monica Basin, California**

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Abstract - Measurements of $\Delta^{14}C$, $\delta^{13}C$ and $\delta^{15}N$ are reported for dissolved (plus colloidal), suspended and sinking particulate, and total sedimentary organic matter in the Santa Monica Basin (mid-basin and shelf sites) on CaBS cruises 1, 3, 4, 7, 8 and 10. These isotopic signatures were indicative of the following processes occurring within the basin regime: (1) terrestrial inputs of organic matter to the sinking and suspended particulate organic matter were of the order of 10% or less, and as high as 25% for the sedimentary organic matter; (2) Δ^{14} C values of the UV-oxidizable dissolved organic matter below 5m were similar to those measured in open ocean waters, while the Δ^{14} C values in the suspended, and, to a lesser degree, in the sinking organic matter decreased markedly with depth. This latter decrease was primarily attributed to episodic resuspension of shelf and slope sedimentary organic matter, and secondarily to natural and/or anthropogenic petroleum inputs; and (3) the isotopic signatures of the UV-oxidizable dissolved organic matter, coupled with total dissolved carbon and amino acid and carbohydrate concentrations were strikingly similar in the deep basin and at an open-ocean site, suggesting a common history for the subsurface $(>300_m)$ and deep water at both sites.

In addition, total mass and organic carbon and nitrogen fluxes from five particle trap deployments are described in detail. Mass fluxes increased with depth, especially on the shelf, suggesting that particle input from the basin slopes may reach the mid-basin site.

We conclude that there is minimal perturbation of all organic phases in the basin from terrestrial sources, and that the properties of the UV-oxidizable dissolved organic matter are not greatly influenced by particles of local origin.

CONTENTS

1. INTRODUCTION

The principal goal of the California Basin Study (CABS) is to delineate the sources, transformation, dispersal and ultimate fate of particulate organic particles derived from marine and terrestrial sources. An understanding of particle dynamics is essential in predicting the impact of energy-derived, possibly deleterious, substances on the southern California borderland regime. Inherent in understanding particle dynamics are concurrent studies on all organic phases in the basin system. This includes sinking and suspended particulate, dissolved (plus colloidal), and sedimentary organic matter. Especially important are transformations between these phases.

This report focuses on the use of multiple isotopic signatures $(^{14}C, ^{13}C, ^{15}N)$ to trace the origin **and cycling of organic phases in the Santa Monica-San Pedro basin system.**

Radiocarbon (14C) is derived from two sources: natural cosmogenic production in the stratosphere, and atmospheric bomb production during the late 1950s and early 1960s. The high levels of ¹⁴C in surface dissolved inorganic carbon (DIC) subsequent to 1960 (NYDAL, LOVESETH **and SKOGSETH, 1980) result in organic matter produced in surface waters during photosynthesis** also containing high levels of ¹⁴C ($\Delta^{14}C^*$ = +50 to +150%). Thus, surface-derived organic matter **photosynthetically-fixed since 1957, and found in sub-surface waters and in the sediments,** contains bomb ¹⁴C. Lower levels of ¹⁴C (Δ ¹⁴C<-75%) indicate pre-bomb levels (BERGER, **TAYLOR and LIBBY, 1966; ROBINSON and THOMPSON, 1981), which in turn, suggests a minimal** turnover of carbon in the past 35 years. Thus, ^{14}C is useful as both a long and short-term tracer because of the natural and bomb-produced components, respectively. The high '4C activity of recently synthesized (<35y) terrestrial organic matter ($\Delta^{14}C \approx +200\%$) can also be reflected in marine organic phases impacted from terrestrial (and/or atmospheric) sources.

Carbon-13 (δ^{13} C)^a in conjunction with nitrogen-15 (δ^{15} N)^a signatures reflect both the origin and fractionation of organic matter as it flows through ecosystems and undergoes phase transformations. Measurements of both $\delta^{13}C$ and $\delta^{15}N$ on the same organic components are obligatory in sorting out organic matter cycles because of the wide spread in the $\delta^{13}C$ and $\delta^{15}N$ signatures for the various terrestrial and marine end-members and within specific trophic levels. Generally speaking, ¹³C isotopic compositions have proven most valuable for delineating dietary sources and less so in following isotopic fractionation along food-chains, while ¹⁵N reflects trophic levels and specific processes such as nitrogen fixation and denitrification and particle transformations (see, for example, FRY and SHERR, 1984; FRY, 1988; ALTABET, 1988).

2.BACKGROUND

Table 1 summarizes previously-published $\Delta^{14}C$, $\delta^{13}C$ and $\delta^{15}N$ values measured in the Southern California Bight regime for various organic pools and end-members which are relevant for interpreting the measurements presented here for the Santa Monica Basin. Some $\delta^{13}C$ and $\delta^{15}N$ data are omitted for the sedimentary column below the upper 0-1cm horizon.

It is evident that $\Delta^{14}C$ values reported to date are sparse for all the organic phases. Few DIC ¹⁴C activities were measured in California coastal waters from 1959 to 1987, and no values are available for sewage or river (storm water) soluble or particulate organic components. Thus it is difficult to rigorously assign $\Delta^{14}C$ values to these important end-members. The $\Delta^{14}C$ measurements of EMERY and BRAY (1962) for sedimentary organic carbon (SOC) are primarily from subsurface samples where surficial $\Delta^{14}C$ values represent extrapolations. Nonetheless, these numbers are valuable in that they represent pre-bomb activities.

There are no reported measurements of $\delta^{15}N$ in dissolved organic nitrogen (DON) - off southern California or anywhere else owing to the difficulty of performing such measurements - and only a few results for suspended particulate organic matter (POM) at a location seaward of the Southern California Bight (SAINO and HATTORI, 1987). There are, however, some δ^{13} C and δ^{15} N measurements which can be used to assign limits to the relevant end-member values necessary for estimating marine versus terrestrial contributions to the Santa Monica mid-basin organic phases.

^a Δ^{14} C (per mil deviation from the ¹⁴C activity of 19th century wood) = δ^{14} C $\%$ - $2[\delta^{13}C(\%)]$ + 25.0] $[1 + \delta^{14}C (\frac{\gamma}{\infty}) 10^{-3}]$; where the Age (BP) = 8033 ln $[1 + \Delta^{14}C 10^{-3}]^{-1}$, and $\delta^{13}C (\frac{\gamma}{\infty}) = [(1^3C)^{12}C)_{\text{max}}]$ \cdot (13 C/¹²C)_{poB}] / (13 C/¹²C)_{poB} x 10³. All Δ ¹⁴C values are corrected for: δ ¹³C of the sample, age to 1950AD (STUIVER and POLACH, 1977), and relevant blanks for quartz filters and/or combustion tubes. $\delta^{15}N$ ($\degree/_{\infty}$) = [($^{15}N/^{14}N$)_{SAMPLE} - ($^{15}N/^{14}N$)_{Air}] / ($^{15}N/^{14}N$)_{Air} x 10³.

Sources and cycling of matter in the Santa Monica Basin

REFERENCES FOR TABLE 1:

- 1. HUBBS, BIEN and SUESS (1965)
- 2. BIEN, RAKESTRAW and SUESS (1965)
- 3. LINICK (1975)
- 4. OSTLUND and STU1VER (1980)
- 5. E. DRUFFEL (unpublished results)
- 6. MANNING *et al* (1990)
- 7. P.M. WILLIAMS (unpublished results)
- 8. WILLIAMS, McGOWAN and STUIVER(1970)
- 9. EMERY and BRAY (1962)
- 10. LIU and KAPLAN (1989)
- 11. LIU and KAPLAN (1982)
- 12. SWEENEY and KAPLAN (1980a)
- 13. WILLIAMS and GORDON (1970)
- 14. SAINO and HATTORI (1987)
- 15, NELSON *et al* (1987)
- 16. CRISP *et al* (1979)
- 17. MYERS (1974)
- 18. SWEENEY *et al* (1980)
- 19. SWEENEY and KAPLAN (1980b)
- 20. EGANHOUSE (unpublished results, 1988, Personal communication)
- 21. EGANHOUSE (1982)
- 22. EMERY (1960)
- 23. EGANHOUSE and KAPLAN (1988)
- 24. NISSENBAUM and KAPLAN (1972)
- 25. VENKATESAN, BRENNER, RUTH, BONILLA and KAPLAN (1980)
- 26. MULLIN, RAU and EPPLEY (1984)
- 27. *ALTABET* and SMALL (1990)
- 28. SCHIMMELMANN and TEGNER (unpublished results)
- 29. RAU, SWEENEY, KAPLAN, MEARNS and YOUNG (1981)

3. METHODOLOGY

3.1 Sampling

Table 2 lists the cruises, dates and samples taken. Note that all mid-basin and shelf samples are from the same two locations for all cruises. The box core (BC-89, CaBS-1) was taken ~10km southwest of the main mid-basin station.

Dissolved organic carbon (DOC) and DIC were sampled with a new, 12 1 Go-Flo Niskin bottle on CaBS-7 (trace ¹⁴C contaminations of DOC samples from CaBS-4 may have resulted from a "used" 30 1 Niskin). Aliquots for DOC were passed directly from the Niskin through ignited GF/ C glass fiber filters (nominal pore diameter - $1.0 \mu m$) into 1 gallon brown glass bottles and frozen at -20°C. Unfiltered, 500ml samples for DIC were taken initially from the same Niskin bottle by overflowing three successive volumes in a 500ml brown bottle. These samples were preserved with 0.5ml of saturated HgCl, solution and stored at 3° C.

Suspended particulate organic matter was collected using an *in situ* filtration system (WILLIAMS, CARLUCCI and OLSON, 1980) based on an earlier version of LAIRD, JONES and JENTSCH (1967). The current system employs two Pelagic Electronics, sealed *in situ* pumps powered by two marine high-amperage, 12-volt lead-acid batteries to pull seawater through four 142mm diameter Whatman, quartz fiber filters (nominal pore diameter $0.8 \mu m$) pre-ignited at 800 $^{\circ}$ C) held in PVC holders. Flow rates are initially 10-15 l m⁻¹ and total filtration volumes are measured using individual $ARAD[®]$ flowmeters. The pumps are turned on and off at depth with a mechanical timer, and at deployment are filled with distilled water which is displaced by ambient seawater after dissolution of a soluble wafer (Lifesaver). The intake water is prefiltered through 505µm pore diameter nitex netting. Contamination is minimized by coating the supporting framework with heat-cured epoxy resin and using stainless steel hardware. The amounts of seawater filtered per single 142mm filter unit varied from 6501 at 100m to 14401 at depth for 3 to 6h of pumping, respectively. After deployment, each filter pad was folded and frozen at -20 \degree C in cleaned glass jars.

Sinking particles were collected using paired, fiberglass"Soutar" cones, each with an effective mouth opening of $0.062m^2$ (see BRULAND, FRANKS, LANDING and SOUTAR, 1981, for basic trap design). The mouth of each trap was baffled with a cellular grid (lcm x I cm x 4cm deep) to restrict internal water flow and constrain particle capture to the trap mouth. The lucite cod-end collectors (21) were charged with 30g of solid HgCl, in a perforated plastic bottle prior to deployment, and filled with surface seawater at launching. On retrieval, the cod-ends were capped and stored at 3-5°C prior to splitting and processing the sample (usually 1 to 14 days later, depending on cruise duration).

The sediment core (8cm diameter by 28cm length) was subsampled from a Soutar box core (SOUTAR, 1979), capped, and frozen at -20°C (collected by R. JAHNKE).

All of the above shipboard sampling procedures were done on the R/V *New Horizon,* where $14C$ productivity studies were routinely carried out. Thus, it was necessary to rigorously clean the samplers with dilute HC1, methanol and distilled water and to use plastic gloves, etc., when appropriate. No ^{14}C contamination was evident in the $\Delta^{14}C$ results documented in this manuscript.

TABLE 2. Sampling information. POC(sink) and PON(sink) = particulate organic carbon and nitrogen in sediment trap particulates; POC(susp) and PON(susp) = particulate organic carbon and nitrogen in filterable, suspended particles; DOC = soluble plus colloidal organic carbon passing 1 µm pore-diameter glass fiber filters; DIC = dissolved inorganic carbon; and SOC and SON = total organic carbon and nitrogen in dried, acidified sediment samples. Note that bottom depths are $\pm 2m$ and lat./ long. are within 0.2'

3.2 Analyses

DOC was oxidized to CO₂ by high-energy UV irradiation following procedures given in WILLIAMS and GORDON (1970) as modified in DRUFFEL, WILLIAMS, ROBERTSON, GRIFFIN, JULL and DONAHUE (1989). Five litre, thawed seawater samples are acidified to $pH = 2.2 - 2.5$ with H₃PO₄, sparged free of DIC with clean N₂, saturated with O₂, and oxidized for 6h with a 1200W Conrad-Hanovia UV lamp at 70° C. The resultant CO₂ is purified and its ¹⁴C content determined at the NSF-TAMS facility at University of Arizona after conversion to graphite. $\delta^{13}C (\pm 0.1\degree/\infty)$ values for the same DOC were measured on a V.G. Micromass 602E isotope ratio mass spectrometer at the Woods Hole Oceanographic Institution (WHOI).

DIC was collected as CO_2 by acidifying 150ml of the preserved samples with 3 ml of 5% H₂PO₄ (final pH \approx 2.3-2.4) in a CO₂-free closed system. The CO₂ was collected and purified as with the DOC-CO₂. $\Delta^{14}C$ and $\delta^{13}C$ measurements were done at the University of Arizona and WHOI, respectively.

3.3 Suspended, filterable POM [POC (susp) and PON (susp)]

At WHOI the thawed quartz fiber filters were acidified with 5ml of 1% H₃PO₄ and dried *in vacuo* overnight to remove inorganic carbon and water. The filters were then oxidized for 1 h with CuO (wire form) and Ag foil in double quartz tubes at 850°C following the procedure of MINAGAWA, WINTER and KAPLAN (1984). The resultant $CO₂$ derived from the POC (susp) was converted to graphite (JULL, DONAHUE, HATHEWAY, LINICK and TOOLIN, 1986) at the University of Arizona and the $\Delta^{14}C$ and $\delta^{13}C$ values measured at the University of Arizona and WHOI, respectively. $\Delta^{14}C$ values for CO, obtained from all closed tube combustions were corrected for blank CO₂ from the quartz combustion tubes and quartz filters. Blanks composed 0.3 to 5.7% of the sample CO, volumes. Δ^{14} C values of blank CO, samples averaged-480%. δ^{13} C and δ^{15} N values for replicate filters were also measured by D. Winter at the Institute of Geophysics and Planetary Physics, University of California, Los Angeles (UCLA). These latter values are those reported in Tables 3, 4 and 5, where the precision is $\pm 0.1\%$ for both the $\delta^{13}C$ and $\delta^{15}N$ measurements.

3.4 Sinking POM [POC (sink)] and PON [PON(sink)]

Approximately 1200-1500ml of the supernatant liquid in the lucite cod-ends was syphoned off, and the remaining 500-800ml mixed and subsampled for isotope analyses, mass and C and N flux measurements (SIO), and trace organic compounds (M.I. VENKATESAN, UCLA). Aliquots for Δ^{14} C, δ^{13} C, and δ^{15} N analyses were acidified to a stable pH = 1.5-3 to remove carbonates and filtered through 42mm diameter GF/C glass fibre filters using a ~15psi vacuum. The collected solids were briefly rinsed with double-distilled water, dried, and pulverized in a mortar. Portions of these homogenized solids were: (1) oxidized to $CO₂$ at WHOI as for the POC (susp), and the $CO₂$ ¹⁴C content measured at the University of Arizona; and (2) oxidized at UCLA and their $\delta^{13}C$ and $\delta^{15}N$ signatures measured. Additional aliquots of the original cod-end samples were analyzed in duplicate for their total mass (dry weight) by drying at 60° C to constant weight (NELSON, BEERS, EPPLEY, JACKSON, McCARTHY and SOUTAR, 1987) and in duplicate for their CHN content (SHARP, 1974) using either a Hewlett-Packard Model 185B or a Perkin-Elmer Model 2400 CHN analyzer.

The sediment core was extruded from its lucite liner after slightly thawing on the outside, rinsed briefly with double-distilled water, and cut into 1.25cm sections with a hacksaw. The outer edges were trimmed, and the centre portions acidified to $pH = 2.6-3.0$ by titration with successive

portions of 50% H_4PO_4 . These slurries were dried to constant weight at 60°C, pulverized, and aliquots analyzed for $\Delta^{14}C$, $\delta^{13}C$, and $\delta^{15}N$ [as for POC(sink)].

All of the above operations concerned with isotopic measurements were carried out at either the Mt Soledad Radiocarbon Laboratory (SIO) or the WHOI Radiocarbon Laboratory. Both of these facilities are free of ^{14}C contamination.

Cruise		Depth (m)	$\delta^{13}C$ (°/∞)	$\delta^{15}N$ (°/∞)	Δ ¹⁴ C $(\%)$	Age (y, BP)	Σ Organic Carbon $(\mu \text{mol } l^{-1})$
POC(susp), PON(susp)							
$CaBS-4$							
(10/86)	S	100	-23.61	7.74	102 ± 7	post-bomb	0.57
	D	80	-25.27	6.78	110 ± 8		0.50
		510	-22.22	7.60	27 ± 6	44	0.21
		700	-22.56	9.64	-46 ± 6	Ħ.	0.25
		850	-23.08	9.88	9 ± 6	Ħ	0.36
DOC							
CaBS-4							
(10/86)	S	100	-21.83				53
					(Contaminated with traces of		
	D	5	-22.19		¹⁴ C from Niskin bottle)		76
		100	-21.20				52
		500	-21.14				42
		700	-20.86				42
		850	-21.39				42
$CaBS-7$							
(10/87)	S	100	-21.96		-323 ± 5	3135 ± 40	53
	D	5	-21.94		-197 ± 9	1760 ± 70	76
		100	-21.74		-305 ± 8	2920 ± 60	55
		500	$-*$		$-*$		46
		700	-21.92		-475 ± 5	5180 ± 40	45
		850	-21.61		-462 ± 5	4980 ± 40	44
			*sample lost				
DIC							
CaBS-7							
(10/87)	D	5	1.9		94 ± 6		
		500				post-bomb	
			-0.4		-139 ± 5	1200 ± 40	
		850	-0.3		-169 ± 6	1485 ± 50	

TABLE 3. δ¹³C, δ¹⁵N, Δ¹⁴C and total organic carbon data: POC(susp) and PON(susp), DOC, and DIC. Δ^{14} C values are corrected for δ^{13} C and age to 1950 AD, according to STUIVER and POLACH (1977). $S =$ shelf, $D =$ mid-basin

4. RESULTS

Tables 3, 4 and 5 contain the original $\Delta^{14}C$, $\delta^{13}C$ and $\delta^{15}N$ measurements for the dissolved, sinking, suspended, and sedimentary organic phases in the Santa Monica Basin. These same isotopic signatures are plotted in Figs 1,2 and 3. Mass and organic C and N fluxes are contained in Tables 6, 7 and 8, and depicted in Fig.4.

Core depth	$\delta^{13}C$	$\delta^{15}N$	Δ ¹⁴ C	Sedimentation age ¹ Age		
$(\pm 0.05 \text{cm})$	(°/0)	$(\%)$	(°/0)	(y, BP)	(y,AD)	
$0.00 - 1.25$	-22.15	6.37	-10 ± 6	80 ± 50	1974	
$1.25 - 2.50$	-22.62	7.18	-21 ± 6	170 ± 50	1960	
$2.50 - 3.75$	-21.95	7.33			1939	
$3.75 - 5.00$	-22.03	7.84			1911	
$5.00 - 6.25$	-22.26	7.32			1879	
$6.25 - 7.50$	-22.39	6.09	-154 ± 5	1345 ± 40	1847	
$7.50 - 8.75$	-21.82	7.34			1818	
$8.75 - 10.00$	-21.98	6.56			1783	
$12.50 - 13.75$	-21.79	7.11	-307 ± 5	2945 ± 40	1637	
$18.75 - 20.00$	-22.11	6.64	-416 ± 4	4320 ± 30	1343	

TABLE 5. $\delta^{13}C$, $\delta^{15}N$, $\Delta^{14}C$ data and chronologies. Sedimentary (SOC,SON), carbonate-free organic matter subsampled from a Soutar box core, No. BC-89, Cruise CaBS-1, $10/14/85$. Δ^{14} C values are corrected as in Table 4

¹Calculated from cumulative mass (mg cm⁻²)/mass flux (mg cm⁻²y⁻¹) using mass flux = 14. Img cm⁻² y-I for box core no. BC-89 (see HUH *et al,* 1990). Cumulative mass values for 1.25cm sections interpolated graphically from 1.0cm sections measured by HUH, ZAHNLE and SMALL (1986). Ages are mean values for 1.25cm sections \pm 3 years.

4.1 Dissolved organic and inorganic carbon (DOC, DIC)

The ¹⁴C activities in DOC (DO¹⁴C) in surface waters ($\lt 5m$) were -167, -197 and -189°/ ∞ in 1986, 1987 and 1988, respectively (Tables 1 and 3). These $DO^{14}C$ values are 16-46 $\%$ more negative than at 3m in the North Central Pacific ($\Delta^{14}C = -151\%$) in 1985 (WILLIAMS and DRUFFEL, 1987) and reflect the lower $\Delta^{14}C$ values for the corresponding DIC in the same samples. The 14 C values in DIC (DI¹⁴C) at 3-5m in surface waters south of San Diego and in the Santa Monica Basin (Tables 1 and 3) were 109 and 94% on 1980 and 1987, respectively, compared to 140±10% at 3m in the North Central Pacific in 1985 and 1987 (WILLIAMS and DRUFFEL, 1987; DRUFFEL and WILLIAMS, 1990). These lower $DI¹⁴C$ values in the coastal areas probably result from both sporadic upwelling and the shoaling of 100m isopycnal surfaces, resulting in low ^{14}C activity, subsurface DIC reading the surface. This low ¹⁴C activity is then reflected in the carbon fixed by photosynthesis which is the source of suspended and sinking particulate organic matter and, eventually, DOC. The bomb- ^{14}C signal is apparent even in the limited measurements of $DI^{14}C$ from surface waters off Southern California (Tables 1 and 3), where $\Delta^{14}C$ increased from \sim -90 \degree / \sim in 1959 to \sim +140 \degree / \sim in 1969 and then decreased to \sim 90 \degree / \sim in 1987. The corresponding average Δ^{14} C values for atmospheric CO₂ during these same years were approximately 230, 550 and 200‰, respectively, reflecting the bomb inputs in the late 1950s and early 1960s (LEVIN, KROMER, SCHOCH-FISCHER, BRUNS, MUNNICH, BERDAN, VOGEL and MUNNICH, 1985; MAN-NING, LOWE, MELHUISH, SPARKS, WALLACE, BRENNINKMELIER and McGILL, 1990). If we assume that photosynthetically-derived terrestrial inputs to the Southern California borderland have the same ^{14}C activity as atmospheric CO₂, then the $\Delta^{14}C$ values for marine and terrestrial end-members are \sim 90 and \sim 200 \degree /₀, respectively. At the other extreme, petroleum hydrocarbons (seeps, spills, chemicals) will probably contain little or no ^{14}C , resulting in $\Delta^{14}C$ values approaching or equal to -1000%o.

FIG.1. Radiocarbon activities (Δ^{14} C, per mil deviation from the activity of 19th century wood) for UV-oxidizable dissolved organic carbon (DOC; ϕ = mid-basin, \otimes = shelf), suspended particulate organic carbon (POC (susp); $o = mid-basin$, $\bullet = shelf$), sinking particulate organic carbon (POC (sink); Δ , ∇ , \Diamond , $x = mid-basin$, \blacktriangle , ∇ , \blacklozenge = shelf), dissolved inorganic carbon (\blacklozenge = mid-basin), and total sedimentary organic carbon (\blacksquare = mid-basin).

FIG.2. δ^{13} C and δ^{15} N signatures for DOC (\otimes), POC (susp) (\bullet) and POC (sink) (o), Cruise CaBS-4; and total SOC (l), Cruise CaBS-1.

FIG.3. δ^{13} C and δ^{15} N signatures for POC (sink): o = CaBS-3, ∇ = CaBS-4, \bullet = CaBS-7, + = CaBS-8, \otimes = CaBS-10. The heavy dashed lines (- - -) represent mean values.

				Deployment depth (m)					
Cruise		Shelf (395m)				Mid-basin (905-910m)			
	100	200	350	100	200	500	700	850	
CaBS-3 (05/86)									
A	1040		2530	531		603	867	822	
B	944		2830	603		654	633	821	
Mean	992		2680	567		629	750	822	
CaBS-4 (10/86)									
A	485		2410	231		467	613	701	
B	646		2360	253		359	468	457	
Mean	566		2385	242		413	541	579	
CaBS-7 (10/87)				$\pmb{\mathfrak{h}}$					
A		1130	2590		354	564	750	555	
B		1050	2420		432	574	618	527	
Mean		1090	2505		393	569	684	541	
CaBS-8 (02/88)									
A								687	
B								586	
Mean								637	
CaBS-10 (10/88)									
A		1230	2680		497	495	519	545	
B		1120	2920		385	433	456	555	
Mean		1175	2800		441	464	488	550	

TABLE 6. Mass fluxes. Soutar-paired (cones A and B) sediment traps. All values are means of duplicates as mg m^2d^1 dry weight

	CaBS-3 (05/86)		CaBS-4 (10/86)		CaBS-7 (10/87)		$CaBS-10$ (10/88)	
	C	N	$\mathbf C$	N	$\mathbf C$	N	$\mathbf C$	N
Shelf: 100m								
А	83.5	11.7	51.5	7.1				
В	83.0	13.0						
A(AF)	119	19.6	52.2	8.6				
B(AF)	95.0	15.8	79.6	13.3				
200m								
A					97.3	26.3	126	16.8
в					84.1	20.9	111	16.4
A(AF)					85.1	34.8	112	19.5
B(AF) 350m					47.9	15.1	108	17.3
A	165	21.4	89.5	12.7	160	54.5		
B	166	18.7	150	20.2	139	31.2	190	24.0
A(AF)	146	24.4	125	19.4	124	63.6		
B(AF)	139	18.2	111	17.4	80.0	29.5	160	22.6
Mid-Basin: 100m								
A	73.4	11.0	33.8	5.5				
B	77.8	13.8	51.1	8.3				
A(AF)	72.3	12.4	44.9	8.0				
B(AF)	64.3	10.8	44.3	8.0				
200m								
A					68.9	16.2	110	17.9
B					59.8	15.8	74.1	11.8
A(AF)					70.2	32.1	126	22.5
B(AF)					31.7	10.3	51.1	10.2
500m	49.0		49.3					
A B	49.1	5.5 5.5	25.0	5.5 3.1	59.6 48.7	8.4 7.3	69.2 68.0	8.7
A(AF)	45.4	5.9	40.0	5.0	40.8	6.8	48.7	8.9 7.0
		6.9	42.2	6.1	40.7	8.7	40.7	
B(AF)	52.6							6.5
700m								
A	61.4	6.4	46.0	5.0	58.6	5.1	67.5	7.3
В	50.5	5.4	40.1	4.1	53.3	6.8	54.6	5.7
A(AF)	62.8	7.5	36.5	4.8	37.9	5.7	44.0	6.0
B(AF)	41.8	5.0	48.2	6.6	36.5	5.9	33.4	4.7
850m A	61.8	6.2	37.0	4.1	44.4	4.1	64.5	6.8
В	59.3	5.9	50.2	4.9	34.3	3.9	62.6	7.1
A(AF)	59.5	7.3	40.2	5.0	30.9	4.3	45.6	6.1
B(AF)	50.0	5.6	38.4	5.1	29.9	4.2	46.9	6.5

TABLE 7. Organic carbon and nitrogen fluxes. Soutar-paired (cones A and B) sediment traps. All values represent duplicate measurements in mg m^2d^1 dry weight. AF = acid-fumed

	$CaBS-3$ (05/86)			$CaBS-4$ (10/86)			$CaBS-7$ (10/87)			$CaBS-10$ (10/88)		
	$\mathbf C$	N	CM	с	N	CM	C	N	C/N	c	N	CM
Shelf												
100 _m	107	17.7	7.0	65.9	11.0	7.0						
200m							66.5	25.0	3.1	110	18.4	7.0
350 _m	143	21.3	<u> 7.8</u>	<u> 118</u>	18.4	7.5	102	46.6	26	$160*$	$22.6*$	$8.3*$
Mean	125	19.5	7.4	92.0	14.7	7.3	84.3	35.8	2.8	135	20.5	7.7
Mid-basin												
100 _m	68.3	11.6	6.9	44.6	8.0	6.5						
200m							51.0	21.2	2.8	88.6	16.4	6.3
500m	49.0	6.4	8.9	41.1	5.6	8.6	40.8	7.8	6.1	44.7	6.8	7.7
700m	52.3	6.3	9.8	42.4	5.7	8.7	37.2	5.8	7.5	38.7	5.4	8.4
850m	54.8	6.5	22	39.3	5.1	21	30.4	4.3	8.3	46.3	6.3	8.6
Mean	56.1	7.7	8.9	41.8	6.1	8.2	39.8	9.8	6.2	54.6	8.7	7.8

TABLE 8. Organic carbon and nitrogen fluxes. Acid-fumed, mean values in mg m⁻²d⁻¹ from Table 7 plus C/N ratios (atoms)

*single measurement

FIG.4. Mass and CN fluxes, all in mgm⁻²d⁻¹, for mid-basin and shelf sites: $o = CABS-3$, $\bullet = CABS-$ 4, \otimes = CaBS-10, \triangle = CaBS-10. Dashed lines (- - - -) are N fluxes, and the heavy dashed lines $(- -)$ represent mean values.

The differences in $\Delta^{14}C$ values (Table 3) between $DO^{14}C$ and $DI^{14}C$ (DOC-DIC) are -291% at 5m and -293°/0o at 850m, differences which are of the same order as those found in the NCP at these depths (WILLIAMS and DRUFFEL, 1987). This suggests that this fraction of the DOC (oxidizable by UV radiation) is recycling throughout the oceanic water column including the contiguous, semi-isolated coastal basins. However, the ¹⁴C activity of the DOC (or some fraction thereof) oxidizable only by high temperature combustion (HTC) (SUGIMURA and SUZUKI, 1988) must be significantly higher than that of the UV-oxidizable fraction to account for the observed covariance between $\overline{DOC}_{\text{m}r}$ concentration with apparent oxygen utilization (AOU) in some oceanic regimes. There is some indirect evidence for this "extra" DOC having an elevated 14C content (DRUFFEL, WILLIAMS and SUZUKI, 1989), but there are no hard data. The significance of this paradox of the dissolved/colloidal organic matter (see WILLIAMS and DRUFFEL, 1988) to organic carbon cycling in coastal basins in general, and the Santa Monica Basin in particular, is in assessing the role of DOC in balancing particle fluxes, *in situ* biochemical oxidation, and sedimentary organic matter burial against carbon fixed by photosynthesis and/or entering the system from non-marine sources (JACKSON, AZAM, CARLUCCI, EPPLEY, FINNEY, GORSLINE, HICKEY, HUH, JAHNKE, KAPLAN, LANDRY, SMALL, VENKATESAN, WILLIAMS and WONG, 1989).

Perhaps the most important impact of the "old" recycled DOC is via its possible association with both suspended and sinking POC which may result in low Δ^{14} C values for these particulate phases at depth (Fig. 1) and hence, ambiguity in reading the bomb- ^{14}C signal or radiocarbon clock of these phases *vis-3-vis* their origin and eventual burial in the sediments.

 δ^{13} C values for UV-oxidizable DOC (DOC-UV) in the basins (Table 3) vary little with depth or location and only slightly between cruises - the mean values for all depths for CABS-4 and CaBS-7 samples were -21.4 \pm .5% (n=6) and -21.8 \pm 2% (n=5) respectively. The average δ^{13} value for the North Central Pacific (3-900m, n=17) in 1985 and 1987 was -21.1 \pm .3% o(n=22) (WILLIAMS and DRUFFEL, 1987, unpublished data); and for the SIO pier and San Diego Trough area (Table 1) in 1967-1968 was -22.5% (WILLIAMS and GORDON, 1970; results which could be 1%o more negative because of earlier procedural problems). The DOC-UV concentrations for CABS-4 and CABS-7 (Table 3) were nearly identical at all mid-basin and shelf depths, and were ~4µmol higher at depth than the North Central Pacific DOC-UV values. Thus, the concept of a common origin for the UV-oxidizable fraction of DOC present in both the open ocean and coastal basin is strengthened by $\delta^{13}C$ values and total DOC-UV content-in addition to the $\Delta^{14}C$ signatures.

4.2 Suspended particulate organic matter: POC(susp) and PON(susp)

Suspended POM, whose carbon concentration is of the order of 1% of the DOC-UV (Table 3), has estimated residence times in the upper mixed layer (photic zone) of 20-39 days (SMALL, LANDRY, EPPLEY, AZAM and CARLUCCI, 1989) and 3 to >100 days (EPPLEY, RENGER and BETZER, 1983) based on new production and sinking fluxes, alternatively 4 to 7 days based on thorium isotope measurements (HUH and BEASLEY, 1987). In the deeper basin waters, these POC (susp) residence times may be of the order of 5 to 10 years, as has been reported for thorium isotope measurements in the open ocean (BACON and ANDERSON, 1982). Particles collected in the SMB by *in situ* filtration were nominally $>$ 1 μ m in size but would include finer particles scavenged on larger ones (McCAVE, 1984) and trapped on clogged filters. Thus, the origin of suspended POM is not necessarily localized to the basin system, but is a combination of: (1) POM advected into the basin by surface currents and deep water exchange across the sills; (2) POM derived from the basin slopes through resuspension and subsequent incorporation into various levels within the water column; and (3) POM resulting from fractionation of sinking POM into finer, suspended particles. Transmissometer measurements within the SMB water column (NELSON *et al,* 1987; HUH, SMALL, NIEMNIL, FINNEY, HICKEY, KACHEL, GORSLINE and WILLIAMS, 1990; B. HICKEY, personal communication) indicate that there are no permanent nephaloid layers beneath the euphoric zone but do not preclude sporadic injections of suspended particles at depth from the basin shelf or slopes. Surface and deep current measurements and tracer experiments give residence times for water parcels (with their associated suspended POM) ranging from 3-20d in the upper 200m, up to several years for sporadic renewal of deep basin waters (JACKSON *et al,* 1989). These renewal times are short compared to estimated suspended particle residence times in the surface mixed layer, suggesting caution in relating chemical and isotopic properties of POC (susp) and PON (susp) to locally-sinking POM or other indigenous sources of suspended organic particles. Clearly, advected particles may dominate those of local origin, especially in deeper waters.

 Δ^{14} C values for POC (susp) decrease significantly with depth (Table 3, Fig. 1) with a minimum value of -46% o at 700m. Neither the δ^{13} C signature nor the POC (susp) concentration is strikingly different at 700m from those same parameters measured in the 510 and 850m samples, suggesting that this particular sample was not significantly "contaminated" with oil or other hydrocarbons. Without replicate samples, this low $\Delta^{14}C$ value cannot be attributable to the filtration of a spurious cloud of"old" suspended particles; nor can it arise from resuspended surficial sedimentary organic particles whose Δ^{14} C values were -10 and -21% oin the upper 2.5cm of bulk sediment (Table 5). Two facts are evident from the POC (susp) 14 C activities: (1) Reduced carbon, recently fixed photosynthetically at the surface, whose $D^{14}C$ value should be similar to the surface water $D^{14}C$ value (94°/oo), does not constitute all of the suspended POC. Low 14C-containing organic particles and/or DOC must contribute to the POC (susp) Δ^{14} C values below 100m assumaing that we are not dealing with spurious oil contamination; and (2) the PO¹⁴C (susp) activities are lower than those for the sinking POC collected on the same cruise at the same depths (Fig. 1). This might seem to support longer turnover times for the POC (susp) than for the POC (sink), but this is only true if inclusion of "old" sedimentary particles and/or DOC are excluded, and if the POC (susp) has a common origin with the POC (sink).

 δ^{13} C and δ^{15} N values for POC (susp) do not reflect the isotopic signatures in either POC (sink) or DOC (Figs 2 and 3). $\delta^{13}C$ values for POC (susp) are more negative by ~1% othan for DOC at comparable depths (Table 3), as was earlier observed by WILLIAMS and GORDON (1970) (Table 1). JEFFREY, PFLAUM, BROOKS and SACKETT (1983), who measured $\delta^{13}C$ values for POC (susp) in numerous shallow profiles (<400m) from various oceans, suggested that biological reworking of POC (susp) in the pycnocline caused fractionation of POC- δ^{13} C towards lighter isotopic values so that δ^{13} C values increased with depth. The opposite was found in the SMB where the two shallow samples (mid-basin and shelf) were lighter in 13 C than samples at 500m and below by 3.0% and 1.39% , respectively. This depletion in δ^{13} C suggests a terrestrial contribution is possible; but, if so, none of the shallow POC (sink) δ^{13} C values (Table 4) is isotopically lighter than those measured in the deeper samples. Flocculents from the ouffalls and suspended particles from Los Angeles River storm waters (Table 1) have δ^{13} C values which vary from -23.7 to $-24.9%$, and $\bar{\delta}^{15}N$ values from 2.4 to 3.0%, but there is no compelling evidence from $\delta^{15}N$ values for PON (susp) supporting an appreciable contribution of ouffall-derived suspensoids (this general question of terrestrial contributions to all organic phases in the Santa Monica Basin system is amplified in the Discussion section). The approximately 2% increase in δ^{15} N at 700 and 850m relative to the 80, 100 and 510m samples (Table 3, Fig.,2) follows previous measurements of lighter $\delta^{15}N$ values in PON (susp) in the euphotic zone than at depth (ALTABET, 1988).

4.3 Sinking particulate organic matter [POC(sink) and PON(sink)], and total mass and organic carbon and nitrogen fluxes

There are two caveats concerning the Soutar particle trap deployments. The first is that the shallower traps (100 and 200m) collected significantly fewer organic particles than smallerdiameter, multicylinder "Vertex" traps (WELSCHMEYER and LORENZEN, 1985; SMALL *et al,* 1989) deployed at these same shallower depths (see LANDRY, PETERSON and ANDREWS, 1992). This apparent "under-collection" by the shallow Soutar cones is probably related to motioninduced orientation problems in the upper 200m. We consider that the deeper traps (500-700 and 850m) did collect representative flux samples based on the following observations. JAHNKE (1990) has shown that organic carbon burial rates correspond to sinking carbon fluxes at 850m adjusted for sediment oxidant consumption (see also JACKSON *et al,* 1988). Also ratios of organic carbon fluxes to total mass fluxes (from Tables 6 and 8) decrease from 0.13-0.20 at 100 and 200m $to 0.055-0.084$ at 850 m, primarily because of a decrease in organic matter trapped at depth coupled with an increase in total mass flux with depth (Fig.4). These ratios do not preclude under-trapping of sinking organic matter in the upper 200m with Soutar traps, but do show an approximately twofold decrease in the amount of organic C trapped relative to total mass at 850m compared to 100 or 200m.

The second caveat is that the 100, 200 and 350m traps contained variable but often significant numbers of swimmers, primarily copepod nauplii, all of which could not be separated from the sinking particles. Such swimmers will have Δ^{14} C values close to that of surface DIC, and δ^{13} C and δ^{15} N values representative of marine end-members, so the isotopic signatures for sinking organic matter will be biased in these shallow samples. The swimmers will also lead to the total organic C and N fluxes for passively sinking particles being over-estimated. Conclusions based solely on fluxes and total organic matter collected in the shallow traps are most subject to these errors.

There are no Δ^{14} C values reported previously for POC (sink) in coastal basins. In the North Central Pacific, PO¹⁴C (sink) at 4120 and 5120m were 85 \pm 7 and 114 \pm 7%_o, respectively (DRUFFEL and WILLIAMS, 1990). These values are higher than those measured at depth in the SMB, possibly reflecting the higher surface $DI⁴C$ content in the North Central Pacific.

 Δ^{14} C values for POC (sink) from five CaBS cruises (Table 4 and Fig. 1) generally decrease to 700m at the mid-basin station with no further reduction in ¹⁴C at 850m. All of the $\Delta^{14}C$ values are greater than -75%, the maximum pre-bomb value for surface DIC prior to 1950 (AD); or, conversely, all of the POC (sink) samples contain bomb- ${}^{14}C$ - as would be expected. The interesting point is that this diminuition of ^{14}C activity with depth requires that some fraction of the POC (sink) contains organic carbon which is not surface-derived and/or derived from surface waters >35 years ago. At $850m$ (Fig.1) the PO¹⁴C (susp) and PO¹⁴C (sink) values converge to a mean $\Delta^{14}C = 27 \pm 21$ % (range = 2-52%, n=4) from a mean value of 96 \pm 14% (range = 78-110%) ∞ , n=4) at 80-200m, the same value as DI¹⁴C at 5m. The general correspondence between the ¹⁴C contents of sinking and suspended POC suggests a common source and similar histories for these phases, although it does not rule out their having disparate sources with closely related isotopic signatures.

One clue to the source of "older" sinking POC is the lower Δ^{14} C values for all of the particle trap POM samples from the shelf. $\Delta^{14}C$ decreased from a mean of 67 \pm 7% oat 100m to 39 \pm $6\degree$ ₀ at 200m and -13 \pm 14% at 350m, ~50m above the seafloor. Perhaps, fortuitously, the differences between the surface and deep samples at mid-basin (69%) and on the shelf (80%) are not significantly different. This might be interpreted as a "common source", e.g. resuspended, low- ¹⁴C activity, shelf sedimentary organic matter (SOM), mixing with recently-fixed organic carbon, where the amount of common-source POM decreases with distance from its origin on the

shelf. Since persistent nephaloid layers have not been observed at depth in mid-basin waters, these low Δ^{14} C values for POC (sink) on the shelf are more likely from resuspended ¹⁴C-poor SOM, while another process (e.g. adsorption of "old" DOC) may also occur with the mid-basin samples.

 δ^{13} C and δ^{15} N values for sinking POM (Table 4, Figs 2 and 3) vary significantly between cruises, between depths, and between the mid-basin and shelf stations. The $\delta^{15}N$ values are particularly variable at mid-basin where $\delta^{15}N$ at 850m (cruise CaBS-3) was 5.50%. and that at 500m (cruise CaBS-7) was 10.20% . Only the CaBS-4 deployment showed smooth $\delta^{13}C$ and $\delta^{15}N$ profiles (Figs 2 and 3). If all measurements at each depth are averaged, vertical changes in $\delta^{15}N$ are much less pronounced (see Fig.3 and JACKSON *et al.* 1989), and the average $\delta^{15}N$ values at 100 and 500m (8.87 and 8.42%) are similar to those measured at the same two depths (8.0 and 8.0% , respectively) for samples from two, 2.5 day, free-floating conical trap deployments in 1983 (NELSON *et al,* 1987).

It is apparent from Fig.3 that the vertical profiles of $\delta^{13}C$ (with the exception of 700 and 850m on CaBS-3) are about $1\overline{°}/\overline{°}$ heavier in 13 C on cruises CaBS-3, 7 and 10 than on CaBS-4, both at mid-basin and on the shelf. No similar differences occur with the $\delta^{15}N$ values. $\delta^{15}N$ on cruise CaBS-4 is not systematically lower as would be expected if the lighter $\delta^{13}C$ values on CaBS-4 originated from terrestrial inputs. It is difficult to attribute variations in $\delta^{13}C$ values, be they dissolved, suspended or sinking organic phases to terrestrial sources, since $\delta^{13}C$ values for the terrestrial end-members (-23.7 to -26.4%), Table 1) are only about 3% or less depleted in ¹³C relative to the dissolved and particulate organic phases in question. Variations in the $\delta^{13}C$ signatures for the sinking organic matter are most likely a function of differing $\delta^{13}C$ values for the various sources compromising the sinking POM, and do not arise from trophic level fractionation processes. These sources include (see Table 1): phyto- and zooplankters ($\delta^{13}C \approx -19$ to -22 \degree /₀₀); kelp ($\delta^{13}C \cong -14$ to -21 \degree /₀₀); sole and prawns ($\delta^{13}C \cong -16$ to -18 \degree /₀₀), resuspended sedimentary organic matter ($\delta^{13}C \equiv -20$ to -23%), and sewage or storm water particles ($\delta^{13}C =$ -23.7 to -26.4 %). The uniform, CaBS-4 δ^{13} C signatures for sinking POM may have been a result of predominantly one source of particles (e.g. copepod-derived organic matter) being trapped during this deployment.

Some variation in the $\delta^{13}C$ signatures could have arisen from changes in CO₂ (aq) concentrations (RAU, TAKAHASHI and DES MARAIS, 1989) which would alter the $\delta^{13}C$ values of the organic phases. However, the small interannual variations in CO , (aq) or temperature in this region would result only in small changes in the $\delta^{13}C$ signatures.

How then, are the corresponding $\delta^{15}N$ signatures interpreted? The large, and seemingly unrelated excursions in $\delta^{15}N$ between deep and shallow trap samples and between deployments must be a function of isotopic fractionation during phase changes, and reutilization and recycling in the euphotic zone coupled with a sporadic input of sewage particulates. Such processes as: (1) ¹⁵N enrichment in higher trophic levels of the order of 3.5% per trophic level (FRY, 1988 and references therein); (2) ¹⁵N depletion in fecal pellets (~1-2%o) relative to the parent zooplankton body tissue coupled with an approximate 2% fecal pellet enrichment over the apparent zooplankton food source (ALTABET and SMALL, 1990); (3) variable $\delta^{15}N$ values in photosynthetically fixed NO₃ and NH₄⁺ reflecting variations in NO₃ and NH₄⁺ during denitrification and recycling of nitrogen in the euphotic zone (LIU and KAPLAN, 1989; CHECKLEY and ENTZEROTH, 1985; CHECKLEY and MILLER, 1989); and (4) ¹⁵N fractionation between sinking and suspended particles (ALTABET, 1988). Any or all of these processes could be operating within the complex nitrogen cycle in the SMB system, making it difficult, if not impossible, to relate any specific $\delta^{15}N$ profile of PON (susp) to any one (or more) direct sources or processes. What is evident is that on cruise CaBS-3, ¹⁵N-depleted particles (presumably sewage-derived) dominated the trapped particles at 350m on the shelf ($\delta^{15}N = 3.55$) and even appeared to have entered the 850m trap at JP0 30~ l/4-d

the mid-basin station. Such "sewage" contributions were not apparent in the other mid-basin PON (susp) profiles (Fig.3), but could have enhanced the regular depletion of ^{13}N in the 350m traps relative to the 100 and 200m samples on the shelf. This depletion could also arise from resuspension of sedimentary organic particles whose δ^{13} C values (e.g. 6.4 at 0-1.25cm, Table 5 for core BC-89) were more similar to the PON (sink) δ^{15} N values at 350m on the shelf (and at 850m) at mid-basin) than to, for example, zooplankton tissue (Table 1). The significant increases in mass and C and N fluxes on the shelf, and in mass fluxes at mid-basin (Fig.4), support the hypothesis for such a sedimentary contribution from the shelf/slope regions; so do the lower ${}^{14}C$ activities in the 350 and 700 and 850m trapped particles and in the surface sedimentary organic matter.

4.4 Sedimentary organic matter (SOC)

 $\Delta^{14}C$, $\delta^{13}C$ and $\delta^{15}N$ values for the upper 20cm of box core No. BC-89 are listed in Table 5 and depicted in Figs 1 and 2.

The Δ^{14} C values measured in the surficial sediments of the SMB (-10 ± 6 and -21 ± 6%, 0 to 2.5cm) clearly show the presence of bomb ¹⁴C. As expected, a Δ^{14} C result obtained for a grab sample collected during the pre-bomb period of 1956 in the SMB $(-147 \pm 19\degree\degree\degree\degree, 1280 \pm 150\degree\degree)$ EMERY and BRAY, 1962) was much lower than our 1985 values. There is, however, reasonable agreement between the 1956 Δ^{14} C values at 1cm and 15cm (-147 \pm 19% of and -258 \pm 19%. respectively, EMERY and BRAY, 1962) and our 1985 Δ^{14} C values at 7cm and 13cm (-154 ± 5%) and -307 \pm 5%.). Our Δ^{14} C value at 20cm appears to be anomalously low (-416 \pm 4%) when compared with any of EMERY and BRAY'S results for the upper 90cm in three cores from the Santa Monica Basin and the adjoining San pedro Basin. This may be evidence of "old", redeposited carbon that EMERY and BRAY (1962) postulated to be in surficial SOC from the basins off Southern California.

For the Santa Monica and San Pedro basins, EMERY and BRAY (1962) calculated six sedimentation rates ranging from 38 to 145cm $10^{-3}y^{-1}$ (mean = 66cm $10^{-3}y^{-1}$) based on the difference in ¹⁴C activities between a surface and deep (>300cm) Δ^{14} C measurement. These sedimentation rates are similar to the 31cm $10³y⁻¹$ calculated for core BC-89 from ²¹⁰Pb measurements in the top 20cm (Table 5, 20cm x $10³/642y$). The ¹⁴C sedimentation rate for Core BC-89 is much less (\sim 4cm 10⁻³y⁻¹) based on near-surface (6.2 to 20cm) Δ^{14} C results. This latter rate may be unique to core BC-89, as large variability in Δ^{14} C results were also observed by EMERY and BRAY (1962) in near-surface SOC.

 δ^{13} C and δ^{15} N values for SOC (Table 5, Fig.2) do not show extreme excursions within the sedimentary column. $\delta^{13}C$ (-21.79 to -22.62%) and = -22.11% and $\delta^{15}N$ (6.09 to 8.74%), mean = 6.98%) values fall within the envelope of data points on a regression plot of $\delta^{13}C$ vs. $\delta^{15}N$ for sedimentary organic matter from continental shelf sediments of the northeast Pacific (PETERS, SWEENEY and KAPLAN, 1978), but are not themselves significantly correlated (Fig.5F). There are no striking correlations of $\delta^{13}C$ or $\delta^{15}N$ with sedimentation events which have occurred during the past 500 years; e.g. the decline in sedimentation rates in core BC-89 which occurred 200 years ago (HUH, ZAHNLE and SMALL, 1990) at the time of an extensive turbidite intrusion into the basin (MALOUTA, GORSLINE and THORNTON, 1981), or with episodic, high, storm-derived run-off at 10-30y intervals (MALOUTA, GORSLINE and THORNTON, 1981). Nor are there any tight correlations of δ^{13} C or δ^{15} N with past productivity maxima (SMITH and EPPLEY, 1982) or total SOC content for the 1922-1979 period. Note that total SOC concentration profiles at mid-basin and shelf sites show a maxima in SOC content in 1965-1970, when inputs of wastewater particulates from the White's Point outfall reached a maximum (FINNEY and HUH, 1989; EGANHOUSE and

KAPLAN, 1988). There is also no reflection in the isotopic ratios for core BC-89 of the SOC and SON concentration maxima and $\delta^{13}C$ and $\delta^{15}N$ minima observed at 6-10cm in a core taken at 60m bathymetric depth on the San Pedro shelf in 1981 (EGANHOUSE and KAPLAN, 1988). These SOC and SON maxima and isotopic minima on the shelf are a direct result of the maximum discharge of terrestrially-derived sewage particles, which occurred in the late 1960s. Thus, the terrestrial C and N isotopic signatures have been poorly preserved in the mid-basin, sedimentary column (at least in 1.25cm sections), implying that significant biochemical oxidation-solubilization of sewage particulates occurs en route to their eventual sequestration in the sediments.

With respect to the isotopic signatures for the mid-basin suspended, sinking and dissolved organic phases (Figs 1,2 and 3), the surficial (0-1.25cm) sedimentary organic matter most closely resembles: (1) the 850m sinking POC from Cruise CaBS-8 in ¹⁴C content ($\Delta^{14}C_{\text{soc}} = -10 \pm 6\%$ _{oo}, $\Delta^{14}C_{\text{POC(sink)}} = 2 \pm 6\degree$ /₀₀); and (2), the 850m suspended POC from Cruise CaBS-4 ($\Delta^{14}C = 9 \pm \degree$ 6% ₀). The SOC δ^{13} C value (-22.15%) is slightly lighter than the mean (n=5) value for the sinking POC at $850m$ (-21.78 \degree /₀₀) or the DOC value at $850m$ (-21.50 \degree / \degree , n=2), but slightly heavier than the suspended POC value at 850m from Cruise CaBS-4 (-23.08 \degree / \circ). δ^{15} N for the 0-1.25cm SON $(6.37\degree/\circ\circ)$ is significantly lighter than the mean (n=5) $\delta^{15}N$ (7.42 \degree / \circ) for the mid-basin sinking particles; however, this mean value is misleading because the two extreme $\delta^{15}N$ values (Table 4) 5.50 and 5.97 are indicative of contamination from terrestrial (sewage) inputs. Thus the source of total sedimentary organic carbon can not be attributed either to any one of the indigenous organic phases in the water column or to the wastewater outfalls. This result was unexpected but makes it difficult to link unequivocally the terrestrial vs. marine sources to the SOM.

5. DISCUSSION

5.1 Terrestrial (sewage, storm run-off, industrial organics) contribution to the SMB *organic phases*

The average $\delta^{13}C$ and $\delta^{15}N$ signatures for White's Point sewage flocculents are -24 and 2.5%, respectively (Table 1). $\delta^{13}C$ in Los Angeles river storm water suspended solids is -25% (Table 1). No values for $\delta^{15}N$ in river solids, or for $\Delta^{14}C$ in sewage or runoff organics are available. Δ^{14} C values in natural oil seeps, anthropogenic petroleum products and spills, and petroleumderived industrial chemicals will be - 1000°/oo, and in modern organic matter (grass, leaves, paper, etc.) will be taken as 200% , equivalent to that of contemporary atmospheric CO₃ (Table 1).

A rough estimate of the contribution of sewage-derived organic flocculents to the SMB organic phases can be calculated using the two-source mixing equation:

$$
X_{s} [\delta^{13}C_{s}] + X_{M} [\delta^{13}C_{M}] = [\delta^{13}C_{SMB}]
$$

$$
X_{s} [\delta^{15}N_{s}] + X_{M} [\delta^{15}N_{M}] = [\delta^{15}N_{SMB}]
$$
 (1)

where X_s and X_w are the fractions of sewage and marine end-members in the SMB organic phases having the appropriate measured isotopic signatures ($\delta^{13}C_{SMB}$ and $\delta^{15}N_{SMB}$). Table 9 lists the percentages of sewage-derived organics in the SMB organic phases and includes end-members and organic phase isotopic signatures. The latter values are means of both mid-basin and shelf measurements.

FIG.5. Plots of $\Delta^{14}C$ vs. $\delta^{13}C$ or $\delta^{15}N$ and $\delta^{13}C$ vs. $\delta^{15}N$ for the various organic phases (all values). A and B: POC (sink), \triangle = mid-basin, \triangle = shelf; POC (susp), \bullet = mid-basin, \blacktriangleright = shelf. C: DOC, o = mid-basin, \otimes = shelf. D: All POC (sink) and POC (susp) values, \bullet = mid-basin, + = shelf. E: SOC, $\blacksquare = \Delta^{14}C$ vs. $\delta^{13}C$, $\square = \Delta^{14}C$ vs. $\delta^{15}N$. F: SOC, x = all values, 0 to 20cm.

Taking the sewage end member signatures as $\delta^{13}C_s = -24\%$ and $\delta^{15}N_s = 2.5\%$ and the marine end member signatures as $\delta^{13}C_M = -21.5\%$ and $\delta^{15}N_M = 8.5\%$, the percentage contributions of sewage organic matter, X_{s} , to the basin organic phases are:

 1 Does not include $\delta^{15}N = 3.55\%$ from 350m, shelf station, Cruise CaBS-3.

The choice of end-member isotopic signatures is largely subjective, and does not include nonsewage terrigenous organic matter. $\delta^{15}N_s$ and $\delta^{13}C_s$ values are from SWEENEY and KAPLAN (1980b, Table 1). For the marine end-members, we have chosen 8.5% of $\delta^{15}N_{\rm M}$, the mean value for NO₂ in upper 100m of the San Pedro Basin (LIU and KAPLAN, 1989), and -21.5% of $\delta^{13}C_{M}$, based on DOC and POC(sink) values at 100 or 200m.

The percentage contribution of sewage flocculents, X_s , to the SMB organic phases (Table 9) is 3-8% for the sinking and suspended POM (excluding the 72% value for POC (susp) based on δ^{13} C) and 25-28% for the surficial SOM. The wider spread in the δ^{13} C end-members makes the percentages calculated using $\delta^{15}N$ values more credible. The 25% calculated for surficial SOM corresponds to the value found by EGANHOUSE and KAPLAN (1988) for SOM at 23-34cm depth in a core from the San Pedro shelf at 60m, where the corresponding percentages for the 0 to 23cm sections varied from -40% at 0-2cm to 95% at 2-4cm. Thus, the contribution of sewage flocculents to the water column organic phases in the mid-basin and shelf waters is probably less than 10%, while the surficial, mid-basin SOM could contain -25% terrestrial components, assuming the terrestrial end-member assignments are valid.

There are also indications from $\delta^{15}N$ values for the POC (sink) of episodic inputs of terrestrial POM at 350m on the shelf ($\delta^{15}N = 3.55\%$, CaBS-3), 850m mid-basin ($\delta^{15}N = 5.50\%$, CaBS-3), and 850m, mid-basin ($\delta^{15}N = 5.97\%$, CaBS-10). Using the $\delta^{15}N_s$ and $\delta^{15}N_M$ end-member values from Table 9, the estimated contribution of sewage to the POM particle trap contents at 350 and at 850m for CABS-3 and 850m for CABS-10 are 83%, 50% and 42%, respectively.

However such high sewage inputs are not reflected in the δ^{13} C signatures of the POC (sink), which suggests that there is reworking and fractionation of the sewage-derived POC without corresponding changes in the $\delta^{15}N$ values (see MYERS, 1974, and SWEENEY, KALIL and KAPLAN, 1980).

Independent of the isotopic evidence, the doubling in the mean mass flux between depths of 100 and 200m to 350m on the shelf, coupled with a 40% increase in the corresponding CN flux (Fig.4), implies that there is export of POM, including terrestrial components, across the shelf. As well as the increased mass flux on the shelf, there is a 40% increase in total mass flux between depths of 100 to 850m at mid-basin (Fig.4), although its origins could be from the seaward slopes of the basin as well as the coastal shelf and slope. These inputs augment the POM derived directly from marine organisms.

With respect to the $\Delta^{14}C$ signatures, sewage inputs cannot be assessed without knowing the Δ^{14} C value for sewage flocculents and solubles. Sewage is composed mainly of faeces, cellulose (toilet paper) and variable quantities of chloroform-soluble hydrocarbons (R. EGANHOUSE, personal communication). Its $\Delta^{14}C$ signature will be a mix of recent ($\Delta^{14}C = 200\%$) and ancient $(\Delta^{14}C = -1000\% \circ)$ components. The hydrocarbon fraction, however, could contribute to lowering Δ^{14} C values in the water column and sedimentary organics (see below).

5.2 Origin of $\Delta^{14}C$ gradients in mid-basin and shelf organic phases (water column)

The most obvious carbon source resulting in the diminution of ¹⁴C activities in the DOC, POC (susp) and POC (sink) is petroleum derived from natural seeps, sewage discharges, oil spills and atmospheric inputs.

As stated earlier, the DOC Δ^{14} C profile can be primarily attributed to the influx of open-ocean water into the basin, rather than to soluble hydrocarbons, whose concentrations (in the boiling point range of n-tetradecane to n-dotriacontane) in 1-3m surface waters and in samples collected 10m off the bottom have been reported to be 0.03 to $80\mu g l^{-1}$ (~0.001 to 3 μ mol C l⁻¹) (RISEBROUGH and BURLINGAME, 1978). Assuming a mean total DOC concentration of 44μ mol $1^{\text{-}1}$ at 500 to 850m (Table 3), and a surface (5m) Δ^{14} C value of -197% of or the source DOC, then it would require an additional 10µmol (23% of the total UV oxidizable DOC!) of hydrocarbon-C per liter ($\Delta^{14}C = -$ 1000 $\%$) to attain the measured value of ~ -470 $\%$ (Table 3) for the deep water DOC. However, the resultant δ^{13} C value of this DOC would then be -23.3°/oo rather than the mean measured value of -21.75 (Table 3), assuming a $\delta^{13}C = -28\%$ for petroleum products.

With respect to the sinking particles, CRISP, BRENNER, VENKATESAN, RUTH and KAPLAN (1979) reported a total hydrocarbon flux of $0.071g$ (~0.006mol C) m⁻²y⁻¹ for the Santa Monica Basin at ~850m. The mean C flux at 850m (Table 7)(is ~15g m⁻²y⁻¹ and 45g m⁻²y=-1 at 350m on the shelf, which gives hydrocarbon contents of $\sim 0.24\%$ (mid-basin) and 0.08% (shelf) assuming the same flux of hydrocarbons at both sites. If the $\Delta^{14}C$ value for the POC sinking from the surface was equal to surface DIC (94%), then the Δ^{14} C for POC (sink) at 850m (or at 350m on the shelf) would be lowered only to 91.3% (and to 93.1% on the shelf) with admixture of 0.24% (or 0.08% on the shelf) petroleum hydrocarbons ($\Delta^{14}C = -1000^{\circ}/\infty$). The measured means of $\Delta^{14}C$ at 850m and 350m, however, are 41 and -13%, respectively (Table 4).

A similar calculation for POC (susp) can be made assuming (1) the $\Delta^{14}C$ source for POC (susp) has a value of 94% with a mean C concentration of 0.27μ mol $1¹$ at 500-850m (Table 3), and (2) the mean concentration of hydrocarbon -C in suspended particles is 0.005μ mol $l⁻¹$, based on data from RISEBROUGH and BURLINGAME (1978) and DeLAPPE, RISEBROUGH and WALKER (1983). These assumptions give a POC (susp) ¹⁴C activity of 74% versus the mean measured $\Delta^{14}C$ value of \sim -3% \circ at 510 to 850m (mid-basin).

These crude estimates of the contribution of petroleum to the organic phases in mid-basin and shelf waters while not precluding it's presence in these phases, do suggest that the contribution is minimal \langle <1%) based on the data available for hydrocarbon contents of DOC, POC (susp) and POC (sink) in the basin.

If natural oil seeps and/or anthropogenic petroleum inputs are not responsible for the d iminuation of ¹⁴C activities with depth, then the most plausible explanation (as mentioned earlier) is that there are contributions of low 14 C activity, surficial sedimentary organic particles which either enter the mid-basin water column sporadically from the basin slopes, or, in the case of the shelf waters, are directly injected into the overlying wters via resuspension by slumping and internal waves. Downslope resuspension of subsurface sediment (5-10cm) injected into the nearbottom water by the activities of benthic animal activity may also contribute significant amounts of low 14C activity SOC. The observed increases in mass and CN fluxes with depth (Tables 6 and 7, Fig.4) are evidence for these processes, most notably at the shelf stations; although the frequency with which these inputs occur, especially the introduction of slope particulates into the deep basin waters, is unknown. The sporadic presence of nephaloid layers in the deep basin waters (B. HICKEY, personal communicaion) lends credence to the interdigitation mechanism.

Assuming the Δ^{14} C values of the POC (susp) derived from the slope surficial sediments to be -15% (the same as the mean value measured for the mid-basin 0-2.5cm SOC, Table 5), and the original source $\Delta^{14}C$ of POC (susp) to be 94% (same as 5m DIC), then the resultant percentage contribution of SOC to the POC (susp) at 510 and 850m is estimated to be 61 and 78%, respectively.

The corresponding percentage contributions of resuspended sedimentary POC to the POC (sink) at 500, 700 and 850m in the basin will be 27, 58 and 50% respectively, where the mean measured Δ^{14} C values at these depths are 65, 31 and 39% respectively (Table 4), and the two source $\Delta^{14}C$ values are again taken as 95% of surface POC (sink)] and -15% of sedimentary POC). For the 350m POC (sink) at the shelf stations, the SOC contribution would be 98% of the total POC (sink) to give its resultant mean Δ^{14} C value of -13%.

Obviously, the $\Delta^{14}C$ value of the SOC derived from the basin slopes and/or shelf may be higher or lower than the assumed value of -15%o, depending upon how thick a surficial layer of sedimentary POC was injected into the deep basin or resuspended on the shelf. The $\Delta^{14}C$ values may also be a function of sedimentary grain size. Coarse particles are rich in fresh plant debris while fine-grained particles contain more fossil organic matter (THOMPSON and EGLINTON, 1978). Thus one might expect that $\Delta^{14}C$ values would vary at any given sediment depth depending on grain size. This mechanism does not account for the ¹⁴C activity ($\Delta^{14}C = -46\%$) of the suspended POC at 700m (Table 3). The only explanation for this anomalously low result is contamination with "dead" (petroleum) carbon. An addition of 6.3% "dead" carbon ($\Delta^{14}C = -$ 1000) is needed to lower the Δ^{14} C of POC (susp) at 700m (assumed to be 20% \circ) to -46% \circ . This invokes a spurious contamination event, probably sampling related, as opposed to the unlikely ubiquitous contribution of petroleum to the POC (susp) at 510m and 850m discussed above.

We feel that the estimated 27, 58 and 50% contributions of SOC to the POC (sink) are high, but not unreasonably so, considering the probability of sporadic SOC inputs occurring during the 98-233d particle trap deployments. However, the estimates of 61 and 78% SOC contributions to the POC (susp) are based solely on a single profile with 6h *in situ* particle filtrations at 510,700 and 850m. This collection may have occurred fortuitously during a period of significant SOC input, so may be unrepresentative of the normal background POC (susp). If a significant fraction of the POC (susp) was derived from near-bottom waters from the slope being advected into the basin, then the resultant isotopic signatures would be strongly influenced by the isotopic characteristics of this advected POC (susp).

There is also the intriguing possibility of adsorption of low ¹⁴C activity DOC-UV onto suspended (or sinking) particles which, if it occurred during the 5 to 10 year residence time of the POC (susp) in the water column, could contribute to the gradient in Δ^{14} C. It would require 12, 25 and 15% of the POC (susp) to be adsorbed DOC at 510, 700 and 850m respectively, to give the measured POC (susp) $\Delta^{14}C$ values (27, -46 and 9%o) at these depths (Table 3), assuming the $\Delta^{14}C$ of the surface-derived POC (susp) to be 94% (same as DIC at 5m). This calculation also assumes a Δ^{14} C of -450% for the DOC-UV at 500m based on the North Central Pacific value at 700m. Again, the SMB 700m POC (susp) $\Delta^{14}C$ value of -46‰ is suspect (it's $\Delta^{14}C$ value would be 12°/00 assuming a 15 % DOC contribution). Although a 12 to 15 % contribution of DOC to the POC (susp) intuitively seems too high, it only amounts to 0.025 to 0.054 μ mol (0.3-0.65 μ g) C l⁻¹ of the total 0.21 to 0.36 μ mol 1⁻¹ of POC (susp), or 0.06 to 0.13% of the total DOC-UV at those depths.

5.3 Origin of the sedimentary organic matter

The contribution of sinking POC reaching the ocean floor at mid-basin is $43mg$ m⁻²d⁻¹(Table 8, mean value, n=4) which may be augmented by unknown, but presumably small, quantities of POC (susp) and DOC. JAHNKE (1990) has calculated that 43% of the total organic carbon reaching the seafloor (18.5mg C m^2d^1) is permanently buried. He concludes that carbon burial rates for the Southern Califomia Bight overall are primarily controlled by input rates and not by variations in *in situ* redox potentials and other preservation variables. This sinking POC includes: (1) terrestrially-derived POC; (2) detritus and associated macro- and micro-organisms derived from the euphoric zone and added during transit to the seafloor; and (3) recycled SOC derived from the basin slopes via episodic injections into the deep basin water.

The contribution of terrestrial organic matter from all sources to the mid-basin sediments, calculated from $\delta^{13}C$ and $\delta^{15}N$ signatures, is about 25% (Table 9), based solely on the $\delta^{13}C$ and δ^{15} N end-member signatures of sewage organics and the surficial SOM. However, the mass emission of sewage carbon $(-5 \times 10^{7} \text{kg y}^{-1})$ into the Southern California Bight calculated from sedimentary coprostanol contents (VENKATESAN and KAPLAN, 1990) has been estimated to be \sim 10³ times less than carbon fixed photosynthetically in the Bight (\sim 1.4 x 10¹⁰kg y⁻¹). This sewage carbon amounts to 1.6% of the mid-basin surficial SOC, which coupled with a 4% organic carbon contribution from terrestrial plants (based on lignin-derived phenol measurements), gives a total of -6% terrestrially-derived organic carbon in the mid-basin sediments, excluding humic substances (VENKATESAN and KAPLAN, 1992). If isotopic fractionation, during *in situ* oxic mineralization of SOM, discriminates against both 13 C and 15 N, it could result in isotopic endmember values 0.5 to 1% heavier than their initial signatures as given in Table 9, so the contribution of terrestrial organic matter would then be even lower than those values calculated in Table 9. For example, if the $\delta^{13}C$ and $\delta^{15}N$ signatures in the 0-3.75cm core section were altered to -21.7 and 8.0% of rom -22.2 and 7.0% by mineralization, then the terrestrial contribution would be reduced from 28% to 8% and from 25% to 8%, respectively, based on these heavier $\delta^{13}C$ and δ^{15} N values. If we assume isotopic fractionation occurs, the estimated upper limit to the amount of terrestrially-derived organic carbon in the surficial SOC of 10% is closer to the sewage and land plant inputs calculated by VENKATESAN and KAPLAN (1992).

Assuming that our previous estimate of recycled SOC in the POC (sink) at 850m (50% of the total) is valid, then 40% of the POC (sink) is unrecycled organic carbon of local origin. How much of each of these three fractions is mineralized and how much is buried is largely conjectural. However, if 57% (24.5mg C $m²d⁻¹$) of the organic matter reaching the ocean floor is mineralized

(JAHNKE, 1990), then there must be nearly complete oxidation of the sinking particles of local origin, plus oxidation of a significant fraction $(-15%)$ of the "already-oxidized", slope-derived SOC and also of a small amount (-2%) of the terrestrial component of the POC (sink). Neither isotopic signatures nor carbon contents of the POC (sink) and SOC (0-2.5cm) can be used to quantify these fractions, largely because we know neither the true isotopic signatures nor the C and N concentrations of the terrestrial and slope inputs. If, for example, the slope-derived surficial SOC had a Δ^{14} C value less than that assumed (-15%) because of contributions of "older" SOC from deeper sediment layers, then the calculated fraction of slope-derived SOC in the POC (sink) would be lower, and the proportion of recycled SOC in the basin sediment (0-2.5cm) reduced. It is clear, however, that the $\Delta^{14}C$ value for the SOC (0-2.5cm) at mid-basin (-15%) does not arise from bioturbation in these distinctly varved sediments, and hence there has to be admixture of prebomb organic carbon with the sinking POC (Δ^{14} C at 850m = 32%). In the simplest case, 57% of pre-bomb carbon ($\Delta^{14}C = -75\%$) plus 43% modern POC (sink) ($\Delta^{14}C = 32\%$) would give an SOC Δ^{14} C value of -29% for the 0-2.5cm accumulated since 1960. This is of the same order as the observed average Δ^{14} C value for this depth horizon (-15%).

This still leaves the question: What is responsible for these "old" $SO¹⁴C$ ages in a rapidly accumulating sediment that is not appreciably mixed by bioturbation or by ventilation with nearbottom water from burrowing organisms? Radiocarbon decay at 20cm (²¹⁰Pb age since AD 1950) =607 years) is equivalent to a decrease of about 73‰ in $\Delta^{14}C$, and an additional decrease of 75%0 (or 625 yrs) is accounted for in pre-bomb SOC owing to the reservoir age of the surface ocean at this site (BERGER, TAYLOR and LIBBY, 1966; ROBINSON and THOMPSON, 1981). Thus, we can account for a Δ^{14} C value for SOC at 20cm of -150% \circ ; instead, our measured value is -416% \circ . EMERY and BRAY (1962) suggested that unexpectedly "old" ages for surficial SOC (mean ^{14}C age of 2500 yrs BP, $\Delta^{14}C = -270°/00$, may result in part from redeposition and mixing of ancient with modern organic carbon. An alternate explanation is to invoke the incorporation of DOC into the POC that sediments onto the sediment/water interface and becomes buried. The large gradient with depth observed in POC Δ^{14} C results suggests that "old" carbon in some form is being incorporated into POC in the water column.

5.4 Phase inter-relationships deduced from isotopic signatures

Figure 5 portrays regressions between $\Delta^{14}C$, $\delta^{13}C$ and $\delta^{15}N$ for the organic phases at the midbasin and shelf stations. These number-6-shot patterns, in general, show common, but not distinctive, sources for the organic matter in all phases. The narrow spread in $\delta^{13}C$ values precludes any meaningful and distinctive regressions of $\delta^{13}C$ vs. $\Delta^{14}C$ for any of the organic phases, and while there is a larger spread in $\delta^{15}N$ values, no distinctive patterns in $\delta^{13}N$ vs $\Delta^{14}C$ regressions emerge which would uniquely characterize the origin(s) of any particular organic phases. There is a tight coupling of $\delta^{13}C$ vs. $\delta^{12}N$ only for the SOC. Thus, these isotopic signatures basically reflect the multiplicity of source organic matter to all phases (at least in the water column), and are not specific enough for interpreting phase inter-relationships.

5.5 C/N ratios in the sinking organic matter

C/N ratios (by atoms) at mid-basin vary from 6.1 to 9.9 (excepting at 200m, CaBS-7), and from 7.0 to 8.3 (excepting at 200 and 350m, CABS-7) at the shelf (Table 8, Fig.4). The three exceptionally low ratios (2.6, 2.8, 3.1) cannot be attributed to analytical error, and must have resulted from both reduced carbon flux and increased nitrogen flux; all are lower than C/N ratios in phyto- and zooplankters (C/N = 5-6) and in pure protein (C/N = 3.5; GNAIGER and BITTERLICH,

1984). No concurrent analyses were done for nitrogen-rich molecules such as ammonia, urea or methyl amines, which, by sorption on highly proteinaceous particles, could have accounted for these anomalously low C/N values. The only unique isotopic signature which appears in these shallow samples from CaBS-7 is a Δ^{14} C value of 2% oat 350m, in comparison to values of -18 and -24% for CaBS-3 and 4. The $\delta^{15}N$ values were relatively high for these three samples; especially at 350m, where $\delta^{15}N$ was 8.06% compared to the CaBS-3, 4 and 10 values of 3.55, 7.40 and 7.86%0 respectively. Thus the most likely source of these highly nitrogenous particles is from the marine organic pool, unlike the terrestrially-impacted sinking particles at 350m for CaBS-3 and 4.

5.6 Comparison of isotopic signatures and other properties between the Santa Monica Basin and the North Central Pacific gyre

One of the more striking observations to result from this study was the close correspondence of $\Delta^{14}C$, $\delta^{13}C$, total UV-oxidizable DOC, total POC (susp), soluble free and combined amino acids, and free plus combined carbohydrates between the mid-basin station in the Santa Monica Basin and at a station at 31^oN, 159^oW in the oligotrophic North Central Pacific (NCP) gyre. Some of these similarities are shown for $\Delta^{14}C$ values (Fig.6) and for dissolved free amino acids (DFAA), total dissolved, hydrolyzable amino acids (THAA) and dissolved free plus hydrolyzable carbohydrates (TCHO) (Fig.7).

The amino acid analyses followed the procedure of LINDROTH and MOPPER (1979), and the carbohydrate determinations were from BURNEY and SIEBURTH (1977). These latter values are reported as glucose equivalents. DFAA, THAA and TCHO for the Santa Monica Basin are from WILLIAMS (1986), and from DRUFFEL *et al* (1989) for the NCP. All DOC-UV and POC (susp) results are from the total CO₂ collected during the UV-oxidation of DOC and the closed-tube combustion of POC (susp). $\Delta^{14}C$ values at the NCP site for DOC-UV, DIC, POC (susp) and POC (sink) are from DRUFFEL and WILLIAMS (1990).

The decrease in DOC-UV and DIC Δ^{14} C values in the upper 900m at both sites follows a similar gradient, such that the SMB values are approximately the same as those 200m deeper in the NCP. This is believed to be the result of the shoaling of isopycnals of open-ocean water entering the basin, and secondarily to local upwelling. Total DOC-UV concentrations in the SMB (Table 3) for cruises CaBS-4 and 7 were 42 to 46 μ mol $1⁻¹$ from 500 to 850m; compared to 52, 47 and 42 μ mol $1¹$ at 450, 600 and 900m in the NCP, respectively. Mean total DOC-UV values at the two sites for the upper 100m waters were 62μ mol 1^{-1} (NCP, n=3) and 65μ mol 1^{-1} (SMB, n=4). There are also some recent, preliminary values for the $\textrm{DOC}_{\textrm{HTC}}$ at mid-basin. These results are from D. HANSELL, UCSC (personal communication), for samples collected on CaBS-11, and analyzed for DOC_{HTC} using a "clone" of Suzuki's 3% Pt/Al,O₃-catalyzed oxidation at 680°C (SUGIMURA and SUZUKI, 1988). The SMB, DOC_{rrc} values decreased from 130µmol 1⁻¹ at the surface to 100µmol 1⁻¹ at 100m and to 85 μ mol 1⁻¹ at 850m. The results for the NCP were 210 μ mol 1⁻¹ at the surface, decreasing to 108 μ mol 1⁻¹ at 482m and to 94 and 90 μ mol 1⁻¹ at 757 and 900m, respectively (DRUFFEL, WILLIAMS and SUZUKI, 1989). Thus, the DOC-UV and DOC_{HTC} concentrations in the 500 to 900m waters in both the SMB and NCP are similar, suggesting that these soluble organic fractions have a common origin, or at least a common biochemical history, while the "extra" DOC_{HTC} in the upper waters may have origins unique to various regions, judging from its elevated concentration in central (DRUFFEL, WILLIAMS and SUZUKI, 1989) and western (SUGIMURA and SUZUKI, 1988) Pacific surface waters. Lastly, the δ^{13} C signatures for the DOC-UV fall within the ranges of -20.86 to -22.19%0 (SMB, Table 3) and -20.4 to -21.6%0 (NCP, DRUFFEL *etal,* 1989) for the upper 900m.

FIG.6. A14C values for the Santa Monica Basin (SMB, mid-basin and shelf sites) and the north central Pacific site (NCP, 31°N 159°W). DOC, $\phi = NCP$, $\phi = SMB$ (mid-basin, CaBS-7), $\bullet = SMB$ (shelf, CaBS-7); DIC, \bullet = NCP, x = SMB (mid-basin, CaBS-7); POC (susp), o = NCP, \bullet = SMB (mid-basin, plus one point at 100m at the shelf site, CaBS-4); POC (sink), $\nabla = NCP$, $\nabla = SMB$ (mid-basin, CaBS-7), ∇ = SMB (shelf, CaBS-7).

With respect to the more labile DFAA, THAA and TCHO values (Fig.7), however, the close correspondence of their vertical profiles between the SMB and the NCP is more difficult to explain. The DFAA concentrations are low at both sites, where the increase below the sill (740m) in the SMB is a result of denitrification and possible benthic contributions. It appears that higher productivity in the coastal waters is not reflected in elevated concentrations of either THAA or TCHO in the surface or deep basin waters; and, in fact, TCHO in the upper 100m of the SMB is lower than in the NCP.

The Δ^{14} C values for POC (susp) in the SMB and NCP both decrease with depth, but have significantly lower ¹⁴C activities in the basin. Aside from contributions of resuspended POC discussed above, some fraction of the POC (susp) in the basin may have had a lower initial $\Delta^{14}C$ value because of the lower surface $DIC^{-14}C$ activity (94% oin the basin at 5m versus 140% oat 3m in the NCP). This assumes that the source of the POC (susp) was from photosynthetically-fixed

FIG.7. Profiles of total dissolved free amino acids (DFAA) total dissolved hydrolyzable amino acids (THAA) and total dissolved hydrolyzable carbohydrates (TCHO, as glucose equivalents) in the SMB and NCP: \bullet = DFAA (NCP), o = DFAA (SMB), \blacksquare = THAA (NCP), \Box = THAA (SMB), \blacktriangle = TCHO (NCP) , Δ = TCHO (SMB).

DIC whose value was indeed 94%. Total concentrations of POC (susp) in the basin deep-waters (500-850m) (Table 3) were 0.21 to 0.36 μ mol l^{-1} compared to values of 0.24 and 0.15 μ mol l^{-1} at 450 and 900m in the NCP. The corresponding δ^{13} C signatures were -22.22 to -23.08% (SMB) and -19.35 and -21.70 at 450 and 900m in the NCP. Unlike the dissolved organic matter, these above comparisons for POC (susp) do not indicate a common origin of POC (susp) for the SMB and NCP regimes.

6. SUMMARY

Isotopic signatures ($\Delta^{14}C$, $\delta^{13}C$, $\delta^{15}N$) of the soluble and particulate organic phases measured in this study did not prove, nor were they anticipated to be, ideal proxies for unequivocally defining the sources and cycling mechanisms of organic matter within the Santa Monica basin system.

However, these isotopic signatures, coupled with organic matter concentrations and fluxes, did provide clues to the sources of certain organic components and, to some extent, set quantitative limits to these sources. For example: (1) terrestrial inputs of organic matter from both natural and anthropogenic sources were estimated to be <5% for dissolved organic matter, <10% for suspended and sinking particulate organic matter, and <25% for sedimentary organic matter; (2) the isotopic signatures and concentrations of UV-oxidizable DOC were strikingly similar in the deep basin and at an open-ocean site in the North Central Pacific, suggesting a common history for a major fraction of the DOC in the subsurface waters at both sites; and (3) episodic resuspension of"old" (14C-depleted) shelf and/or slope sedimentary organic matter appeared to be reflected in the low ^{14}C activities of the POC (susp) and POC (sink) in the basin subsurface waters.

There were no significant correlations for the $\Delta^{14}C$, $\delta^{13}C$ and $\delta^{15}N$ signatures between the suspended and sinking particulate organic matter, sedimentary organic matter, and soluble organic matter which would have been useful in delineating phase transformations among these organic pools. The multiplicity of fractionation processes within and between organic phases, plus the wide ranges in end-member isotopic signatures, makes it difficult, if not impossible, to rely upon isotopic measurements alone for future studies of this nature; studies which must couple isotopic measurements with chemical analysis of process-oriented tracers (e.g. organic biomarkers).

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