

Terrestrial Organic Carbon Inputs to Marine Sediments

Reading List

Hedges J.I. and Oades J.M. (1997) Comparative organic geochemistries of soils and marine sediments. *Org. Geochem.* **27**, 319-361.

Hedges J.I., Keil R.G. and Benner R. (1997) What happens to terrestrial organic matter in the ocean? *Org. Geochem.* **27**, 195-212.

Other reading:

Goni M.A., Ruttenger K.C. and Eglinton T.I. (1997) Sources and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico. *Nature*, **389**, 275-278.

Leithold & Blair (2001) Watershed control on the carbon loading of marine sedimentary particles. *GCA* **65**, 2231-2240.

Goni et al. (2005) The supply and preservation of ancient and modern components of organic carbon in the Canadian Beaufort Shelf of the Arctic Ocean. *Mar. Chem.* **93**, 53-73.

Schefuss et al. (2003) Carbon isotope analyses of *n*-alkanes in dust from the lower atmosphere over the central eastern Atlantic. *GCA* **67**, 1757-1767.

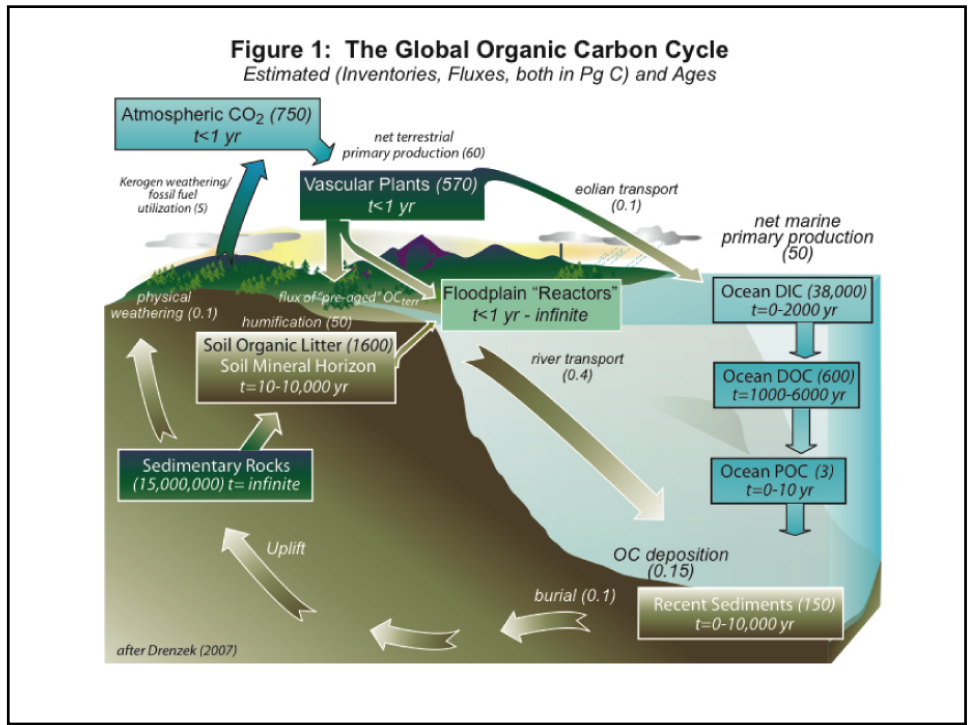
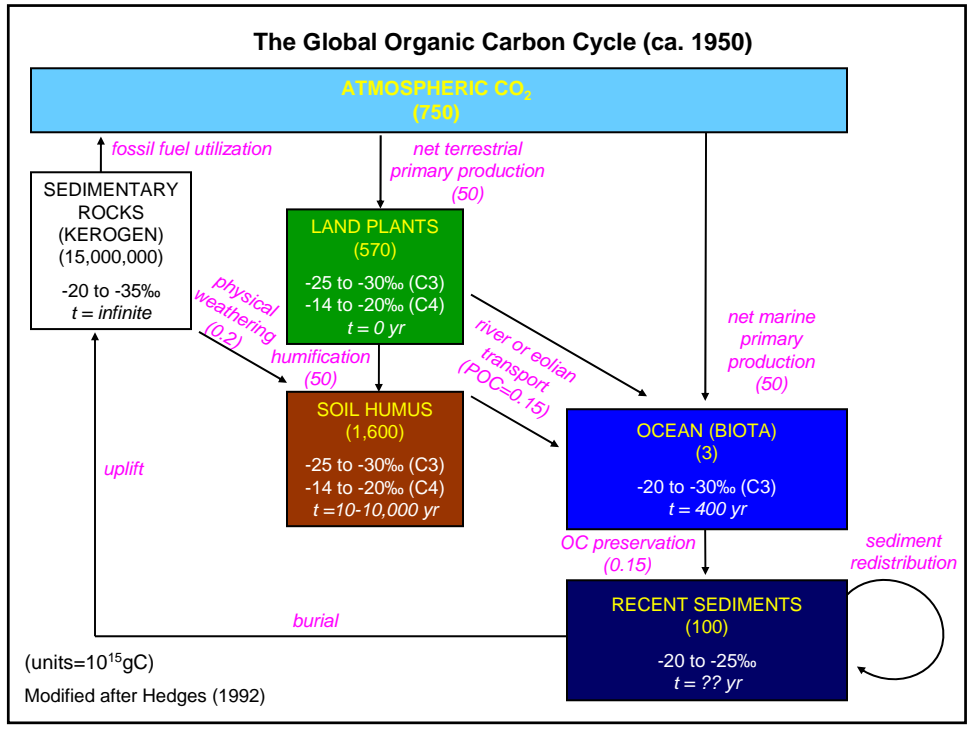
Hopmans E.C., Weijers J.W.H., Schefuss E., Herfort L., Sinnighe Damste J.S. and Schouten S. (2004) A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids. *EPSL* **224**, 107-116.

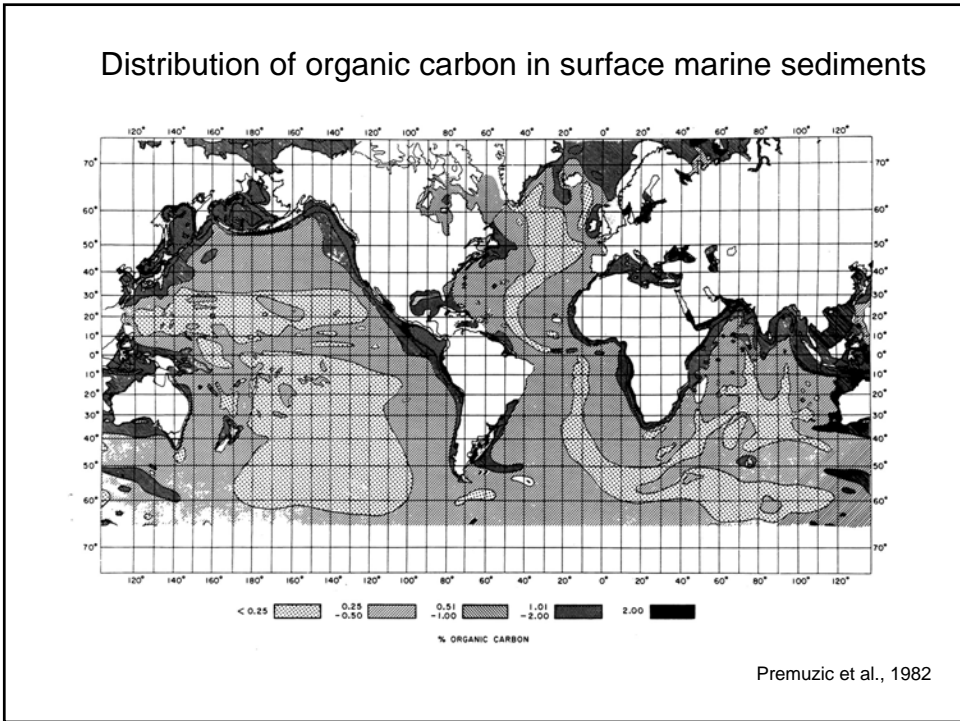
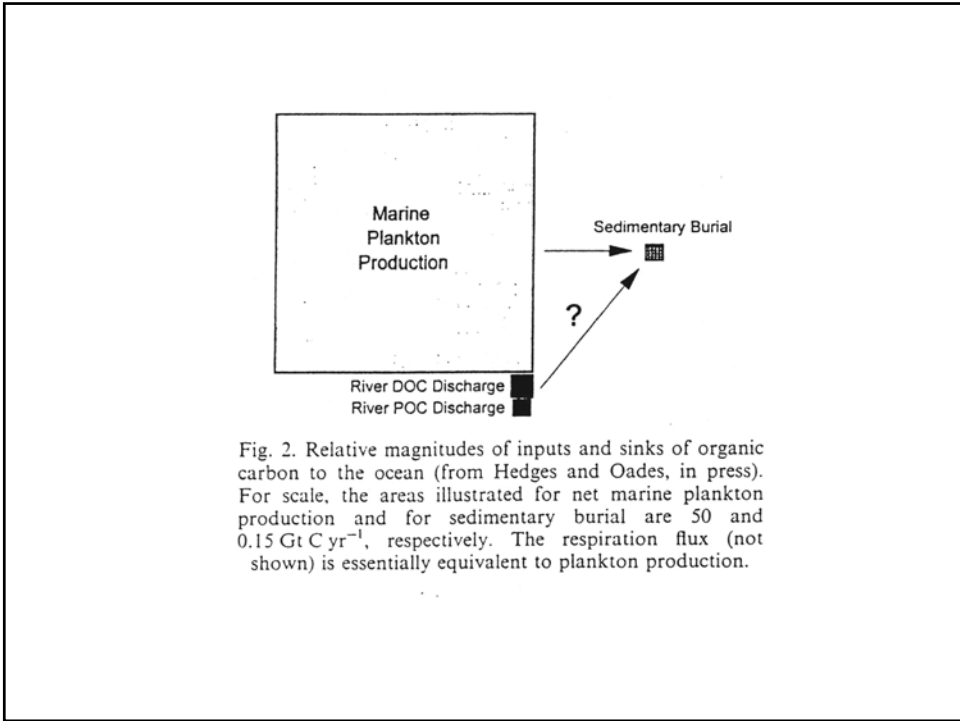
Significance of Terrestrial Organic Carbon

- Most (ca. 90%) of the OC burial in present-day marine sediments occurs on continental margins and in deltas.
- Because they lie at the land-ocean interface, these depositional environments have the potential to be strongly influenced by terrestrial organic carbon inputs.
- The flux of POC from land is sufficient to account for all the OC being buried in marine sediments.
- Terrestrial OM is relatively poor in N relative to marine OM, and hence might be expected to be less susceptible to (re)cycling (reduced respiration) and preferentially accumulate in marine OC reservoirs.
- This doesn't appear to be the case, so what happens to terrestrial OC?

Implications:

- Global carbon budgets
- Long-term controls on atmospheric CO₂ and O₂.
- Estimates of export of primary production from surface ocean.
- Inferences of past productivity in the oceans from OC-based sediment records.
- Interpretation of records of terrestrial and marine productivity from marine sediments.





Organic carbon burial in marine sediments

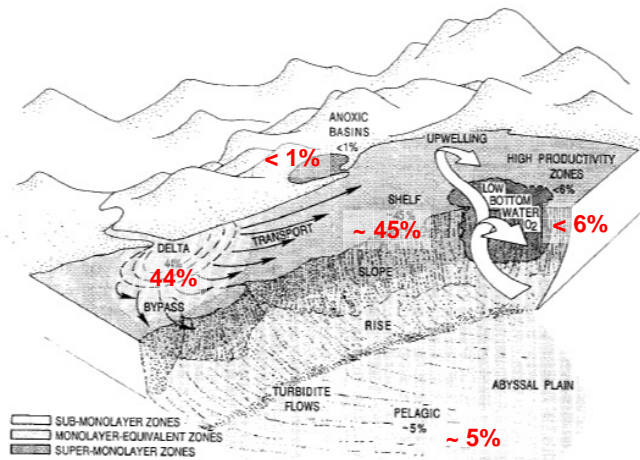


Fig. 1. Idealized diagram depicting current estimates of the percentage of total organic matter burial occurring within various marine sediment types (see Table 2). Light sections represent sediments which contain organic loadings lower than a monolayer equivalent. Stippled sediments contain monolayer-equivalent loadings, and dark sediments contain loadings that are more than monolayer-equivalent.

Important Considerations

- Organic compounds synthesized by organisms are subject to biological and physicochemical processes that alter their chemical composition, and complicate their recognition and quantification in downstream organic carbon (OC) reservoirs such as soils and sediments.
- This "pre-conditioning" that modifies organic matter prior to burial may influence its reactivity in the sub-surface (e.g., by physical association or chemical reaction).
- The time-scales over which organic matter is processed prior to burial may also vary substantially, depending on its origin.
- As a result, contemporaneously deposited organic material of terrestrial and marine origin may exhibit a range of ages and reactivities.
- In seeking to quantify the proportions of organic matter preserved in the sub-surface that stem from different sources it is important to find tracer properties that are largely independent of degradation.
- Continental margins contain significant quantities of "pre-aged" organic carbon.

Approaches to quantify OC inputs to marine sediments

Bulk parameters

- $C_{\text{organic}}/N_{\text{total}}$
- Stable carbon isotopic composition of total organic carbon ($\delta^{13}C_{\text{TOC}}$)

Molecular parameters

- Regression of terrestrial biomarker concentrations vs bulk properties ($\delta^{13}C$, C_{org}/N)
- Extrapolation to zero marker concentration yields a bulk marine end-member elemental or isotopic value that can be inserted into isotopic/elemental mass balance.
- Direct use of concentration measurements for biomarkers in “representative” end-member samples (e.g. plant wax biomarkers in riverine suspended sediments) to determine extent of dilution by marine OC.

Limitations:

- Typically, only 2 end-members are considered (marine and vascular plant), and terrestrial end-member biased towards vascular plant inputs.
- Constancy in composition is assumed along transects.

Bulk properties used to quantify terrestrial OC inputs

C_{org}/N ratios

- Principle:
 - Vascular plant biomass is depleted in nitrogen (mainly comprised of cellulose and lignin), compared to [protein-rich] marine phytoplankton.
- Limitations:
 - Diagenetic influences - proteins are relatively labile, resulting in increased C_{org}/N ratios with degradation.
 - Impact of microbial processes on C_{org}/N ratios.
 - Inorganic N bound in clays can affect ratio, especially in low TOC sediments.

$\delta^{13}C$ TOC composition

- Principle:
 - OC from marine primary production typically enriched in ^{13}C relative to C_3 vascular plant carbon.
- Limitations:
 - Complications due to mixed inputs of C_3 and C_4 higher plant carbon.
 - Past and present-day variations in $\delta^{13}C$ value of marine end-member.
 - Potential diagenetic influences due to intermolecular isotopic variations (e.g. selective preservation of ^{13}C -depleted lipids over ^{13}C -enriched proteins)

Elemental and stable carbon isotopic composition of size and density fractionated sediments

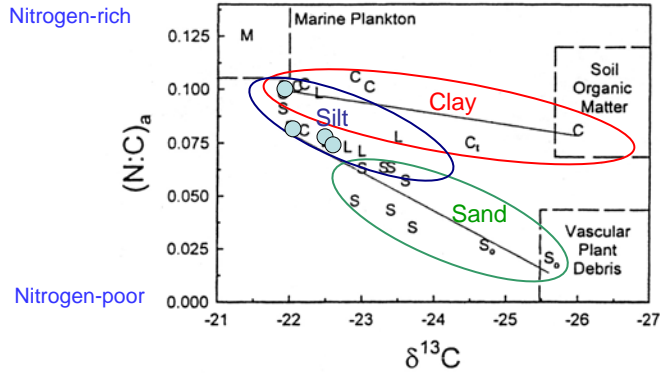
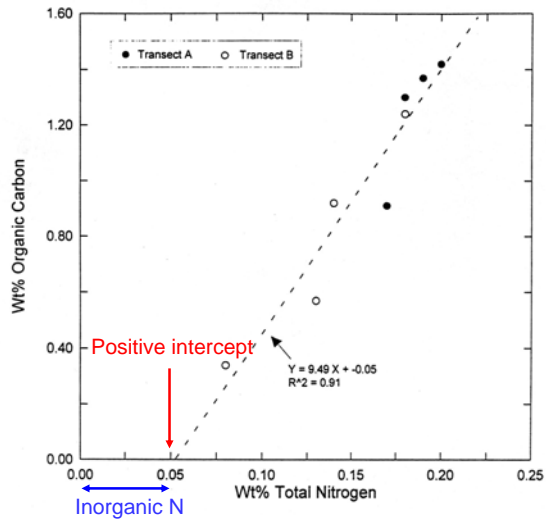


Fig. 5. Atomic N/C ratio versus stable carbon isotopic composition ($\delta^{13}\text{C}$, ‰) of organic matter in size and density fractions isolated from Washington coast sediments (Keil *et al.*, 1994). M is marine material, B is bulk sediment, C is clay-, L is silt- and S is sand-sized sediment. Subscript t is high density ($\rho > 2.6$) fraction and subscript o is low density ($\rho < 1.5$) fraction.

%C_{organic} and %N_{total} in surface marine sediments (Gulf of Mexico)

Inorganic N especially problematic in sediments with low OC content (< 1% TOC)

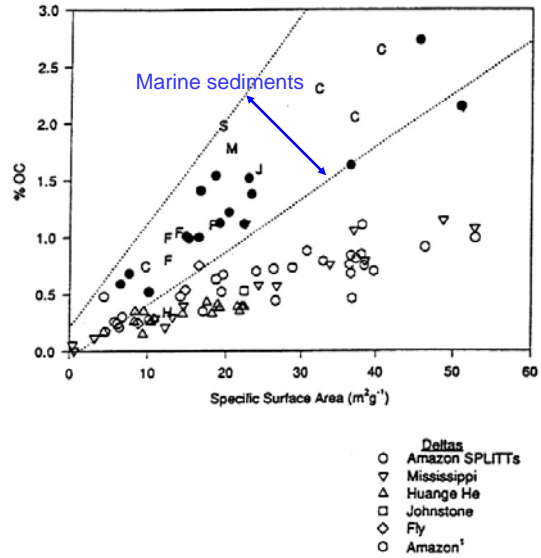
Determination of N_{organic} problematic due to losses associated with acidification procedures (hydrolysis of labile N-bonds)



**%OC vs specific mineral surface area
for river (solid symbols) and delta (open symbols) sediments.**

Organic C contents in sediments are generally tightly coupled to mineral surface area (implies close association of organic matter with mineral surfaces – sorption? occlusion?)

Lower OC/SA ratios for delta vs river sediments suggests significant loss of [terrestrial] carbon upon discharge to the delta



Loss of terrestrial OC and replacement by marine OC in deltaic systems

(assumes mineral surface area is conserved during weathering and transport to the oceans)

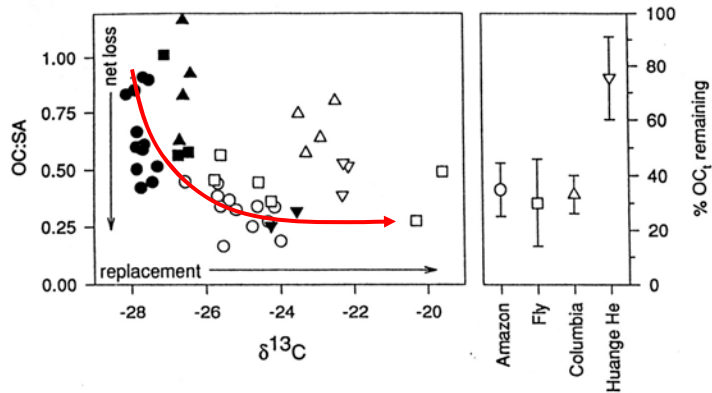


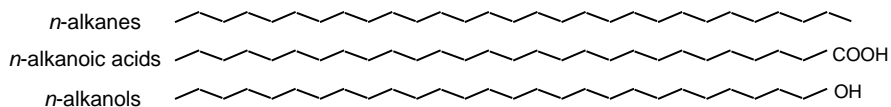
Fig. 2. Organic carbon to mineral surface area ratio (OC:SA) plotted against organic matter stable carbon isotope composition. River samples are as filled and delta samples are as open symbols. A shift downward in OC:SA denotes net loss of organic matter in the sediment mineral fractions, and a shift toward more positive isotopic compositions indicates addition of marine organic matter. The right hand side of the figure illustrates the average (± 1 std) total amount of terrestrial organic matter (OC_t) remaining in deltaic sediments after accounting for both shifts in OC:SA and $\delta^{13}C$ between river and delta sediments for the coupled river-delta systems studied to date.

Biological markers as tracers of terrestrial OC inputs

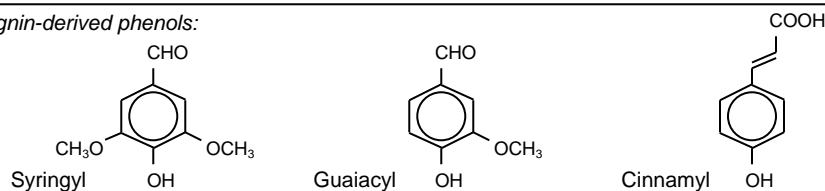
Compound types

- Plant waxes (long-chain *n*-alkanes, *n*-alcohols, *n*-alkanoic acids)
- Terpenoids (e.g., abietic acid, retene, taraxerol)
- Branched and isoprenoid ether lipids
- Lignin phenols
- Cutin
- Tannins, Suberins

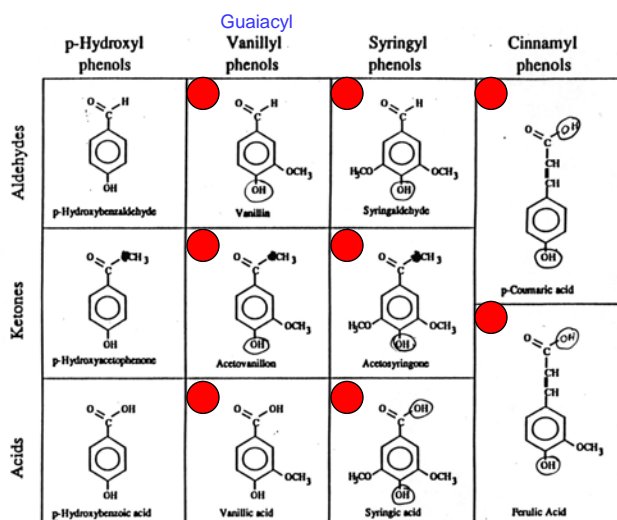
Higher plant epicuticular leaf waxes:



Lignin-derived phenols:



Lignin-derived phenols from CuO oxidation



● Used in determination of λ_8 (expressed as mg phenols per 100 mg OC)

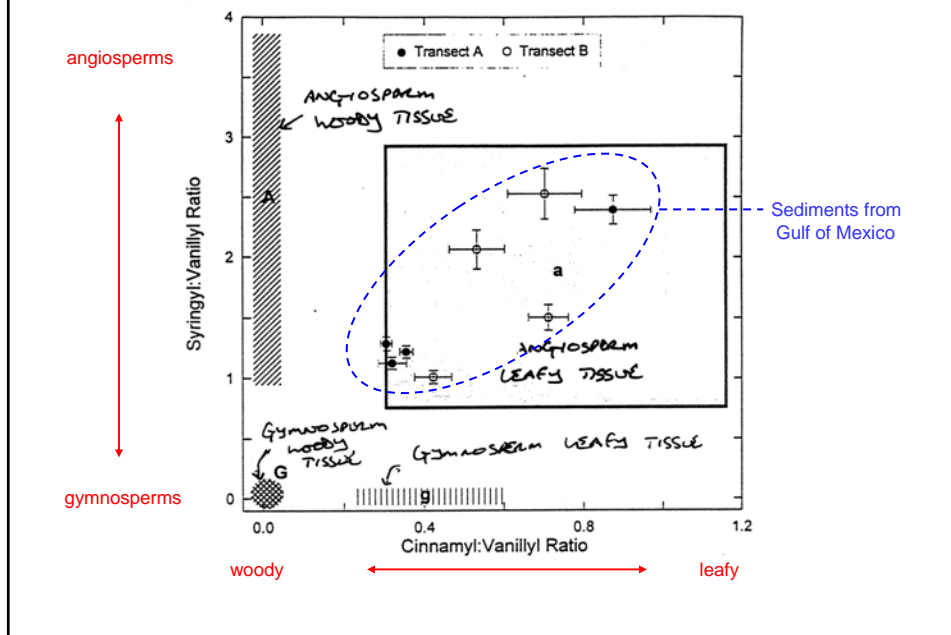
Molecular markers of terrestrial vegetation

Lignin Compositional Parameters

Lignin-derived phenols

- syringyl/guaiacyl ratio (S/V): angiosperm vs. gymnosperm
- cinnamyl/guaiacyl ratio (C/V): leafy vs woody vegetation
- acid/aldehyde ratio (Ad/Al)_v: extent of lignin degradation
- $\delta^{13}\text{C}$: Determination of C3 vs C4 vs CAM inputs

Compositional parameters derived from CuO oxidation products



Stable carbon isotopic analysis of individual lignin-derived phenols

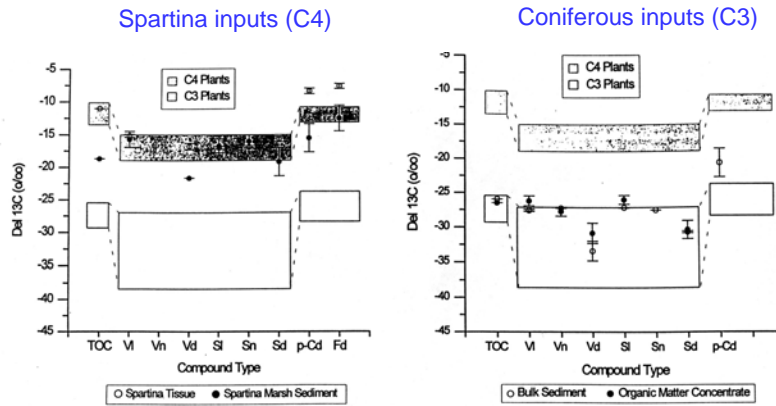


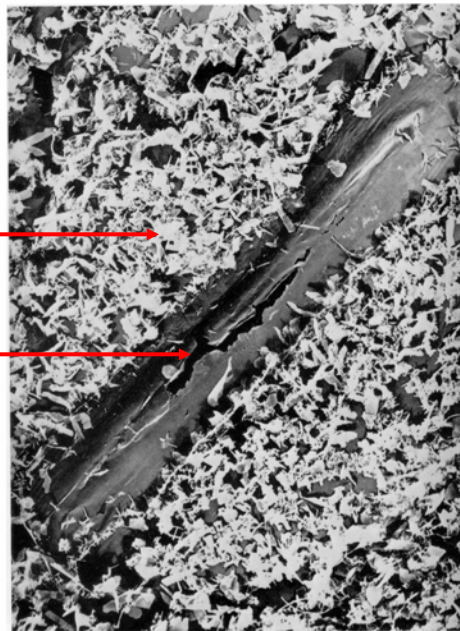
Fig. 4. Plot of $\delta^{13}C$ of TOC and individual lignin CuO oxidation products of organic matter concentrates from living *Spartina alterniflora* tissue (open symbols) and *Spartina* marsh sediment (closed symbols). Error bars represent \pm one standard deviation from average $\delta^{13}C$ (‰). Included are shaded areas representing the compositional ranges of C₃ and C₄ plant tissues (Table 4).

Fig. 6. Plot of $\delta^{13}C$ of TOC and individual lignin CuO oxidation products of bulk sediments (open symbols) and sedimentary organic matter concentrate (closed symbols) from Lake Washington. Error bars represent \pm one standard deviation from average $\delta^{13}C$ (‰). Included are shaded areas representing the compositional ranges of C₃ and C₄ plant tissues analyzed (Table 4).

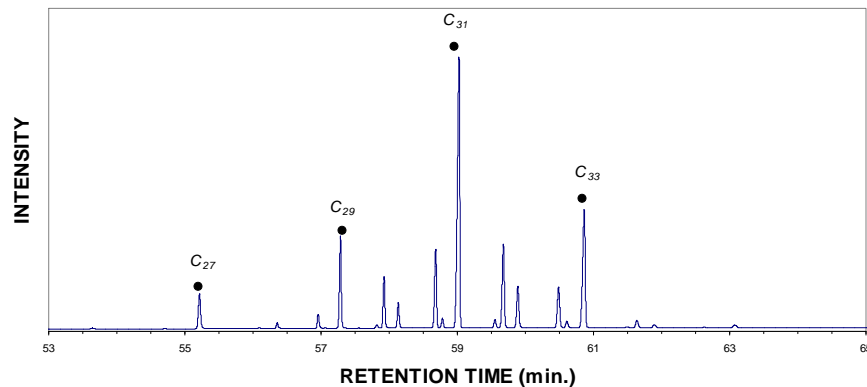
Epicuticular waxes on corn leaf surface

Waxes on leaf surface (white) →

Leaf stomata →



Example gas chromatogram of waxes (alkane fraction) from Tobacco leaves



This figure shows a typical gas chromatography trace of a hydrocarbon (alkane) fraction extracted and purified from a higher plant leaf sample. Note the predominance of long-chain (>C₂₄) odd-carbon-numbered *n*-alkanes (marked with circles) that is highly characteristic of higher plant leaf waxes. The chain-length distribution of these compounds is indicative of growth temperature.

Molecular markers of terrestrial vegetation

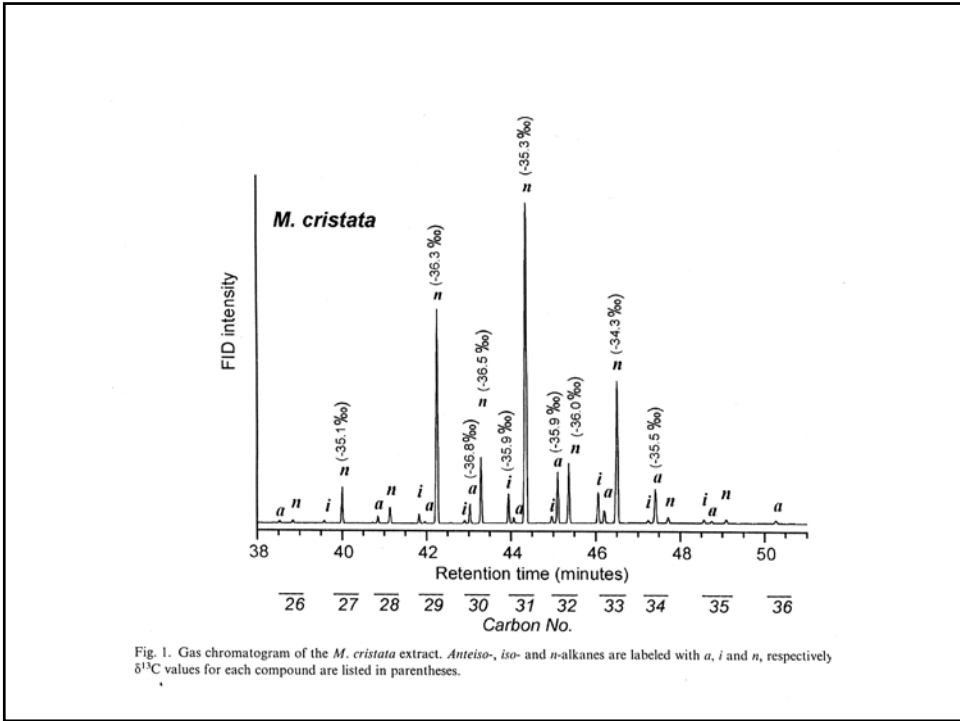
Plant Wax Compositional Parameters

Plant wax n-alkanes/n-alcohols/n-acids

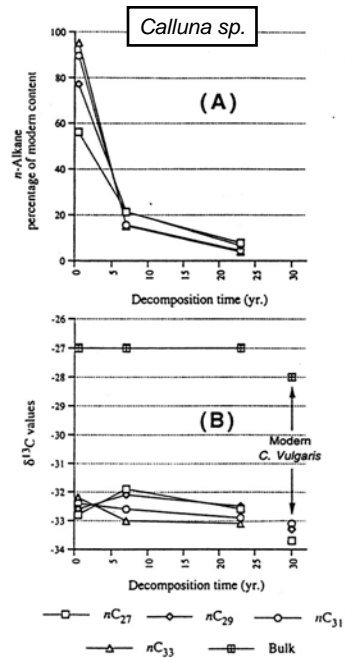
- Carbon Preference Index (CPI) or Odd-over-Even Predominance (OEP)

$$\text{CPI} = \frac{2\sum \text{odd } C_{21}\text{-to-}C_{35}}{(\sum \text{even } C_{20}\text{-to-}C_{34} + \sum \text{even } C_{22}\text{-to-}C_{36})}$$
- Average chain length (ACL)

$$\text{ACL} = \frac{(\sum [C_i] \times i)}{\sum [C_i]}$$
 where:
i is the range of carbon numbers (typically 23-35 for alkanes)
C_i is the relative concentration of the alkane containing *i* carbon atoms.
- δ¹³C: Determination of C3 vs C4 vs CAM inputs
- δD: aridity/water stress



Influence of long-term degradation on isotopic composition of leaf-wax biomarker lipids



The Columbia River/Washington margin system

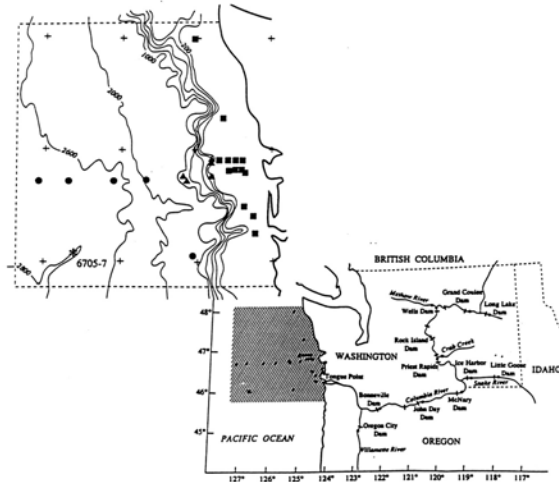
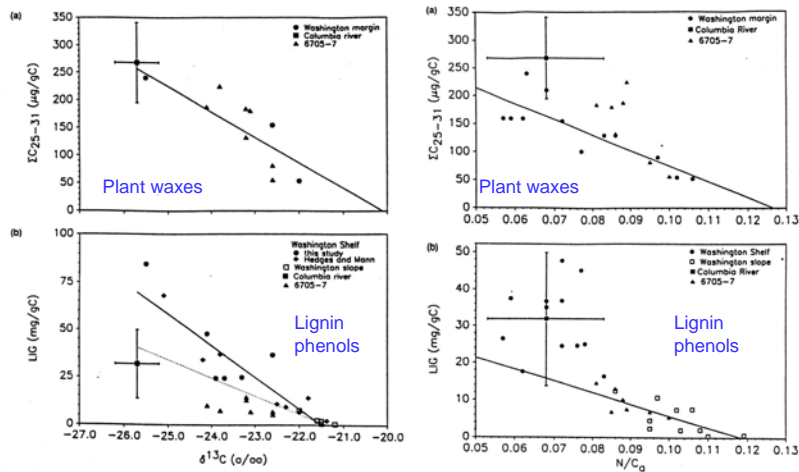


FIG. 1. Map identifies fourteen sampling locations behind major dam sites within the Columbia River drainage basin. The cross-hatched area and corresponding inset indicates twenty-three offshore sites on the Washington margin also examined in this study. The specific coordinates of shelf (filled squares), slope (filled triangles), and Cascadia Basin (filled circles) sampling locations are given in Table 1. The location for gravity core 6705-7 collected from the Cascadia Seachannel on the Astoria Fan (2688 m water depth; 46°03.6'N 126°57.9'W) is identified by the asterisk.

Higher plant biomarkers in Washington Margin sediments



Prahl et al. 2004, GCA

Lignin phenol contents and isotopic compositions of Gulf of Mexico sediments

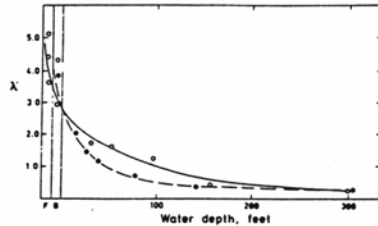


Fig. 4. Plots of λ against water depth at the sampling site for sediments from the Atchafalaya River and Terrebonne Bay transects. Open circles and solid line correspond to the Terrebonne Bay transect. Solid circles and dashed line correspond to the Atchafalaya Bay transect. Abbreviations: F, freshwater or brackish water sediments; B, bay sediments.

Hedges and Parker, 1976

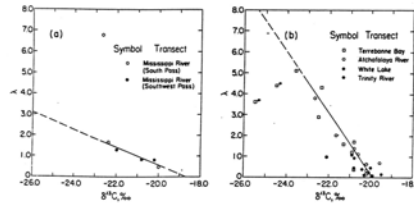


Fig. 5. Plots of λ against $\delta^{13}\text{C}$ for sediments from the (a) Mississippi River and (b) southwest Gulf depositional zones. Correlation lines were determined as the best least-squares fit to a straight line. Freshwater swamp sediments from the Terrebonne Bay transect are denoted in (b) by an asterisk and were not used to determine the correlation line. Southwest Pass sample no. 1 was not used to determine the Mississippi River correlation line.

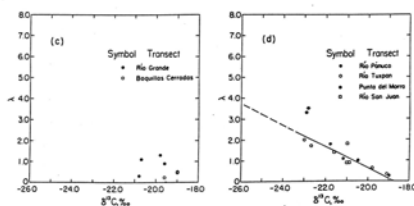
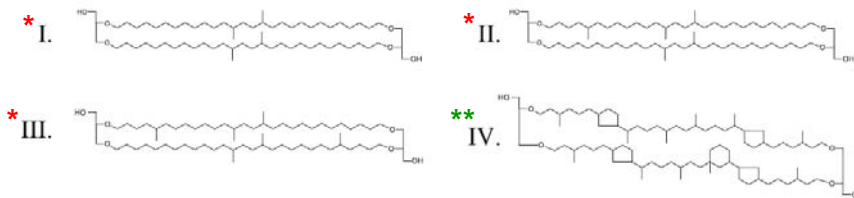


Fig. 6. Plots of λ against $\delta^{13}\text{C}$ for sediments from (c) the Rio Grande and (d) the southwest Gulf depositional zones. Punta del Mero sample no. 1 (*) contained large fragments of gymnosperm wood and, therefore, was not used to determine the correlation line in (d).

A novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid tetraether lipids

E.C. Hopmans et al. / Earth and Planetary Science Letters 224 (2004) 107–116



The Branched and Isoprenoid Tetraether ("BIT") index:

$$\text{BIT} = \frac{[\text{I} + \text{II} + \text{III}]}{[\text{I} + \text{II} + \text{III}] + [\text{IV}]}$$

***** Derived from anaerobic soil bacteria

****** Derived from derived from non-thermophilic crenarchaeota

BIT index in soils and sediments

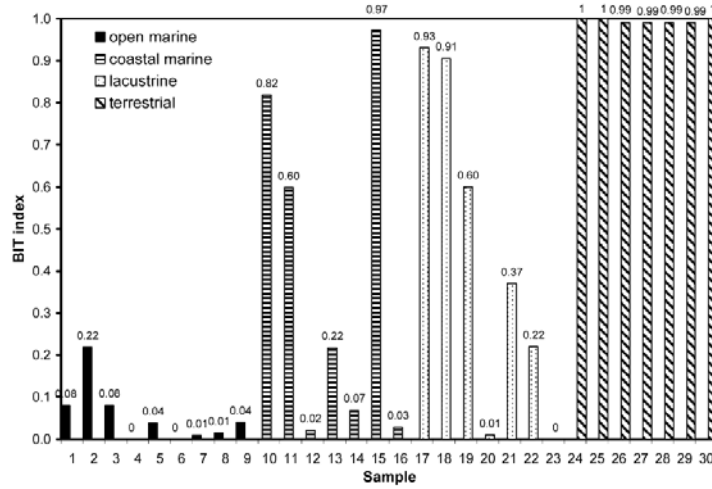
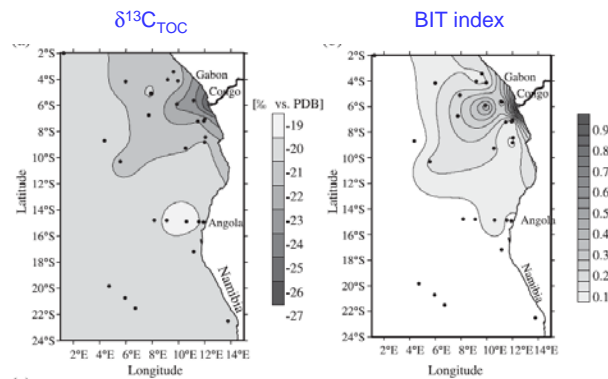


Fig. 4. Bar graph showing the BIT index measured on Holocene sediments from a range of environments. Data points are from: 1, Black Sea; 2, Skagerrak (North Sea); 3, Arabian Sea; 4, Peru Margin; 5, Cariaco Basin; 6, Aegean Sea; 7, Goban Spur (North Atlantic); 8 and 9, Iberian Margin; 10, Wadden Sea (the Netherlands); 11, Mok Bay (Texel); 12, Saanich Inlet (Canada); 13, Drammensfjord (Norway); 14, Skan Bay (Alaska); 15, Kyllaren Fjord (Norway); 16, Kau Bay (Indonesia); 17, Lake Paloma (Chili); 18, Siso Lake (Spain); 19, Lake Michigan (USA); 20, Lake Issyk Kul (Kyrgyzstan); 21, Lake Superior (USA); 22, Lake Malawi (Malawi); 23, Ace Lake (Antarctica); 24, Carbury peat (Ireland); 25, Meerstalblok peat (the Netherlands); 26, Etang de la Gruere peat (Switzerland); 27, Bergvennen peat (the Netherlands); 28, Saxnas Mosse peat (Sweden); 29, Bear Meadows wetland (USA); 30, Texel forest soil (the Netherlands).

Hopmans et al 2004

Tracers of terrestrial OC supply to marine sediments



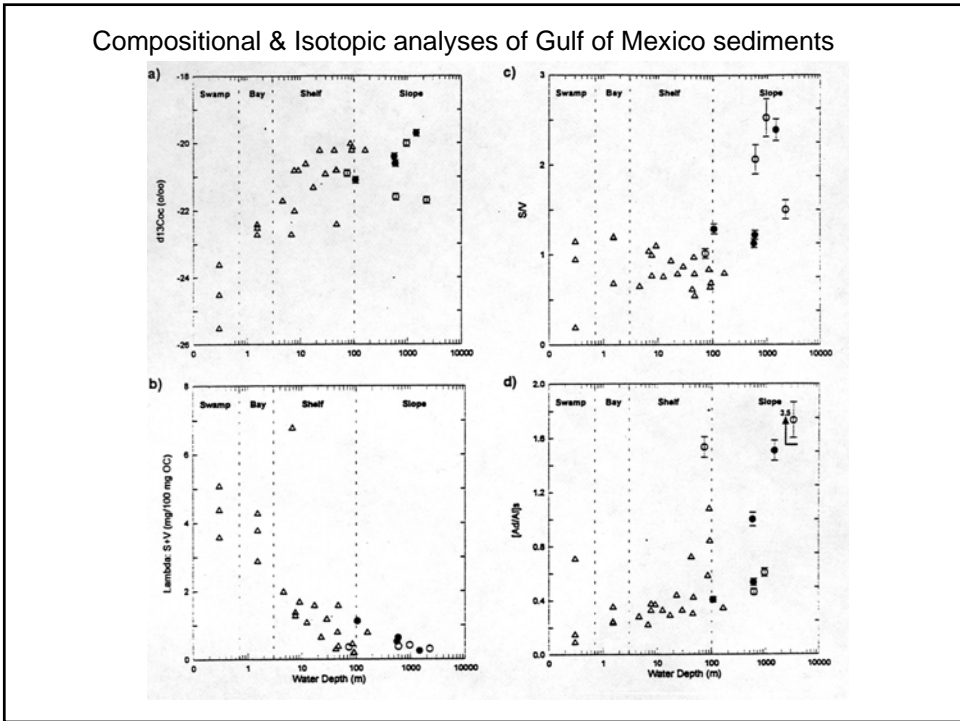
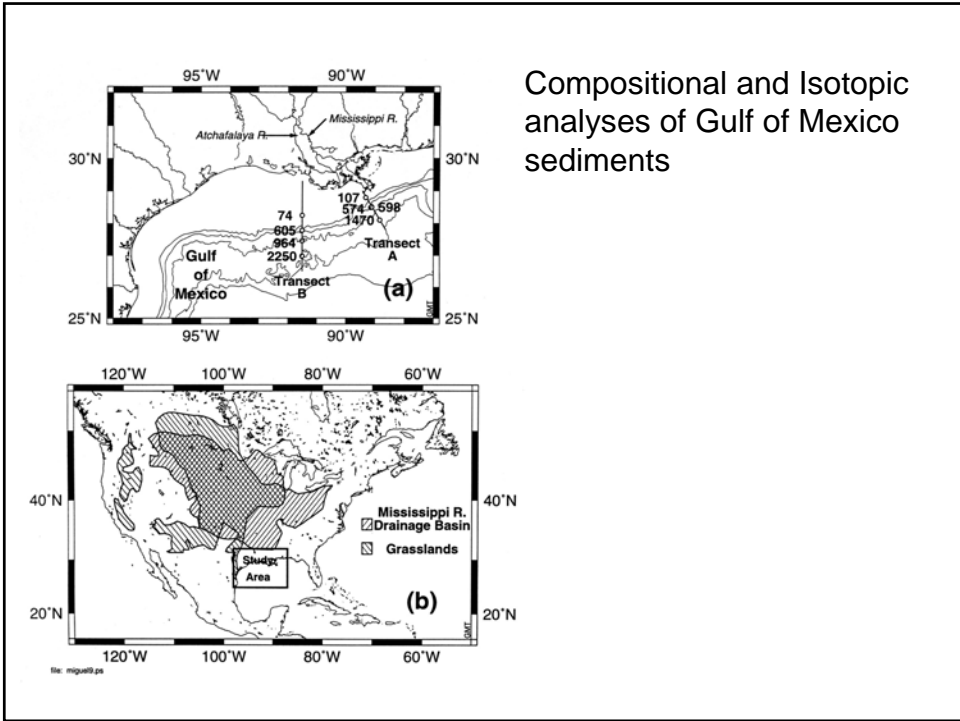
Hopmans et al 2004

Evidence for minimal terrestrial OC contributions to marine sediments

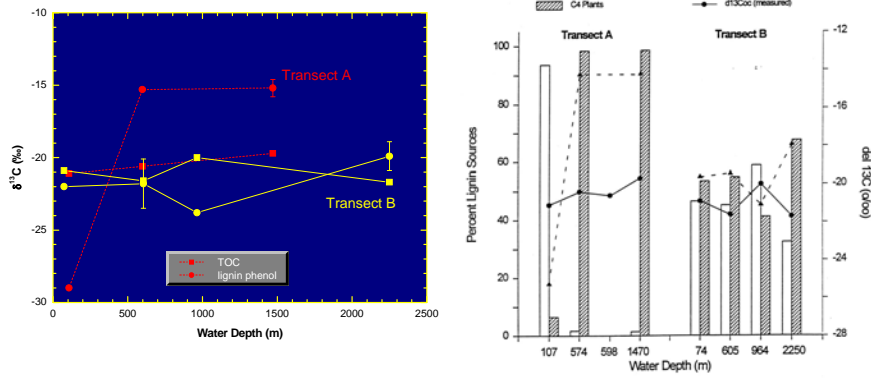
- Variations in OC:SA and $\delta^{13}\text{C}_{\text{OC}}$ in estuaries ("loss & replacement hypothesis").
- Low $\text{C}_{\text{org}}/\text{N}$ values for marine sediments.
- Enriched $\delta^{13}\text{C}$ values of marine sedimentary OC relative to terrestrial (C_3 OC).
- Rapid decrease in lignin phenols and other molecular proxies of terrestrial organic matter with increasing distance offshore / from river mouth.

Evidence for significant terrestrial OC contributions to marine sediments

- Unknown contributions from ^{13}C -enriched (C_4) terrestrial OC sources.
- Importance of hydrodynamic processes in differential export terrestrial organic components.
- Old core-top ages for continental margin sediments (topic of separate lecture).
- Global influence of small, mountainous rivers.
- Arctic ocean under-sampled, yet surrounded by major drainage basins/soil reservoirs.
- Widespread distribution of plant wax lipids in ocean sediments.
- Greater importance of terrestrial OC in glacial times (low sea-level stand, direct river discharge to continental slope)?



Bulk & molecular isotopic compositions of Gulf of Mexico surface sediments



Stable carbon isotopic characteristics of riverine SPOM

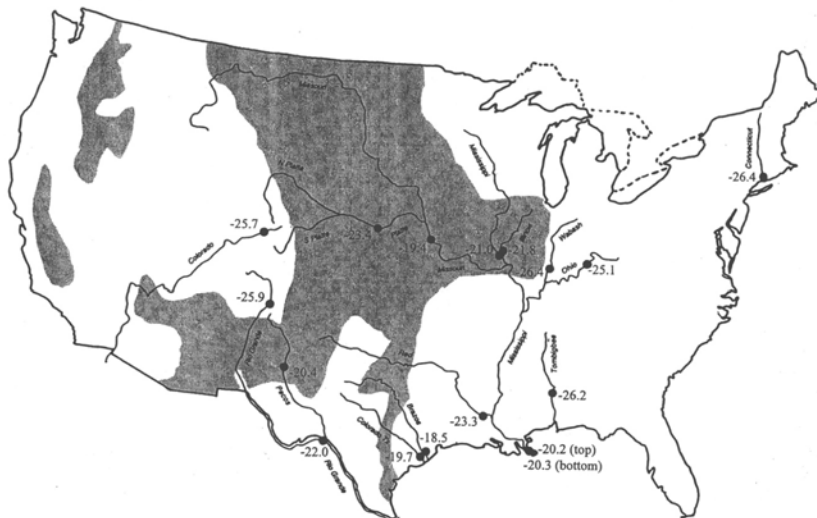
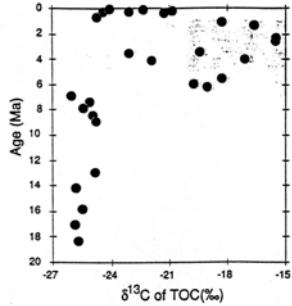


Fig. 1. Map of the continental United States with river sample sites (Canfield, 1997), and $\delta^{13}\text{C}$ values of suspended POM from those sites, illustrated. The distribution of C4 grasslands (shaded area) is adapted from Coupland (1979).

Isotopic compositions of Bengal fan sediments and the emergence of C4 plants



The Himalayan drainage basin is characterized by a predominance of physical transport over chemical weathering, and sequestration of OC exported from this drainage basin is of such a magnitude that it may account for up to 15% of the global burial flux (Aucour et al., 2006).

France-Lanord & Derry (1997) have argued that Himalayan erosion alone exerts a dominant control on the global C cycle through terrestrial OC export and burial.

Recent studies indicate that OC export and burial are extremely efficient in the Himalayan system compared to other large drainage basins on earth (Galy et al., 2007).

A substantial fraction of the terrestrial OC exported and buried by be C4 derived.

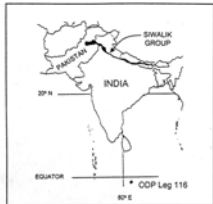


Fig. 3. Map of the Indian subcontinent showing outcrop pattern of Swalik Group and sample localities for both paleosol and marine sediments (short map).

Isotopic compositions of Bengal fan sediments and the emergence of C4 plants

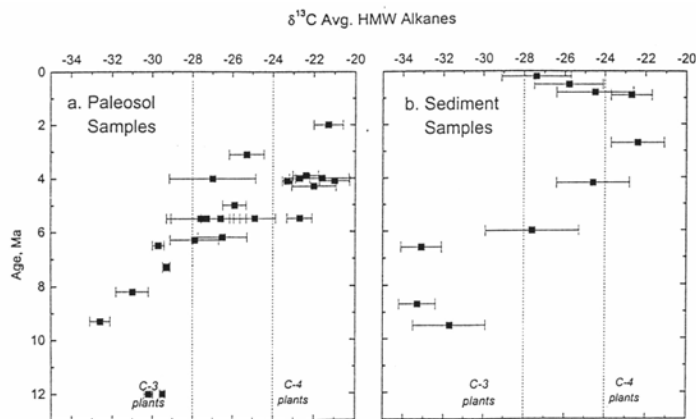
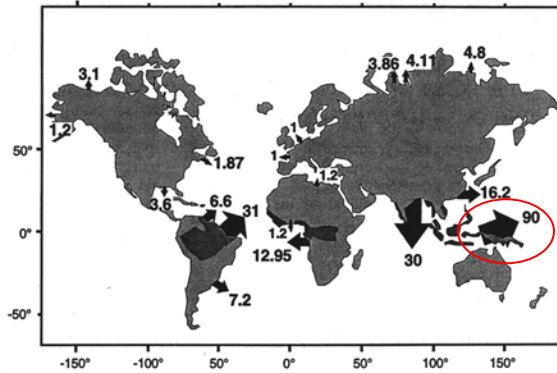


Fig. 6. $\delta^{13}\text{C}$ values representing the average of odd-carbon-numbered HMW alkanes plotted as a function of sample age for both the paleosol and sediment samples. Dotted line represent the approximate limits of n -alkane $\delta^{13}\text{C}$ values expected for C-3 and C-4 plants (see text and Table 14). Paleosol samples with evidence for significant contribution of n -alkanes from parent materials are not included.

Importance of tropical small mountainous river systems in terrigenous OC export to the oceans

Fig. 1 Annual discharge of total organic carbon of major world rivers to the oceans (organic carbon fluxes are in 10^{12} gC year⁻¹; wet tropics are underlain in *dark grey*). Data are from: Telang et al. (1991; Mackenzie, Yukon, St. Lawrence, Mississippi); Depetris and Paolini (1991; Orinoco, Parana); Richey et al. (1991; Amazon); Martins and Probst (1991; Zaire, Niger); Degens et al. (1991; Rhine + Elbe, Seine + Loire + Gironde); Telang et al. (1991; Ob, Yenisei, Lena); Gan-Wei-Bin et al. (1983; Yangtze); Subramanian and Ittekkot (1991; Ganges + Brahmaputra + Indus); Bird et al. (1995; Oceania)



40-70% of the sediment delivered to the oceans is transported by numerous small rivers (Milliman and Syvitski, 1992).

These systems transport OC that is distinct in composition from the world's largest and better studied rivers (Blair et al., 2004).

Milliman et al

Key characteristics of large and small river systems

Large rivers:

- Develop on passive margins with extensive floodplains, estuaries and deltaic systems that serve as efficient "reactors" for remineralization of terrestrial organic matter.
- Well-developed soils for (re-)processing of organic matter.
- Soil erosion a major source of terrestrial OC.
- Gradual (seasonal) variations in fluvial supply

Small Mountainous rivers:

- Develop on active margins with steep relief and often narrow continental shelves and restricted flood plains.
- Highly episodic sediment delivery, little time available for storage/oxidation in intermediate reservoirs prior to export to the ocean.
- Erosion of bedrock as well as poorly developed soils (old carbon supply).

Importance of tropical mountainous river systems in terrigenous OC export to the oceans

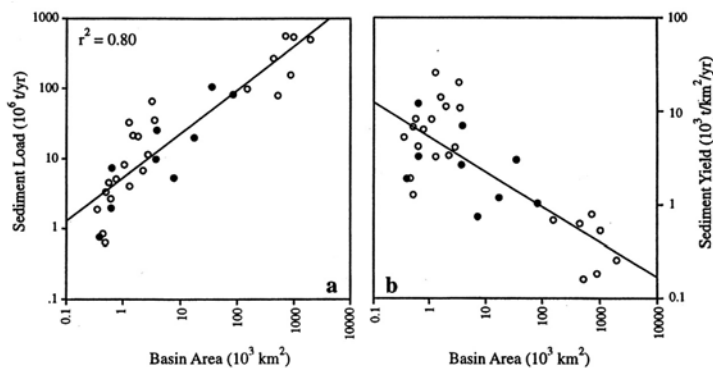
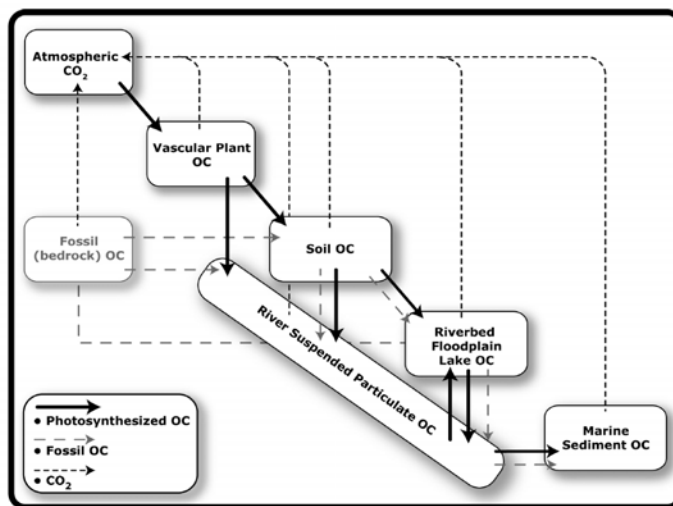


Fig. 1. Relationship between annual sediment load (a) and sediment yield (b) and basin area for various southeast Asian and Indonesian/Papua New Guinean humid (>500 mm y⁻¹ run-off), mountain (>1000 m headwater elevation) rivers. Note that the East Indies rivers (Fly, Purari, Solo, Citamandy, Cimanuk, Cimuntur, Cilutung, Cijolang, and Agno; solid dots) have loads and yields very near values predicted based solely on southeast Asian river (open circles) algorithms; see text for further discussion. Data from Milliman and Syvitski (1992), somewhat modified by Milliman and Farnsworth (in prep.).



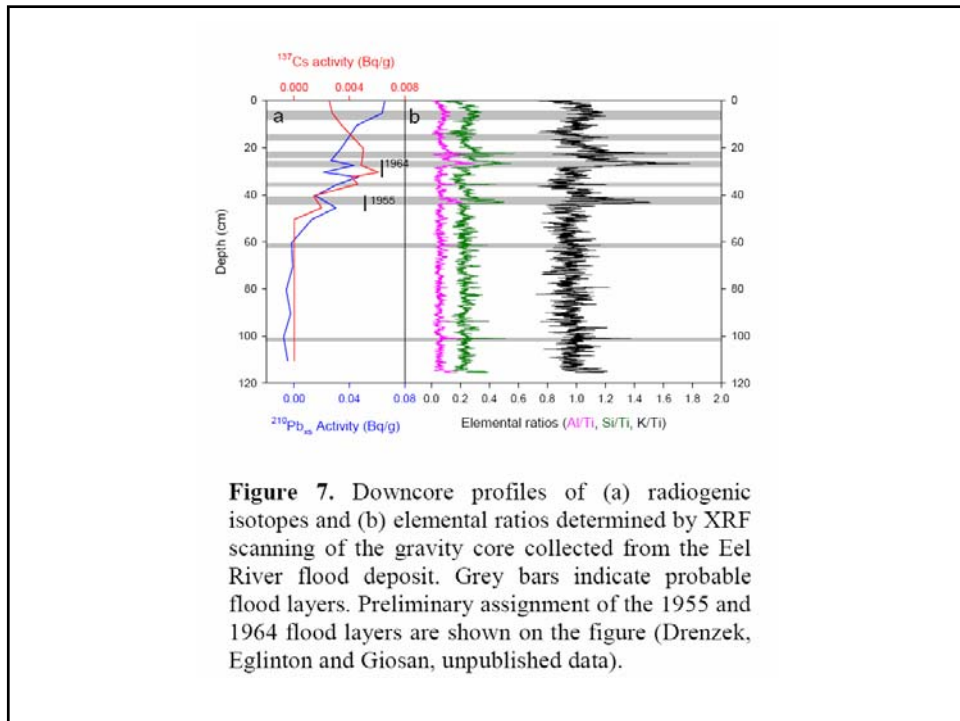
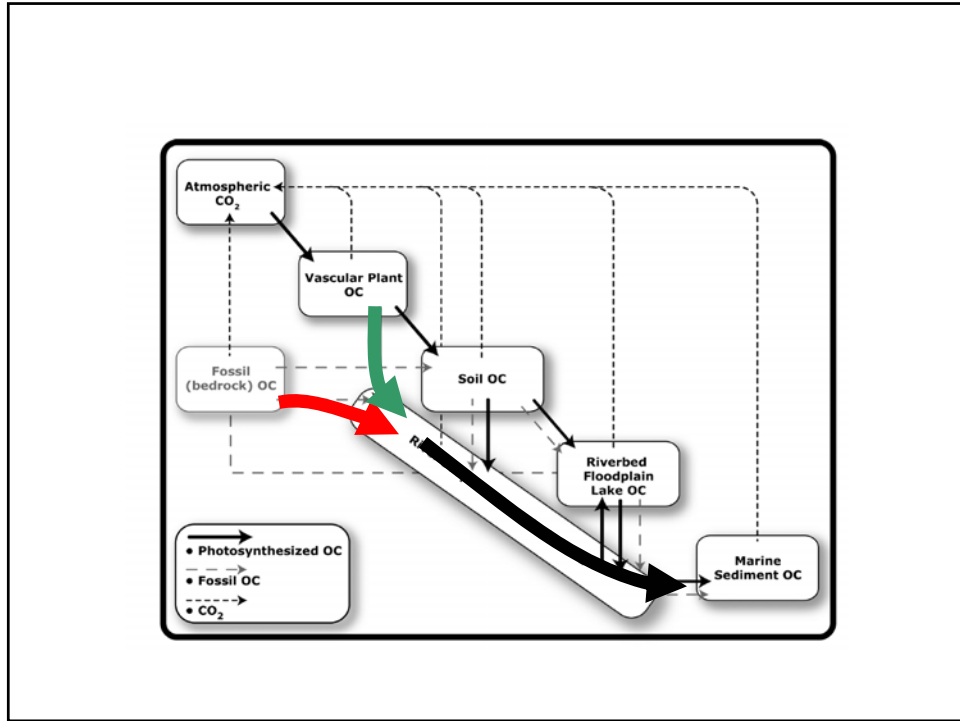
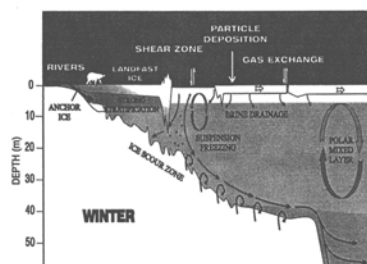
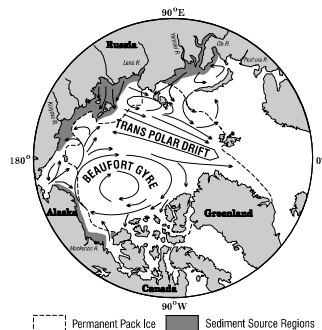
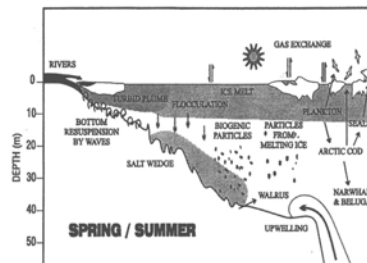
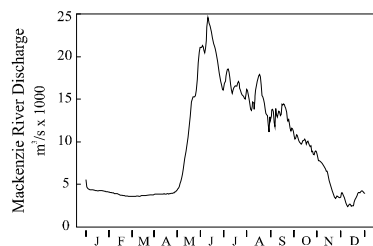


Figure 7. Downcore profiles of (a) radiogenic isotopes and (b) elemental ratios determined by XRF scanning of the gravity core collected from the Eel River flood deposit. Grey bars indicate probable flood layers. Preliminary assignment of the 1955 and 1964 flood layers are shown on the figure (Drenzek, Eglinton and Giosan, unpublished data).

Terrestrial OC inputs to the Arctic Ocean

- The Arctic Ocean receives proportionately ten times more freshwater input than any other ocean basin. They also deliver large amounts of organic carbon.
- About half of the global inventory of terrestrial organic carbon is stored in the soils of Arctic watersheds (Dixon, 1994). Much of this carbon is sequestered in permafrost and is inaccessible. However, permafrost destabilization will make a larger fraction of terrestrial organic carbon available in the future.
- Organic loadings in Arctic rivers are among the highest in the world. Annually, Arctic rivers export some $20\text{-}30 \times 10^{12}$ g of terrigenous DOC along with $4\text{-}6 \times 10^{12}$ g of particulate organic carbon (POC) to the shelf.
- Arctic rivers discharge > 90% of their freshwater during the spring/summer melt (freshet) between May and July. Episodic delivery analogous to small mountainous rivers. Low temps and rapid supply decrease opportunity for degradation of terrestrial OC.
- Some arctic rivers drain organic-rich sedimentary rocks (e.g., Mackenzie) – additional source of refractory OC?
- In addition to usual particle dispersal mechanisms, ice-rafting can result in long-distance transport of terrestrial OC.

Riverine delivery and transport of OC (Mackenzie/Beaufort)



The Mackenzie/Beaufort System

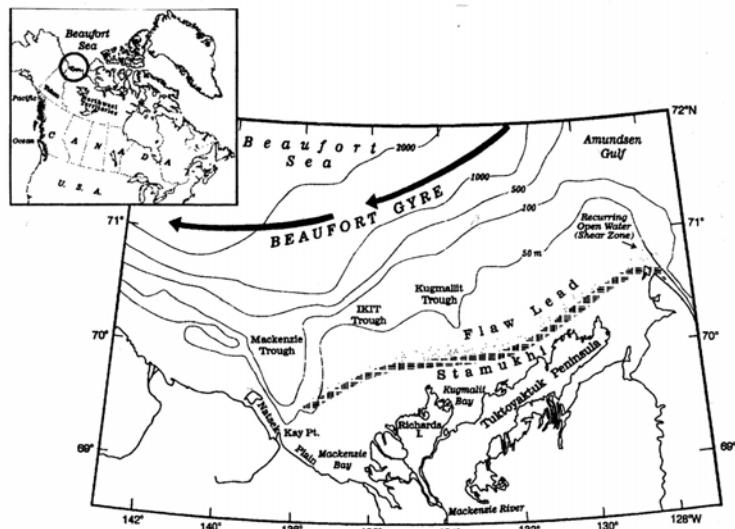


Fig. 1. Location map of the Mackenzie Shelf in the Canadian Beaufort Sea showing the various features discussed in the text.

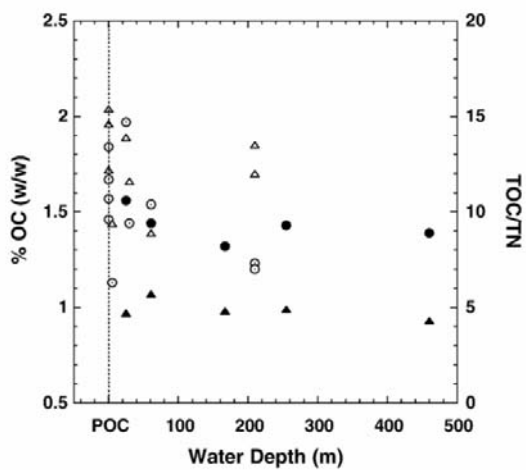
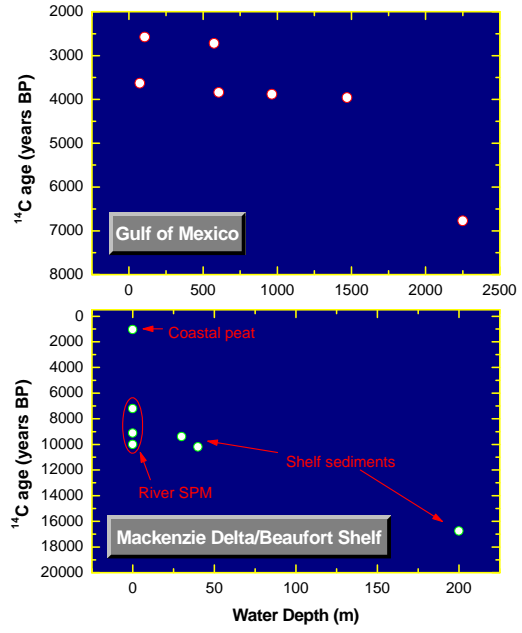
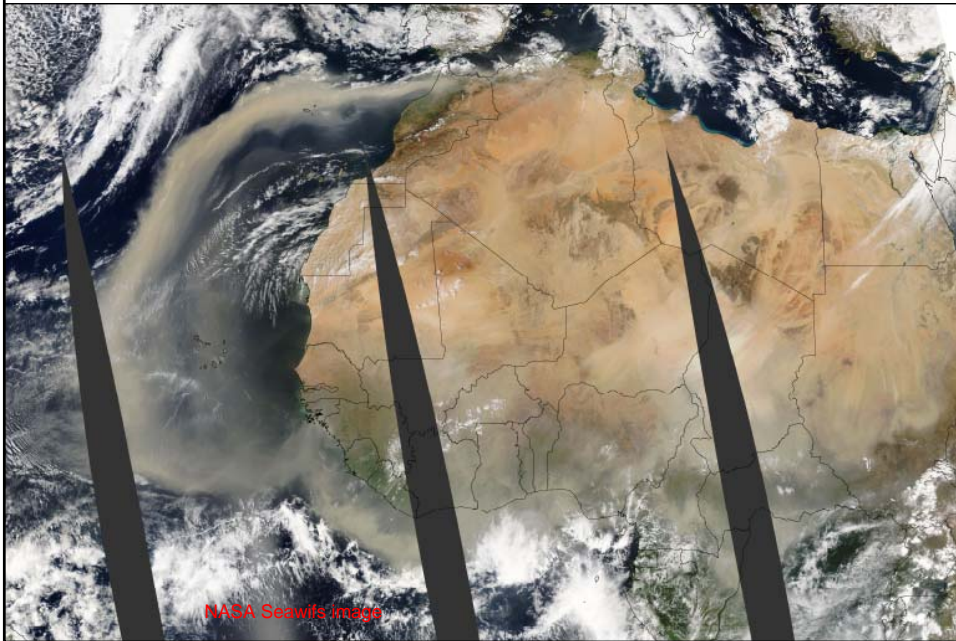


Fig. 2. Trends in sedimentary %OC (circles) and TOC/TN (triangles) with water depth from this study (closed symbols) and Goñi et al. (2000) (open symbols), along with %OC and TOC/TN for Mackenzie River POC samples from Goñi et al. (2000).

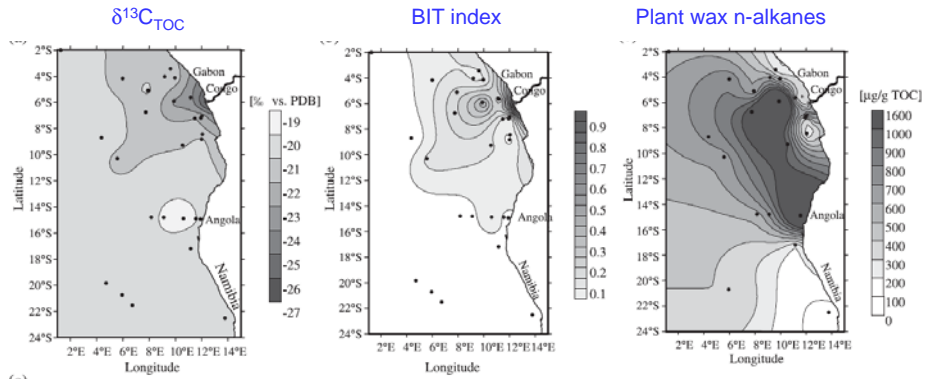
^{14}C ages of suspended particulate and sedimentary OC in river dominated systems



Eolian supply of terrestrial organic carbon to the oceans



Tracers of terrestrial OC supply to marine sediments



Hopmans et al 2004

Long range transport and preservation of plant wax alkanes in marine sediments

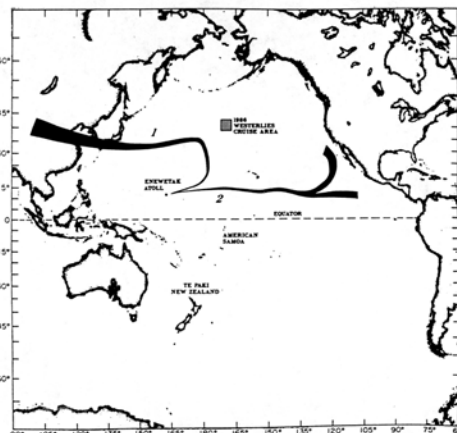
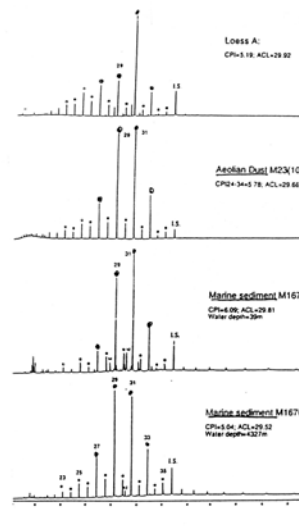


Fig. 1. Locations of the major SEAREX sampling sites and some of the typical air mass trajectories for the Enewetak site: (1) dry season; (2) wet season.

Gagosian and Peltzer

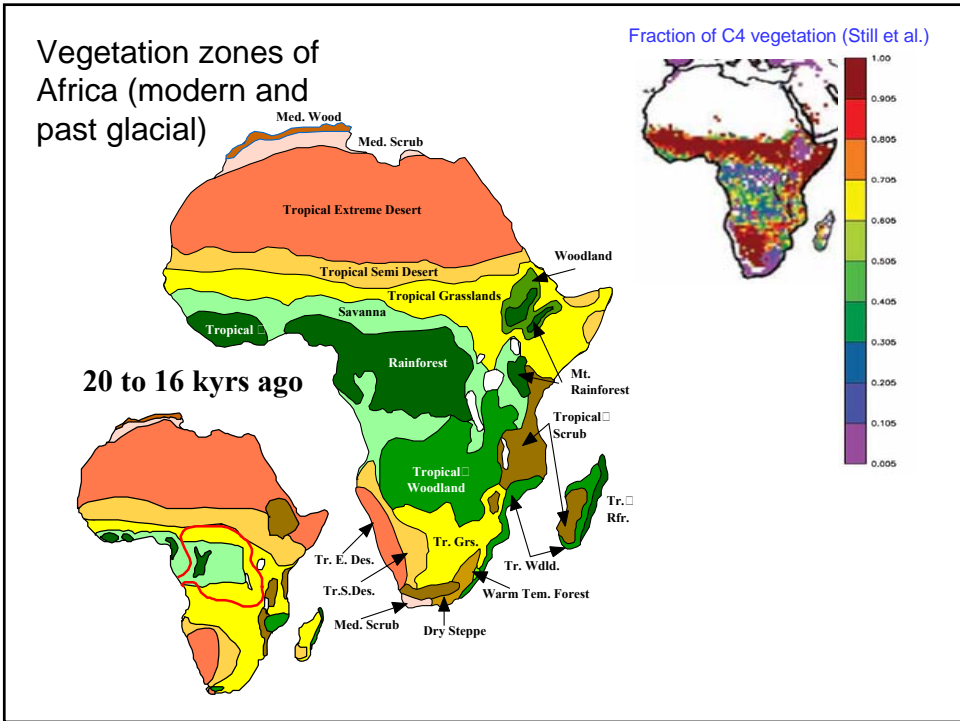
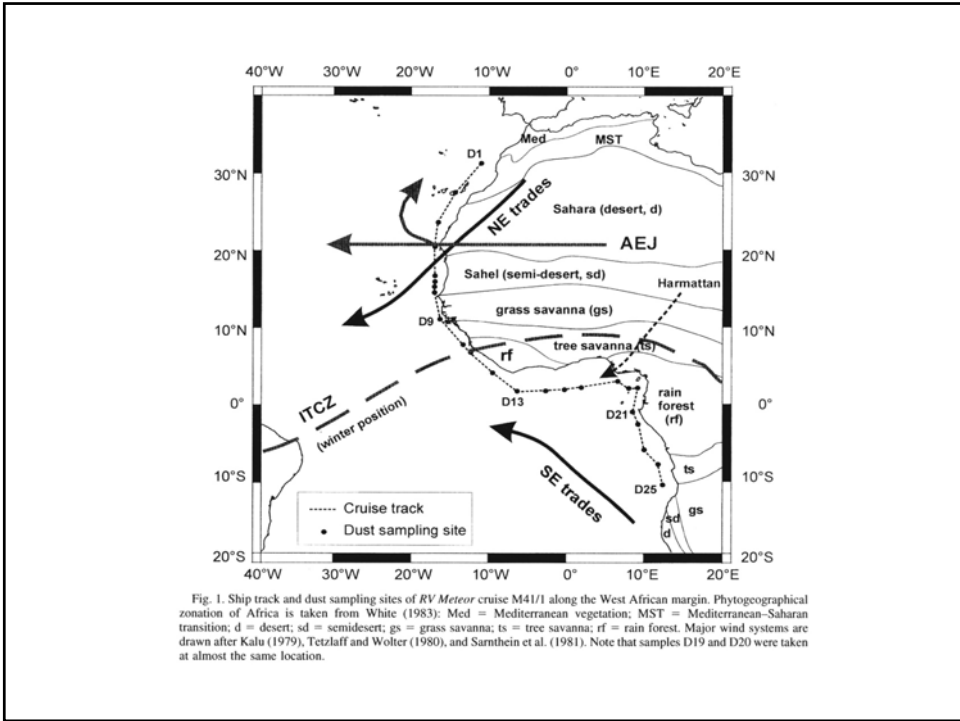


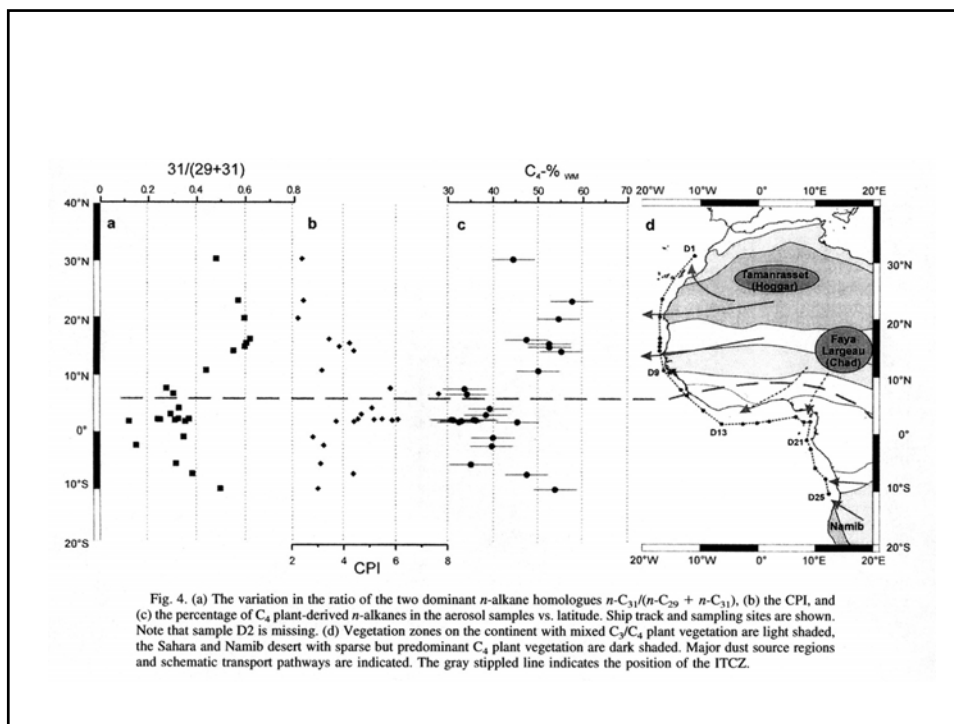
HYDROCARBON FRACTIONS

*: n-alkane with strong odd/even predominance, presumably from aeolian dust transportation.

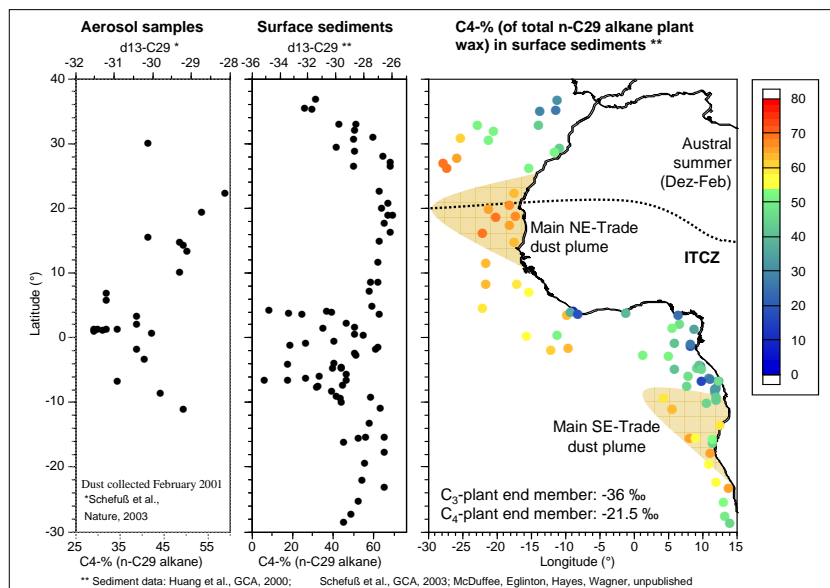
n1=22,29,30-trinorhop-17(21)-ene n2=C30 Hop-17(21)-ene

Eglinton et al



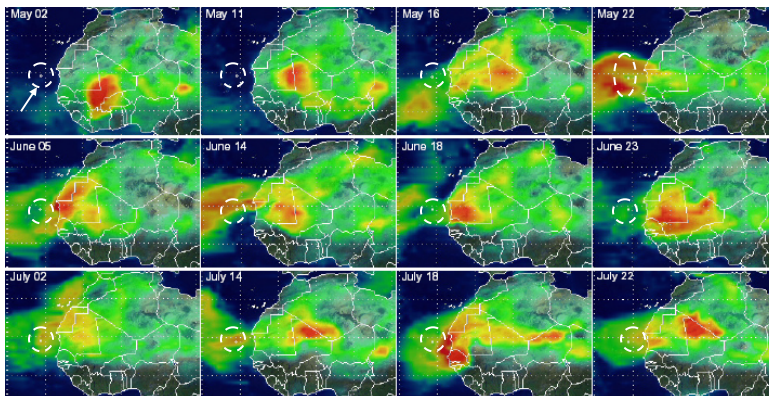


Plant wax (C_{29} *n*-alkane) carbon isotopes of African dust and E-Atlantic surface sediments



Carbon isotopic composition of dustfall sample off NW Africa

Fractions	Concn. (gdw basis)	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	^{14}C age (yr BP)
Total Organic Carbon	1.02 %	-18.93	-149.6	1260 \pm 40
Black Carbon	0.24 %	-15.13	-231.7	2070 \pm 35
Plant wax alcohols	12 μg	-27.9	-80.8	649 \pm 143



Eglinton et al., G³, 2002

Summary

- The annual export of terrestrial OC by rivers to the oceans is more than sufficient to account for all the OC buried in marine sediments.
- The majority of OC burial in marine sediments takes place on the continental margins, particularly in deltaic systems.
- Together, these two observations imply that terrestrial organic matter may comprise a major fraction of OC buried in marine sediments.
- Nevertheless, a range of evidence indicates that terrestrial organic carbon is efficiently remineralized before or upon entering the ocean.
- Current estimates for terrestrial OC burial may be incorrect/too low due to:
 - Inadequate sampling of small [tropical] mountainous river systems
 - Inadequate characterization of rivers draining into the Arctic Ocean
 - Variable inputs of C3 and C4 terrestrial vegetation
 - Compositional transformations attending dispersal of terrestrial organic matter in the oceans.
- Variations in terrestrial OC burial over glacial/interglacial cycles?