

Radiocarbon evidence of fossil-carbon cycling in sediments of a nearshore hydrocarbon seep

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WIDESPREAD seepage of petroleum and natural gas in the southern California continental borderland¹⁻⁴ provides an opportunity to study the long-term fate and biogeochemical effects of hydrocarbons in nearshore sedimentary environments. The hydrocarbons that enrich seep sediments have been hypothesized to serve as a carbon and energy source for sediment metabolism and infaunal populations⁵⁻⁹. Here we present ¹⁴C natural abundances in sediment total organic carbon (TOC), pore-water dissolved inorganic carbon (DIC) and infauna from in and around a hydrocarbon seep off southern California which were measured to help test this hypothesis. Concentrations of ¹⁴C in each pool reflect the admixture of fossil (¹⁴C-depleted) seep-derived carbon with carbon from the euphotic zone. The ¹⁴C depletion in TOC and DIC increased with proximity to the seepage zone and with sediment depth; ¹⁴C abundances differed between meiofauna and macrofauna, suggesting that the two groups incorporate fossil carbon in different ways. The results indicate that fossil carbon can indeed comprise a major component of these carbon pools in nearshore seep sediments.

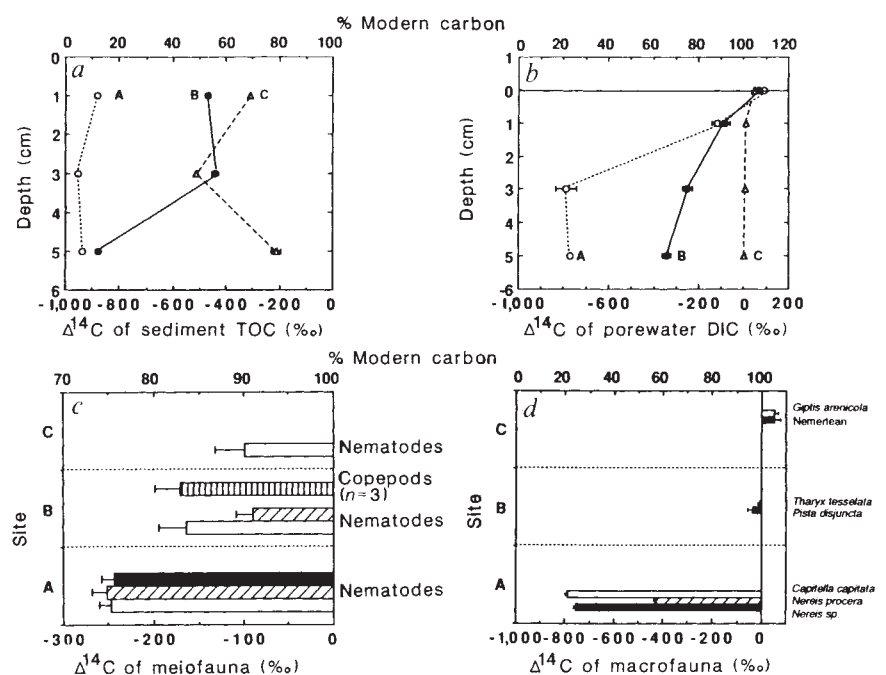
The Isla Vista hydrocarbon seep (34°19' N, 119°50' W), located offshore from Santa Barbara, differs from the deeper, well studied seeps of the Gulf of Mexico^{10,11} in its shallow depth

(16 m) and nearshore location (~0.5 km) and in the absence of vent-type fauna. The area is characterized by fine, well sorted Quaternary sands which are directly underlain by highly fractured Miocene Monterey shale, and the major seep trends in the region lie along active strike-slip and thrust faults^{2,4,12}. Total rates of petroleum seepage for the Coal Oil Point region, of which the Isla Vista seep is a discrete seep, range from 15 to 400 barrels per day⁴. Sediment hydrocarbons at the Isla Vista seep consist of abundant natural gases (C₁-C₅) and higher molecular weight aliphatic and aromatic compounds^{13,14} (J.E.B., manuscript in preparation).

We obtained samples of TOC, DIC, meiofauna and macrofauna for ¹⁴C analysis from cores collected at three sites: A, at the centre of the Isla Vista seep where extensive petroleum and hydrocarbon gas seepage occur; B, 20 m to the north of A on the periphery of the seep where there is little oil and gas evolved but large numbers of weathered tar particles; C, 1 km to the east of A and B, which served as a control site. In nearshore environments, ¹⁴C is a more useful carbon tracer for biogeochemical and trophic-dynamic studies than is ¹³C because its sources are distinct and because it has a greater natural dynamic range¹⁵. We measured the ¹⁴C abundances of 58 samples, some as small as 25 µg, by accelerator mass spectrometry to precisions of 1-10% depending on their size¹⁶. Although the qualitative nature of carbon and energy flow through Isla Vista seep sediments was inferred from previous studies^{8,9} of community metabolism, quantitative estimates were not possible. Here we use natural abundances of ¹⁴C to provide estimates of the extent of fossil-carbon cycling in the major carbon pools of seep and non-seep sediments.

The quantity and ¹⁴C content of TOC at the three sites provides a basis for estimating the type of sediment organic carbon available for subsequent sediment metabolism and faunal incorporation (Fig. 1a; Table 1). The depth-averaged (0-6 cm) ¹⁴C of TOC at site C (mean = 65.6 ± 15.4% modern, modern ¹⁴C is defined as the 1950 AD atmospheric ¹⁴C concentration) was comparable to other California borderland surficial sediments, including those from the Santa Barbara (0-19 cm; 72.1% modern) and San Nicolas (0-5 cm; 70.3% modern) basins¹, but

FIG. 1 Natural ¹⁴C abundances, expressed as percent modern carbon and $\Delta^{14}\text{C}$, in a, sediment TOC, b, pore-water DIC, c, meiofauna and d, macrofauna in sediments at sites A, B and C near the Isla Vista hydrocarbon seep. Values for TOC and DIC represent the mid-point of the depth interval sampled. Organisms were collected from the 0-2 cm depth interval only. Bars indicate a measurement error of 1 standard deviation for individual samples (TOC, DIC and macrofauna) or composite samples (meiofauna). Sediments were dried, treated with dilute HCl to remove carbonates and stored dry and in the dark. Pore waters were collected by filter-centrifuging core sections through combusted GF/F glass-fibre filters and stored under N₂ at 5 °C in the dark using HgCl₂ as a preservative. Organisms were separated from surface sediments (0-2 cm) by elutriation and hand-sorting into clean 0.2-µm-filtered sea water where they were allowed to clear their guts for 24 h. Animals were then transferred to distilled water and dried at 60 °C for 48 h. Sediment and faunal samples were subsequently combusted at 900 °C, and pore waters were acidified with concentrated phosphoric acid. The evolved CO₂ was reduced under an atmosphere of H₂ to graphite²⁶, which was subsequently analysed using the Simon Fraser University accelerator mass spectrometry facility at McMaster University²⁷. Measurements of ¹³C content, required for ¹⁴C normalization, were not made directly on the samples owing to the small amounts of material available. Instead we used published measurements^{1,20-22,28,29} for ¹³C content representative of each sample type. The ¹⁴C determinations were not affected by uncertainties



in ¹³C content within the total precision of the radiocarbon measurements. Radiocarbon contents and apparent ages of the samples are expressed in conventional notation³⁰. $\Delta^{14}\text{C}$ is the per mil deviation from the 'standard' nineteenth century wood.

TABLE 1 Profiles of Isla Vista seep sediments

Site	Depth (cm)	TOC (%)	DIC (mM)	Bacteria ($\times 10^8 \text{ cm}^{-3}$)	^{14}C Activity		TOC oil fraction (%)	Respired DIC (%)
					TOC (% modern)	DIC (% modern)		
A	0	—	2.2±0	—	—	109.3±0.2	—	—
	0-2	1.8	7.4±1.7	32.0±3.4	12.1±0.3	88.5±2.5	84	14
	2-4	1.9	7.6±2.2	37.0±0.6	4.6±0.3	21.4±4.7	92	81
	4-6	1.8	9.4±0.9	51.0±13.0	6.2±0.3	23.0±0.8	90	79
B	0	—	2.2±0	—	—	107	—	—
	0-2	0.3	3.7±0.9	20.0±4.1	53.0±1.0	91.8±2.4	24	25
	2-4	1.6	2.9±0.7	13.0±3.0	56.0±1.3	75.0±2.1	40	67
	4-6	2.8	4.3±0	8.6±2.0	12.4±0.4	65.9±2.0	90	43
C	0	—	2.2±0	—	—	104.9±1.9	—	—
	0-2	0.2	2.2±0	9.0±1.8	69.1±0.8	101.0±4.1	—	11
	2-4	0.2	2.2±0.3	8.0±1.4	48.8±0.8	100.7±4.4	—	7
	4-6	0.2	2.2±0.1	6.6±2.0	78.9±1.7	100.4±2.6	—	14

TOC and DIC were determined using standard methods²⁴; bacteria were enumerated by epifluorescence microscopy²⁵. The fraction of TOC derived from petroleum carbon (0% modern C) for each depth at sites A and B was estimated using a mass-balance relationship which assumed that linear mixing of average site-C-type sediment (mean TOC=0.2%, mean ^{14}C =65.6±15.4% modern) TOC with petroleum carbon results in TOC having the measured activities at sites A and B. The maximum potential fraction of DIC derived from respired organic carbon at each depth was also calculated by mass balance assuming that linear mixing of organic-carbon-derived DIC with sediment surface water (0 cm) DIC takes place to give the observed pore-water DIC concentration and ^{14}C activity at sites A, B and C. Values for TOC at all sites and for DIC at site C were determined previously⁹. TOC, DIC and bacteria are means of replicate cores with an uncertainty of 1 standard deviation. DIC ^{14}C activity at 0 cm at site B was not measured but was assumed to be the average of the activities measured at 0 cm at sites A and C.

did not show a regular ^{14}C pattern with depth. Assuming that the average sediment at site C typifies non-seep sediments in the region, the ^{14}C concentrations of sediments at sites A and B may be used to estimate the amount of petroleum carbon in site A and B sediments (Table 1). The TOC at site A contained 84–92% seep-derived, non-volatile carbon and was depleted in ^{14}C at even the shallowest depths. The TOC from site B resembled normal borderland (site C) sediment near the surface but was similar to the hydrocarbon-rich sediment of site A at 4–6 cm.

The abundance of ^{14}C in DIC (Fig. 1b) allows us to estimate the maximum potential remineralization of sediment organic carbon. We assumed that DIC derived from the complete oxidation of 'average' bulk TOC at each depth mixes linearly with DIC from the sediment/seawater interface (Table 1). At site C, advective and diffusive mixing of pore-water DIC with DIC from overlying sea water limited the steady-state contribution of DIC from TOC remineralization to no more than 14%. If we assume that DIC is produced locally in seep (sites A and B) sediments, up to ~80% of the steady-state DIC in site A pore waters is potentially derived from the remineralization (presumably mediated by high rates of sulphate reduction at site A⁹) of TOC and pore-water dissolved organic compounds (J.E.B., manuscript in preparation). In contrast, up to ~70% of DIC from site B may be derived from organic carbon respiration, but this is under suboxic rather than sulphate reducing conditions⁹. Another potential mechanism contributing to elevated fossil DIC in pore waters is its transport from the deep sub-surface reservoir to shallow sediments in formation waters¹⁷. Although our data show significant concentrations of fossil DIC near the seep centre, they do not distinguish between potential sources of DIC as all ultimately arise from fossil organic carbon. The high DIC concentrations, bacterial abundances (Table 1) and rates of metabolism^{8,9} at site A suggest, however, that at least a portion of the fossil DIC in these sediments is produced by recent remineralization of organic carbon.

Nematodes comprised the bulk of meiofauna sampled, and harpacticoid copepods were present in sufficient quantities for ^{14}C measurement at site B only (Fig. 1c). Meiofauna (63–500 μm equivalent spherical diameter, 0.8–1.0 μg per organism) feed by selecting material from the surfaces of sediment grains or in sediment interstices.¹⁸ The ^{14}C contents of meiofauna at site C indicate that their primary source of nutritive carbon was contemporary. Without specifying trophic or assimilatory pathways, we deduced the net incorporation of sedimentary, and hence

fossil, organic carbon at the seep (sites A and B). To estimate the fraction of meiofauna carbon derived from sedimentary TOC we assumed that organisms incorporated carbon from a mixture of sediment TOC and euphotic organic carbon, which was similar in ^{14}C content to the surface DIC¹⁹ (Table 2). The meiofauna from all three sites obtained 60–65% of their carbon from other than average bulk TOC, whether the sediment carbon was 82% fossil (at site A) or was typical borderland sediment (at site C). Stable-carbon isotope evidence indicates that meiofauna can select specific subfractions of sediment organic matter^{20–22}, which, in the seep environment, may include more assimilable and nitrogen-rich organic matter²³ than hydrocarbons. Alternatively, meiofauna may not feed in the most hydrocarbon-rich microenvironments to avoid effects of toxicity. Either scenario suggests that certain meiofauna regulate their incorporation of carbon in hydrocarbon-rich environments.

The ^{14}C abundances of deposit-feeding macrofauna (primarily polychaetes) were more variable than meiofauna (Fig. 1d). The fraction of their carbon derived from fossil carbon (Table 2) equalled the fraction of oil in surface sediment (0–2 cm) TOC (Table 1), within reasonable uncertainty. Site C macrofauna were not depleted in ^{14}C at all with respect to hypothetical euphotic organic matter suggesting, along with the ^{14}C DIC data for site C (Table 1, Fig. 1b), that this TOC is refractory and of low nutritive value, accounting for its mean 3,550-yr equivalent age. Of the organisms analysed, the greatest amounts of fossil carbon were incorporated by site A polychaetes

TABLE 2 ^{14}C in fauna and surface sediment

	Site		
	A	B	C
Surface sediment ^{14}C (% modern C)	12.1±0.3	53.0±1.0	69.1±0.8
Meiofauna ^{14}C (% modern C)	75.3±0.7	84.5±4.2	90.1±3.3
Carbon from sediment TOC (%)	35	37	41
Macrofauna ^{14}C (% modern C)	34.7±14.0	98.2±2.1	105.2±1.6
Carbon from sediment TOC (%)	77	16	0

The percentage of carbon derived from surface-sediment TOC in each faunal group was estimated by assuming that organisms use carbon from a mixing line with the carbon of surface sediment TOC and sediment-supplied organic carbon (assumed to be similar in radiocarbon signature to sediment-surface DIC¹⁹) as endmembers.

(Fig. 1d). The data show that macrofauna, unlike meiofauna, do not discriminate among sources of organic matter with different fossil-carbon contents and sequester their body carbon in direct proportion to sediment TOC, regardless of the specific quality of the organic matter (for example, C/N is ~ 20 at site A⁹).

The large number of documented hydrocarbon seeps in the southern California continental borderland²⁻⁴ indicates that the extensive biogeochemical cycling of hydrocarbon-derived carbon described here in Isla Vista seep sediments could be a widespread regional, if localized, phenomenon. Rates of important geochemical processes including community oxygen meta-

bolism and sulphate reduction are significantly enhanced in seep sediments⁹. Although sediments at the Isla Vista seep have similar types of organisms as non-seep coastal sediments, the numbers of organisms and the distribution of individual taxa are significantly altered⁵⁻⁷. We suggest that these processes and distributions result, at least in part, from extensive incorporation of fossil carbon into seep sediments and its subsequent use as a carbon and energy source by sedimentary assemblages. Careful extrapolation of the information derived from studies of natural hydrocarbon seepage may also provide information on the fate and effects of chronic hydrocarbon inputs to other nearshore sedimentary environments. □

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Evidence from chronosequence studies for a low carbon-storage potential of soils

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OVER most of the Earth's land surface, the amount of carbon stored in soil organic matter exceeds by a factor of two or three the amount stored in living vegetation. This pool of soil carbon is large (1.5×10^{18} g)^{1,2} and plays a dynamic part in the geochemical carbon cycle. Prentice and Fung³ have suggested that terrestrial vegetation and soils would act as a large sink for atmospheric carbon dioxide if its concentration were twice the present level. Here I use data from chronosequence studies to show that the production of refractory humus substances in soils sequesters only $\sim 0.4 \times 10^{15}$ g C yr⁻¹ from the atmosphere, accounting for just 0.7% of terrestrial net primary production. Moreover, agricultural practices tend, on balance, to cause a release of soil carbon to the atmosphere^{4,5}. Thus if the terrestrial biosphere is indeed to act as a carbon sink under future elevated levels of carbon dioxide, this would be more likely to be the result of changes in the distribution and biomass of terrestrial vegetation than of changes in the accumulation of soil organic matter.

The carbon stored in soil organic matter represents the long-term net balance of photosynthesis and total respiration in terrestrial ecosystems. Radiocarbon dates of humic materials in the lower soil profile are frequently $>1,000$ years⁶. New land surfaces produced by disturbances such as volcanic eruptions or glacial retreat yield youthful soils with little or no organic matter. In these soils, the long-term average rate of accumulation of soil organic matter is easily calculated from measurements of bulk density and the percentage of organic carbon at each depth in the soil profile of depth N . Soil organic carbon (g C m^{-2}) = $\sum_{D=0}^N 10,000 D \rho(D) P(D)$ where $\rho(D)$ and $P(D)$ are the bulk density in g cm^{-3} and the percentage of organic carbon,

respectively, in depth interval D . The long-term average rate of accumulation is obtained by dividing the carbon content of the profile by the estimated or measured age. Interval-specific accumulation rates can be calculated from the difference between two soil profiles in the same chronosequence, divided by the difference in their ages.

During soil development, organic matter often shows an initial period of rapid increase for up to 3,000 years, followed by a lower rate of accumulation that may continue for millennia⁷. At any time, the long-term average rate of accumulation is an overestimate of the current rate of accumulation in most soils (Fig. 1). As most soils are at least 3,000 years old, however, the average long-term rate for 3,000- to 10,000-year-old soils provides an upper limit for estimates of soil carbon accumulation during the Holocene and in possible future climates.

In upland ecosystems, the long-term rate of carbon storage varies from $0.2 \text{ g C m}^{-2} \text{ yr}^{-1}$ in some polar deserts to $>10 \text{ g C m}^{-2} \text{ yr}^{-1}$ in some forests (Table 1). Considering the paucity of studies and the range of environments represented, the rates are surprisingly uniform. The long-term rate for 16 soils that are 3,000 to 10,000 years old, $2.4 \pm 0.70 \text{ g C m}^{-2} \text{ yr}^{-1}$ (1 s.e.) (Table 1), can be used to calculate the maximum potential for the present accretion of soil organic matter.

An annual production of $2.4 \text{ g C m}^{-2} \text{ yr}^{-1}$ of humic substances implies a total storage of $0.32 \times 10^{15} \text{ g C yr}^{-1}$ in upland ecosystems under natural vegetation ($133 \times 10^6 \text{ km}^2$; ref. 5). The actual net storage of organic carbon in upland soils is probably less than $0.32 \times 10^{15} \text{ g C yr}^{-1}$, because this value assumes that all upland soils are only 3,000-10,000 years old. Following a similar approach, Armentano and Menges⁸ found that before recent disturbance, soils in wetlands, bogs and peatlands ($3.5 \times 10^6 \text{ km}^2$) were a sink for up to $0.08 \times 10^{15} \text{ g C yr}^{-1}$. Their value may be too low, given recent higher estimates of global wetland area⁹. Nevertheless, assuming these estimates are reasonable, the total storage of soil organic matter ($0.40 \times 10^{15} \text{ g C yr}^{-1}$) is $\sim 0.7\%$ of recent estimates of net primary production on land ($60 \times 10^{15} \text{ g C yr}^{-1}$; ref. 10), but 20% of that storage occurs in wetland ecosystems which cover only 2% of the land surface. A similar approach shows that the net storage of carbon in desert-soil carbonate is also a minor flux in the global carbon cycle ($<0.023 \times 10^{15} \text{ g C yr}^{-1}$; ref. 11).