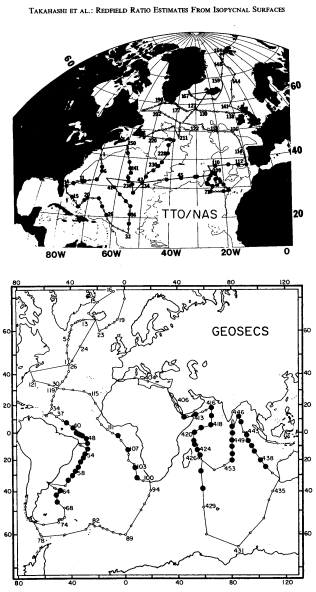
Today:

- Quick review: “Redfield” ratios on isopycnal surfaces
  OM flux estimates from sediment traps

- Selective degradation of OM?

- Turnover times.

- Importance of terrestrial OM (biomarker and ^{13}C data).



1. Takahashi et al., 1985

Estimate C:N:P:-O_2 regeneration ratios from thermocline nutrient chemistry.

(O_2:P along isopycnals)

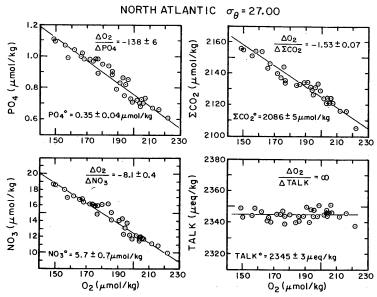
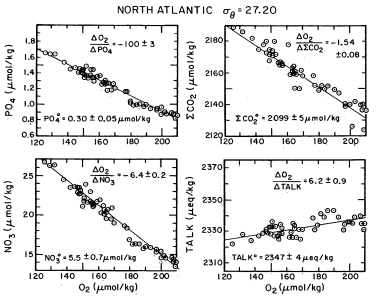


Fig. 4a



O_2:P = -138

O_2:P = -100

Observed slopes reflect decomposition + mixing

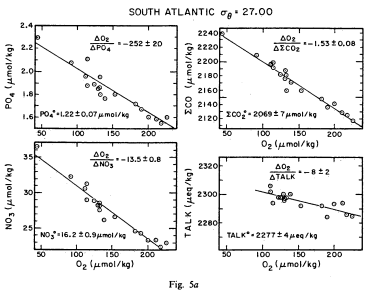
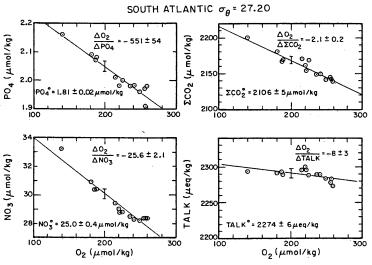
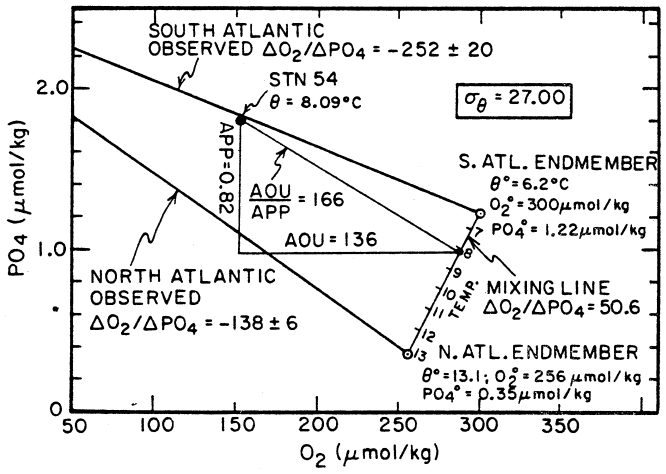


Fig. 5a



O_2:P = -252

O_2:P = -551



Use potential temperature to account for mixing

TAKAHASHI ET AL.: REDFIELD RATIO ESTIMATES FROM ISOPYCNAL SURFACES

TABLE 5. Molecular Ratio of P, N, C, O_2, and $CaCO_3$ Changes in the Atlantic and Indian Oceans

	Number of Stations	σ_θ	P	N	CO_2	$(O_2 - 2N)$	$-O_2$	$CaCO_3$	
Redfield ratio*	—	—	1	16	106	106	138	—	138
North Atlantic	32	27.00	1	17.6 ± 0.6	97 ± 9	130 ± 6	165 ± 7	15 ± 4	
	57	27.20	1	16.8 ± 0.5	88 ± 6	139 ± 6	173 ± 6	8 ± 3	
South Atlantic	16	27.00	1	16.7 ± 0.7	102 ± 7	131 ± 6	165 ± 6	8 ± 2	
	14	27.20	1	16.7 ± 1.2	95 ± 10	150 ± 2	182 ± 9	8 ± 4	
Atlantic mean	119	27/27.2	1	17.0 ± 0.4	96 ± 6	138 ± 9	171 ± 8	10 ± 4	
South Indian	22	27.00	1	15.2 ± 0.6	112 ± 6	138 ± 7	169 ± 8	15 ± 4	
	21	27.20	1	14.5 ± 0.5	125 ± 7	145 ± 5	174 ± 6	19 ± 6	
Indian mean	43	27/27.2	1	14.9 ± 0.4	119 ± 5	142 ± 5	172 ± 5	17 ± 4	
Atlantic and Indian mean	162	27/27.2	1	16.3 ± 1.1	103 ± 14	140 ± 8	172 ± 7	12 ± 5	172

For the oxidation of nitrogen a reaction $NH_3 + 2O_2 = NO_3^- + H_2O + H^+$ (i.e., $N : O_2 = 1 : 2$) is assumed.

*Utilization by plankton after *Redfield et al.* [1963].

2. OM flux estimates from sediment traps

Annual biogenic particle fluxes to the interior of the North Atlantic Ocean; studied at 34°N 21°W and 48°N 21°W

SUSUMU HONJO* and STEVEN J. MANGANINI*

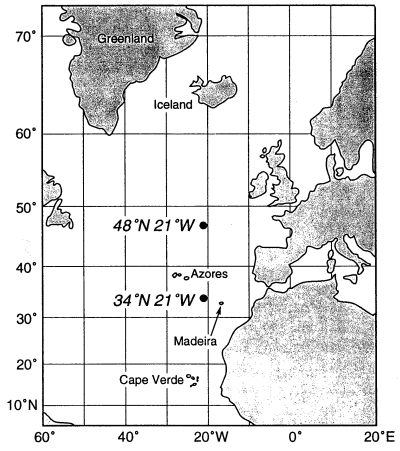


Fig. 1. Location of NABE time-series stations.

Particle fluxes in the North Atlantic Bloom Experiment

Moored sediment trap array, year-long deployments

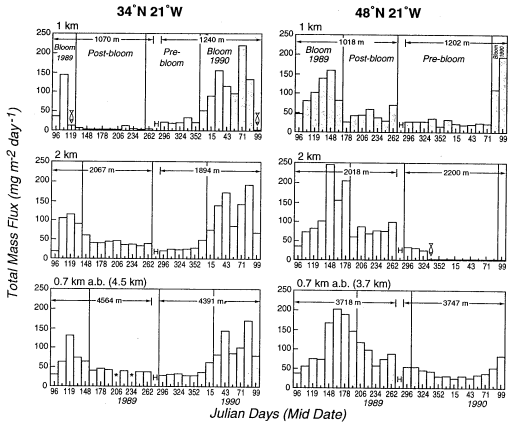


Fig. 3. Annual variability of mass flux at 34°N and the 48°N at three depths with distinction between bloom, pre- and post-bloom episodes with 14 days' resolution (HONJO and MANGANINI, 1992). The boundaries of each episode were first defined at 1 km; then these boundaries were shifted to one period later for the 2-km depth; and then again to one more period later for the 0.7 km a.b. depth. The fish symbol indicates the period when the argentine fish (*Argentina sphyraena*) was accidentally caught, spoiling the flux data thereafter. The same species was caught in all three incidents. *Sample lost during transportation. H: hiatus in deployment due to change of arrays.

Short (1 cup) offset in total mass fluxes w. depth => fast sinking (50 – 200 m/d)

Implies packaging / ballasting

Strong seasonality in total mass flux

Total flux increases with depth (1-2 km)

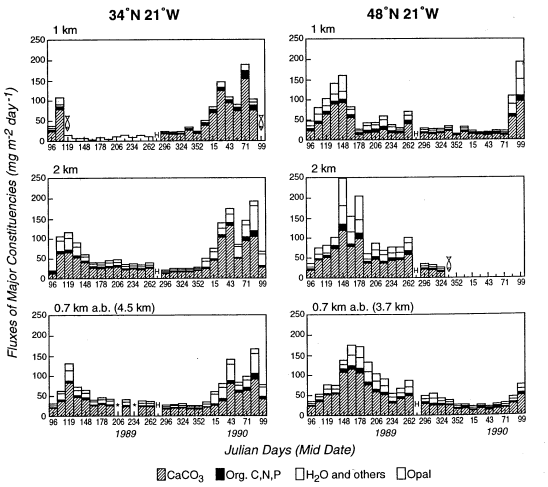
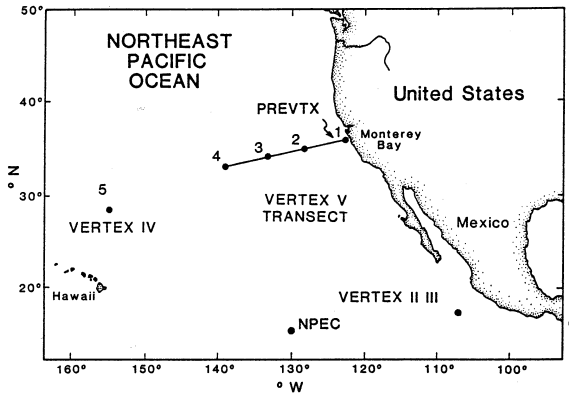


Fig. 6. Annual variability of the major biogenic fluxes at the 34 and 48°N stations at three depths. "H_2O and others" includes water from organic matter (reconstructed from hydrogen flux obtained from elemental analyzer), opaline skeletons and other ignition losses. A small-to-trace mass flux of lithogenic particles, such as clay and air-borne minerals, is included in the category (Honjo and Manganini, 1992). The fish symbol indicates the period when an argentine fish (*Argentina sphyraena*) was accidentally caught, spoiling the flux data thereafter. *Sample lost during transportation. H: hiatus in deployment due to change of arrays.

Strong seasonality in biogenic fluxes (note mass units, not moles of C)

$CaCO_3$ flux increases with depth @ 48N

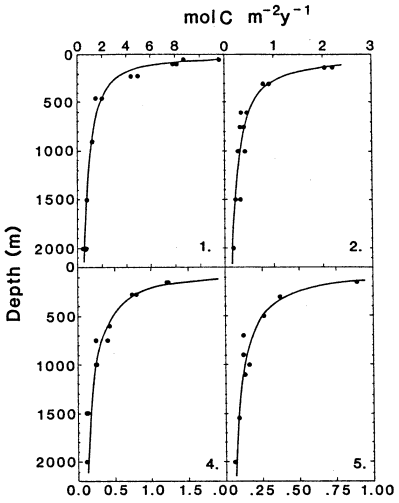
(trapping efficiency)



VERTEX: carbon cycling in the northeast Pacific

John H. Martin,* George A. Knauer,*‡ David M. Karl† and William W. Broenkow*

Short deployments of floating arrays of sediment traps



C flux data fitted with the normalized power function, $F = F_{100}(z/100)^b$

Dramatic attenuation of the POC flux with depth at each site

Fluxes decrease moving offshore

Derived similar curves for C, N, P, and O_2 demand

$-O_2$:P and $-O_2$:C

> Redfield

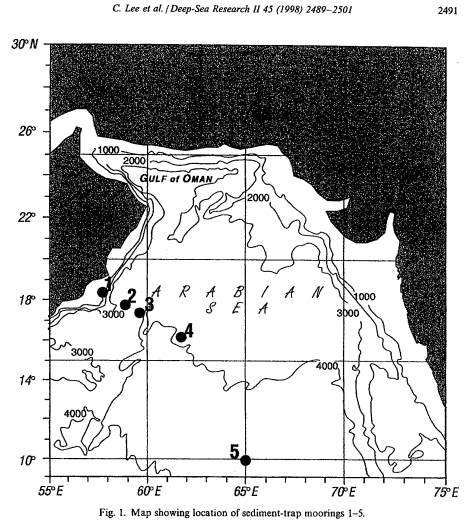


Fig. 1. Map showing location of sediment-trap moorings 1–5.

Lee et al. (1998)
Wakeham et al. (1997)
Lee et al. (2004)

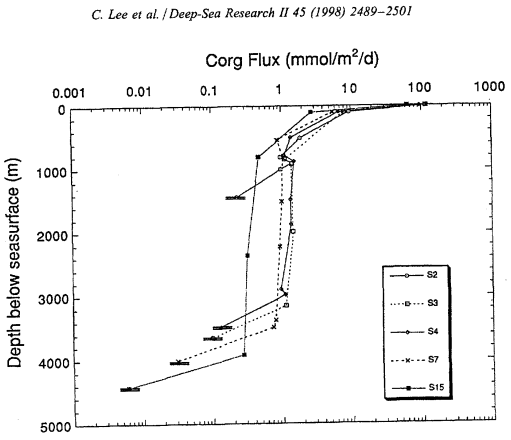


Fig. 2. Average organic carbon fluxes at all sites as a function of depth. The double bars indicate the depth of the sea floor at each mooring location. Numerical values for fluxes in this and other figures appear in Table 2.

^{14}C Pri. Prod.

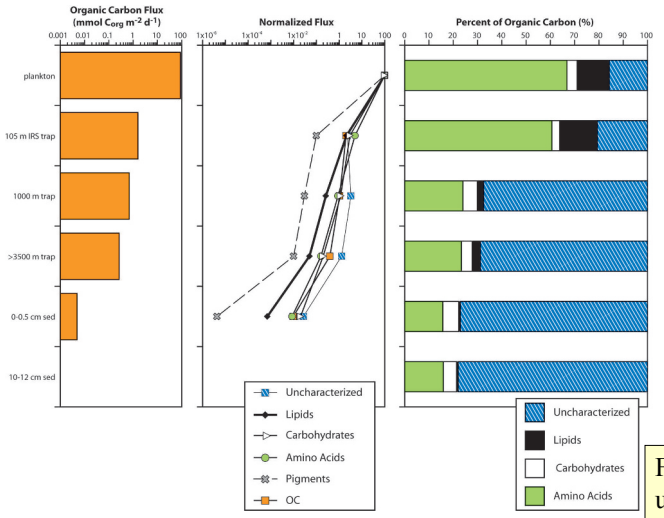
^{234}Th scavenging model

Moored traps

%C x Holocene sed rate

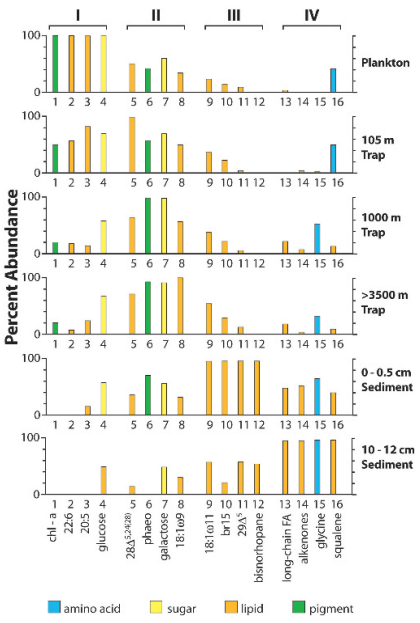
Strong attenuation (at top and bottom)
Different methods reflect different timescales

All compound classes show attenuation; amounts differ



Lee et al., 2004, from Wakeham et al., 1997

Fraction uncharacterized increases w. depth



Empirical groupings of biochemicals by "behavior" – patterns include:

I. Selective degradation

II. Mid-depth maximum

III. Enriched in surface seds

IV. Most resistant

Lee et al., 2004, from Wakeham et al., 1997

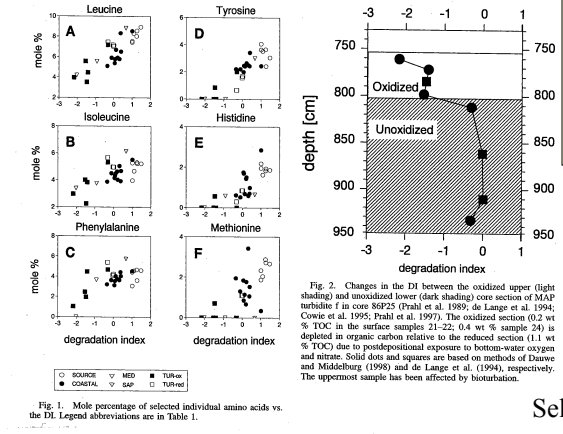


Fig. 1. Mole percentage of selected individual amino acids vs. the DI. Legend abbreviations are in Table 1.

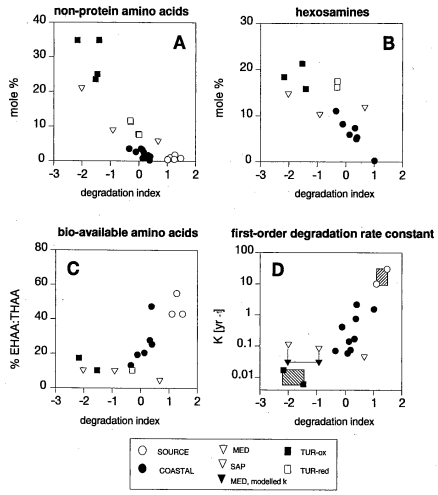
Fig. 2. Changes in the DI between the oxidized upper (light shading) and unoxidized lower (dark shading) core section of MAP turbidite f in core 86P25 (Prahl et al. 1989; de Lange et al. 1994; Cowie et al. 1995; Prahl et al. 1997). The oxidized section (0.2 wt % TOC in the surface samples 21–22; 0.4 wt % sample 24) is depleted in organic carbon relative to the reduced section (1.1 wt % TOC) due to postdepositional exposure to bottom-water oxygen and nitrate. Solid dots and squares are based on methods of Dauwe and Middelburg (1998) and de Lange et al. (1994), respectively. The uppermost sample has been affected by bioturbation.

Principal Components Analysis of amino acid composition of sediments;

Factor 1 loadings interpreted as "degradation index"

Selective preservation:

Dauwe et al., 1999 mostly coastal, but also sapropel, turbidite



More strongly degraded OM (low DI values) correlates with low OM decomposition rate constant. (Selective degradation, with consequences – a decrease in reactivity of the remaining OM)

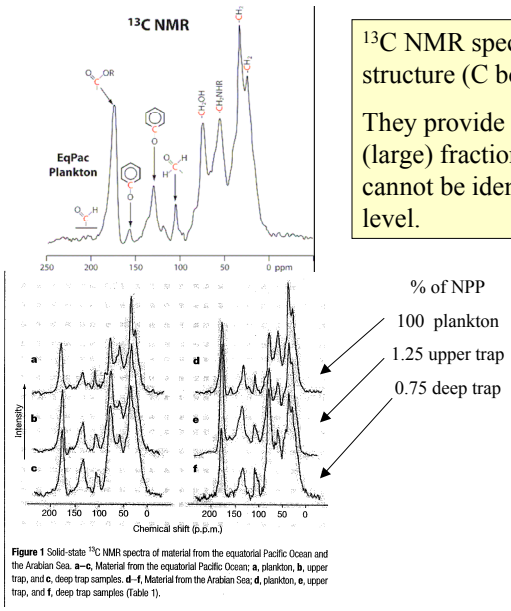


Figure 1 Solid-state ^{13}C NMR spectra of material from the equatorial Pacific Ocean and the Arabian Sea. **a–c**, Material from the equatorial Pacific Ocean; **a**, plankton, **b**, upper trap, and **c**, deep trap samples. **d–f**, Material from the Arabian Sea; **d**, plankton, **e**, upper trap, and **f**, deep trap samples (Table 1).

^{13}C NMR spectra reflect bulk chemical structure (C bonds).

They provide a way to see "into" the (large) fraction of sedimentary OM that cannot be identified at the compound level.

% of NPP
100 plankton
1.25 upper trap
0.75 deep trap

Hedges et al., 2001 – "Evidence for non-selective preservation of organic matter…"

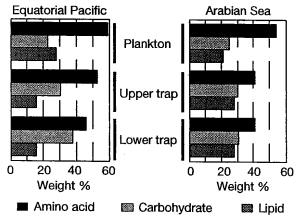


Figure 2 Calculated weight percentages of biochemicals in the samples from the equatorial Pacific Ocean and the Arabian Sea. See Methods for a description of the techniques used to acquire and model these spectral data.

Use the ^{13}C-NMR spectra to calculate "nominal biochemical equivalents" (AA, carbohydrate, lipid).

Plankton, upper trap, and deep trap all very similar, despite ~ 98% OM loss

No evidence of enrichment of a trace (aliphatic) residue, or of increased unsaturation (humification)

Hedges et al., 2001
Non-selective preservation of organic matter

Clear selectivity at compound level (e.g., AA patterns, Dauwe), but not between broad compound classes?

They suggest physical protection of (~representative) OM.

What does bulk composition tell us?
Arnosti and Holmer (2003)

OM oxidation rates (O_2, SR, Fe, Mn) and extracellular DOM hydrolysis rates in Skagerrak sediments.

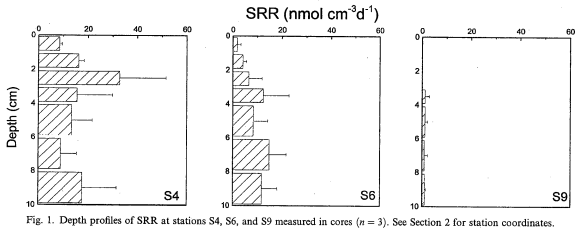


Fig. 1. Depth profiles of SRR at stations S4, S6, and S9 measured in cores ($n = 3$). See Section 2 for station coordinates.

O_2:	7.8	9.6	8.0	mmol O_2 /m^2/dy
SR:	2.9	2.3	0.2	
Fe:	7.5	4.1	0	mmol C /m^2/dy
Mn:	0	0	6.4	

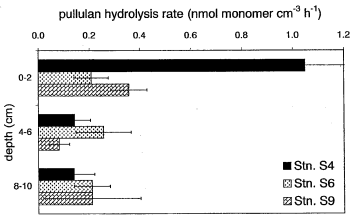


Fig. 2. Pullulan hydrolysis rates at three depth intervals in cores from stations S4, S6, and S9. Error bars show variation among three cores.

Measure the hydrolysis rates of fluorescently labeled polysaccharides in cores and homogenized sediment (drop in molecular weight), combine with DOC data to estimate DOC turnover rates (dy^{-1})

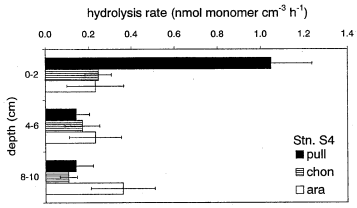


Fig. 3. Pullulan, chondroitin sulfate, and arabinogalactan hydrolysis rates at three depth intervals in intact cores from station S4. Error bars show variation among three cores.

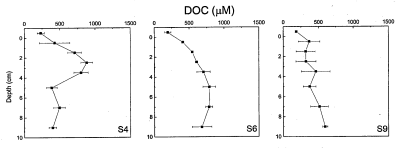


Fig. 6. DOC in porewater from stations S4, S6, and S9. Error bars show variation among three cores.

C. Arnosti, M. Holmer / Estuarine, Coastal and Shelf Science 58 (2003) 197–208

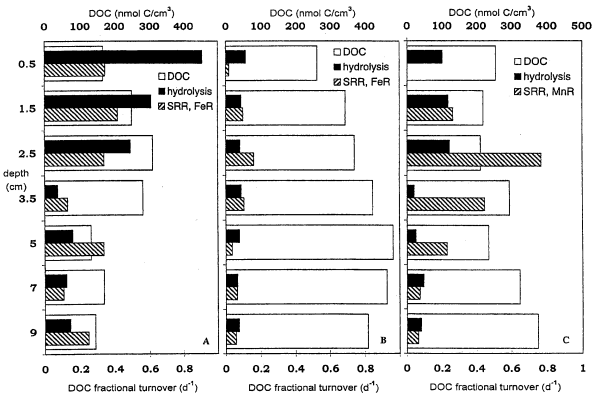
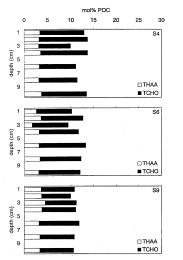


Fig. 7. DOC concentration and fractional turnover: (a) station S4; (b) station S6; (c) station S9. DOC concentration on a sediment-volume basis (white bars), theoretical fractional turnover of the DOC pool via hydrolysis (black bars), and 'real' fractional turnover via terminal remineralization (striped bars; SRR, sulfate reduction rate; FeR, iron reduction rate; MnR, manganese reduction rate). See text for details of turnover calculations.

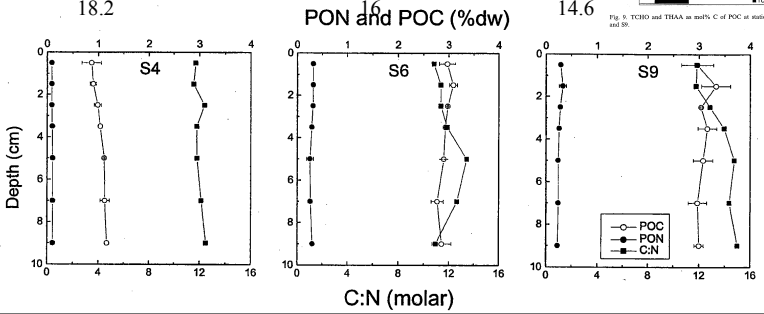
[DOC], and DOC turnover from hydrolysis and from remineralization rates

None of these cores seems rich (THAA and THCO are both low; C:N high; % POC not correlated with decomposition rate) yet the remineralization rates and DOC turnover rates are high



Total decomp rate (mmol/m2/dy):

18.2 16 14.6



Bulk chemistry solid-phase composition not a good indicator of quantity and quality of substrates for microbial communities.

Moodley et al (2002) – experimental study of benthic response to phytodetritus input

^{13}C-enriched phytoplankton slurry injected into benthic flux chambers – rapid processing (6% per day) (of solid-phase addition, not of DOC pool) including CO_2 release, and uptake by bacteria, foraminfera, and metazoans.

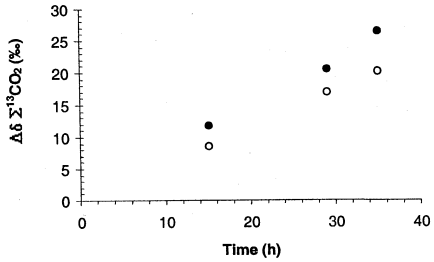


Fig. 1. ^{13}C-enrichment of total inorganic carbon ($\Delta\delta\Sigma^{13}CO_2$) versus time. Values from experimental chambers, ALBEX 2 (○) and ALBEX 3 (●)

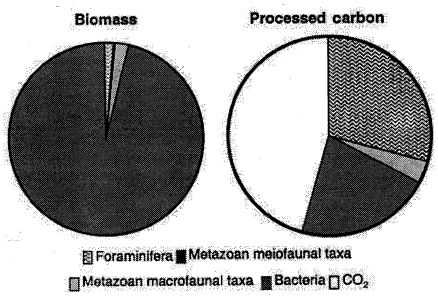


Fig. 2. Proportional division of biomass and processed carbon among the different benthic compartments. Fauna are those retained on a 300 µm sieve and values are average of the 2 experimental chambers

Biomass is dominated by bacteria. Processing includes CO_2 release (46%, mostly bacterial?), and uptake by bacteria (22%) and foraminifera (29%). A disproportionate role for foraminifera in rapid POC processing after phytodetritus input.

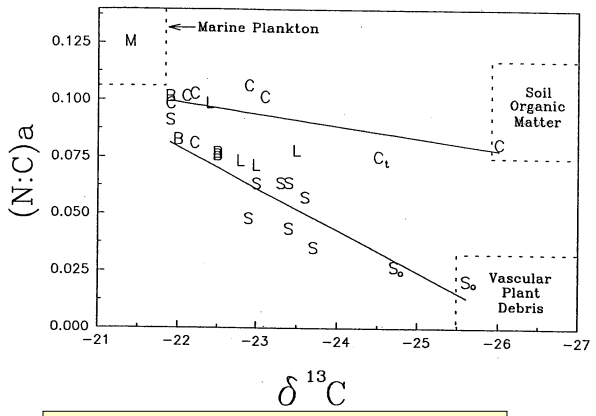
Contribution of terrestrial OM?

C:N ~ 106:16 ~ 6.6 (N:C ~ 0.15)

C:N

10

80



$\delta^{13}C$ mar ~ -20 o/oo, terr ~ -27o/oo

Keil et al., 1994

CAM

C3

C4

Grasses, corn, spartina

Marine plankton

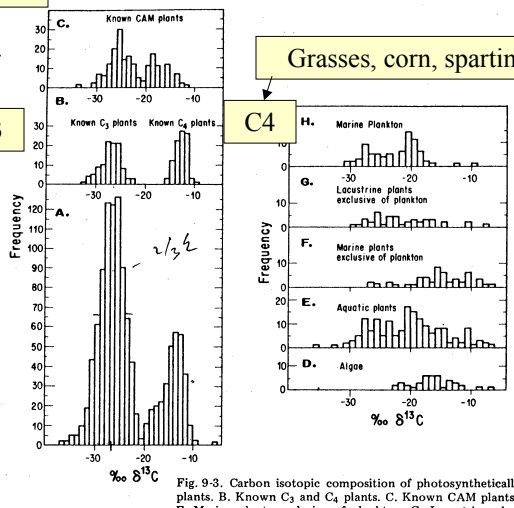
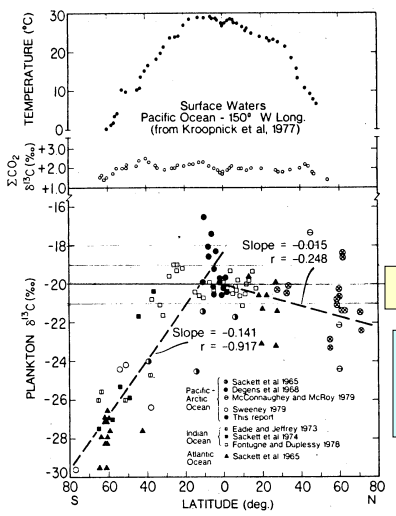


Fig. 9-3. Carbon isotopic composition of photosynthetically fixed carbon A. Terrestrial plants. B. Known C_3 and C_4 plants. C. Known CAM plants. D. Algae. E. Aquatic plants. F. Marine plants exclusive of plankton. G. Lacustrine plants exclusive of plankton. H. Marine plankton. Data from Bender (1968, 1971), Bender et al. (1973), Brown and Smith

"all" terrestrial plants

Deines, 1980

Plankton ^{13}C: ^{12}C ratio changes with latitude



Plankton $\delta^{13}C$ not constant

CO_2 availability (pCO_2, growth rate) (Goericke et al.)

Rau et al.

Goni et al. – lignin, bulk $\delta^{13}C$, biomarker $\delta^{13}C$, bulk ^{14}C

M. A. Goñi, K. C. Ruttenberg, and T. I. Eglinton

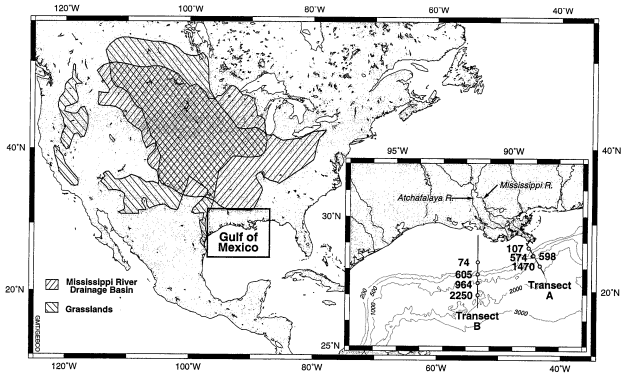


Fig. 1. Map of the drainage basin of the Mississippi River (U.S. Geological Survey Circular 1001), the extent of grasslands in North America (Sims and Coupland, 1979) and the marine sediment sampling locations in the Gulf of Mexico.

Impact of C4 plants on $\delta^{13}C$(terrestrial) and on interpretation of bulk sediment $\delta^{13}C$

Lignin composition – terrestrial vascular plants

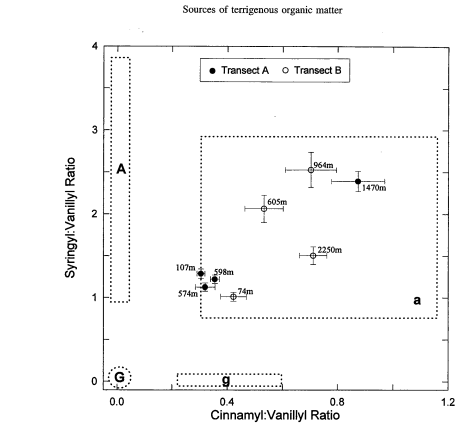


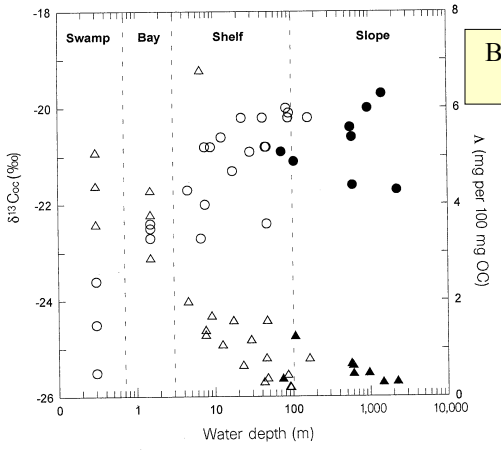
Fig. 6. Plot of cinnamyl:vanillyl (C/V) vs. syringyl:vanillyl (S/V) phenol ratios for Gulf of Mexico sediments. Included are the compositional ranges (delineated by dotted lines) of major vascular plant tissues (Hedges and Mann, 1979; Hedges et al., 1986; Goñi and Hedges, 1992) Tissue abbreviations: G, gymnosperm woods; g, gymnosperm needles; A, angiosperm woods; a, angiosperm leaves and grasses.

angiosperm

gymnosperm

woody

non-woody

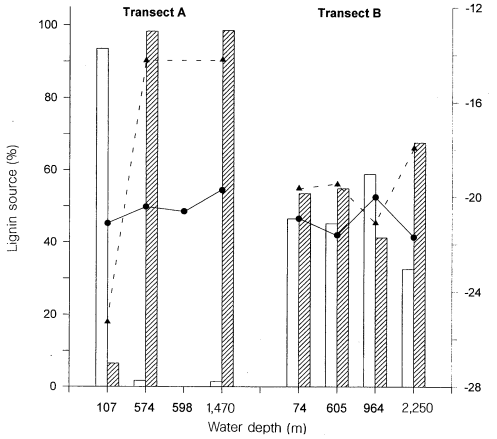


Bulk $\delta^{13}C$ near -20 o/oo by 100 m

Total lignin near 0 by 100 m

Hedges and Parker, Goni et al.

Evidence of little terrestrial organic matter in marine sediments?



Lignin-predicted $\delta^{13}C$ of C3-C4 terrestrial mixture matches observed bulk $\delta^{13}C$ of -20 o/oo

Measure the $\delta^{13}C$ of lignin (known terrestrial) in marine sediments, and use to estimate C3:C4 ratio of all terrestrial OM (bars). (assume lignin representative of all terrestrial OM)
C3 (-30 o/oo) white
C4 (-15 o/oo) shaded

An important role for fine-fraction C4 terrestrial OM in Gulf of Mexico marine sediments – is this global?