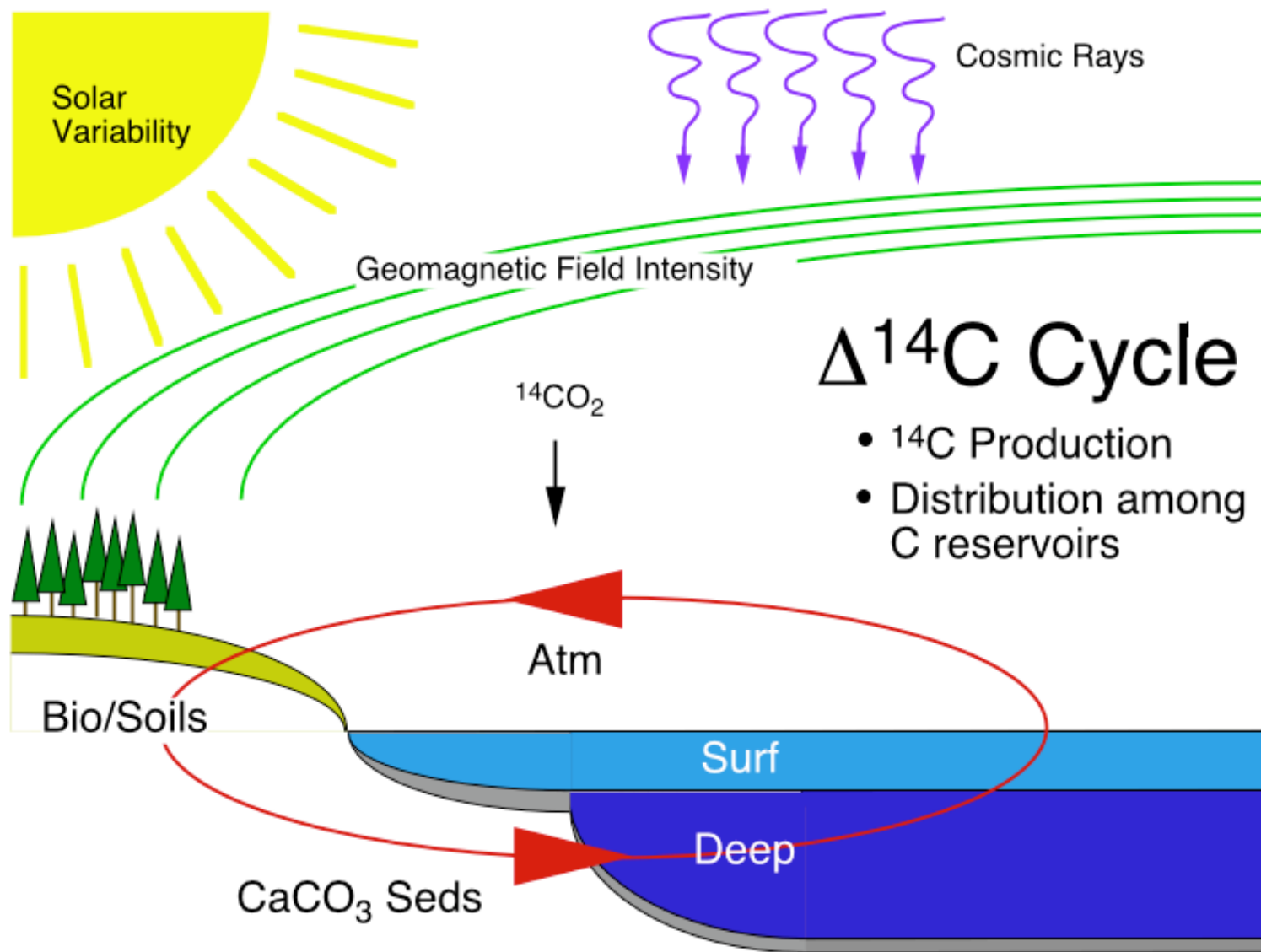
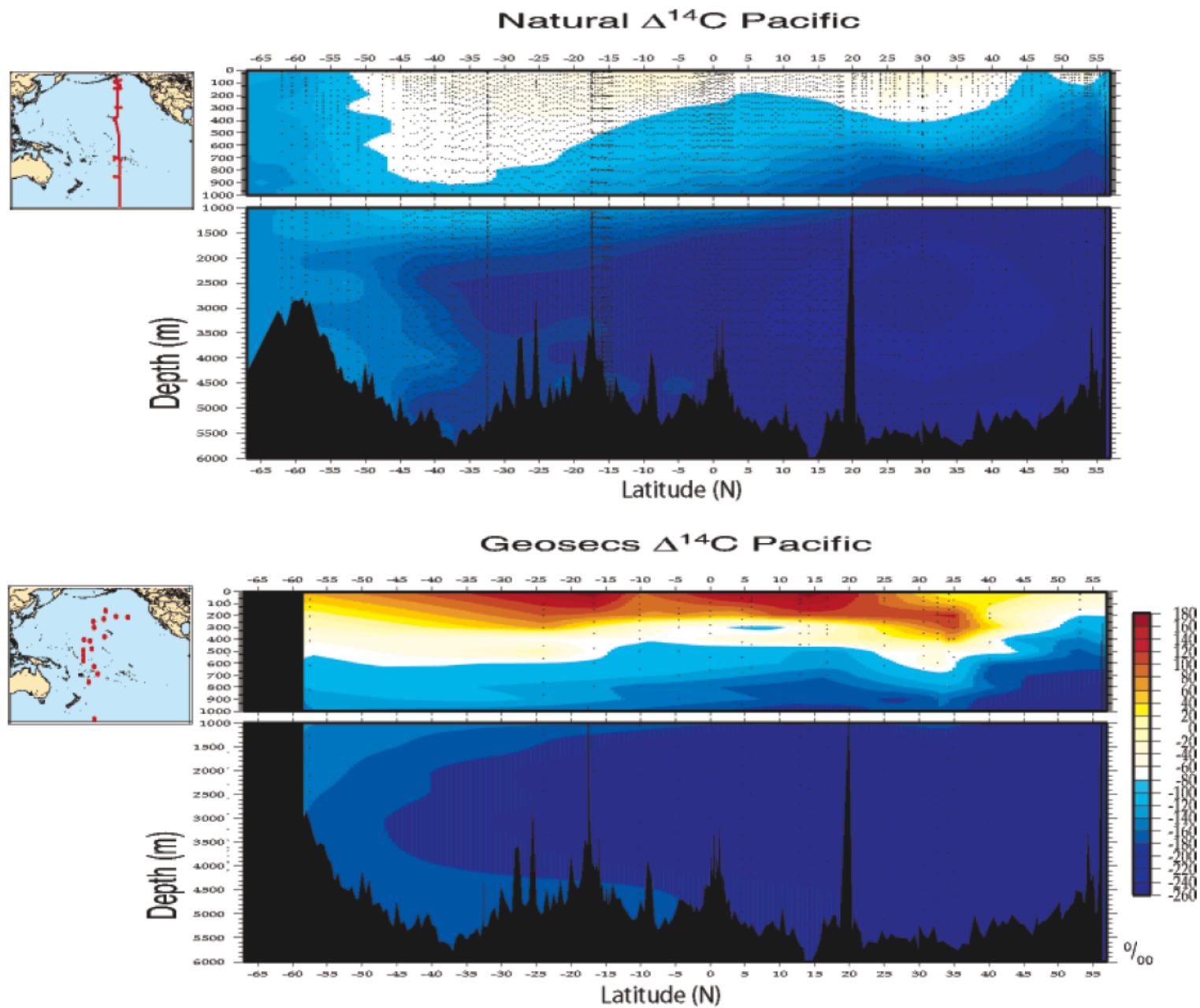


# Natural abundance radiocarbon and DOC





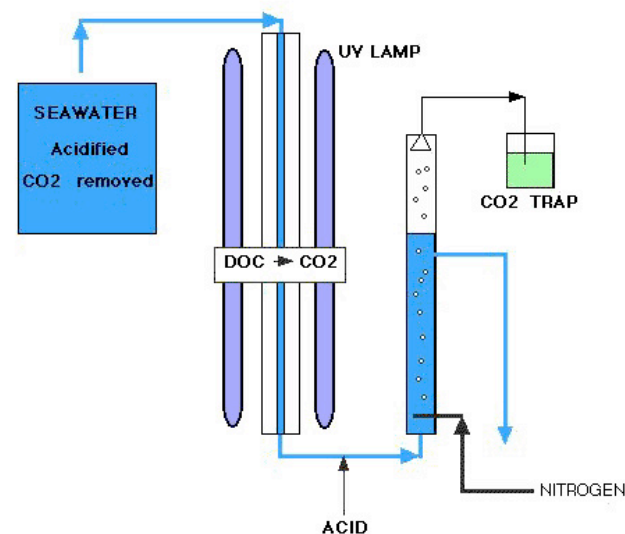
# DOC cycling via $\text{DO}^{14}\text{C}$

## Natural Radiocarbon Activity of the Dissolved Organic Carbon in the North-east Pacific Ocean

THE "age" of the dissolved organic matter in the deep sea relative to its origin in the euphotic zone has been a matter of conjecture for some time<sup>1-3</sup>. Photosynthetic fixation of carbon dioxide into plant carbon by phytoplankton and subsequent biochemical oxidation or solubilization of organic carbon takes place primarily in the upper 0-300 m of the sea. A small, as yet unknown, fraction of this organic carbon is transferred into the deep water by physical processes such as turbulent mixing and sinking of surface water at high latitudes. In addition, particulate organic carbon which sinks from the surface may be converted into dissolved organic matter at depth. In order to determine how "old" this dissolved organic carbon is, its natural radiocarbon activity has been measured for two deep-water samples taken off southern California.

The dissolved organic carbon was converted to carbon dioxide (and subsequently to methane for radiocarbon counting) by photo-oxidation with high energy ultraviolet radiation<sup>4</sup> (Fig. 1). Seawater was collected with a 100 l. stainless steel sampler and stored in 200 l. pre-leached steel drums lined with polythene (no increase in organic carbon was detected during the storage period before analysis). Pre-filtration to remove particulate organic matter was not necessary because its concentration was less than 5 µg/l. The seawater was acidified to pH 2 with hydrochloric acid, sparged free of inorganic carbon (99-97 per cent) with oxygen gas and irradiated in 60 l. batches for 20 h. using a 1,200 W mercury-arc lamp (Hanovia Engelhardt '189 A'). The carbon dioxide so formed was sparged from the seawater with oxygen gas and trapped in strontium hydroxide as strontium carbonate. Complete oxidation was ascertained by comparison of the carbon dioxide in the irradiated seawater (detected by a Beckman model 16 infrared analyser) with the amount of carbon dioxide resulting from the wet combustion of the organic carbon in the seawater before oxidation<sup>5,6</sup>. The strontium carbonate was collected by filtration, washed with water in a nitrogen atmosphere and then dried *in vacuo*.

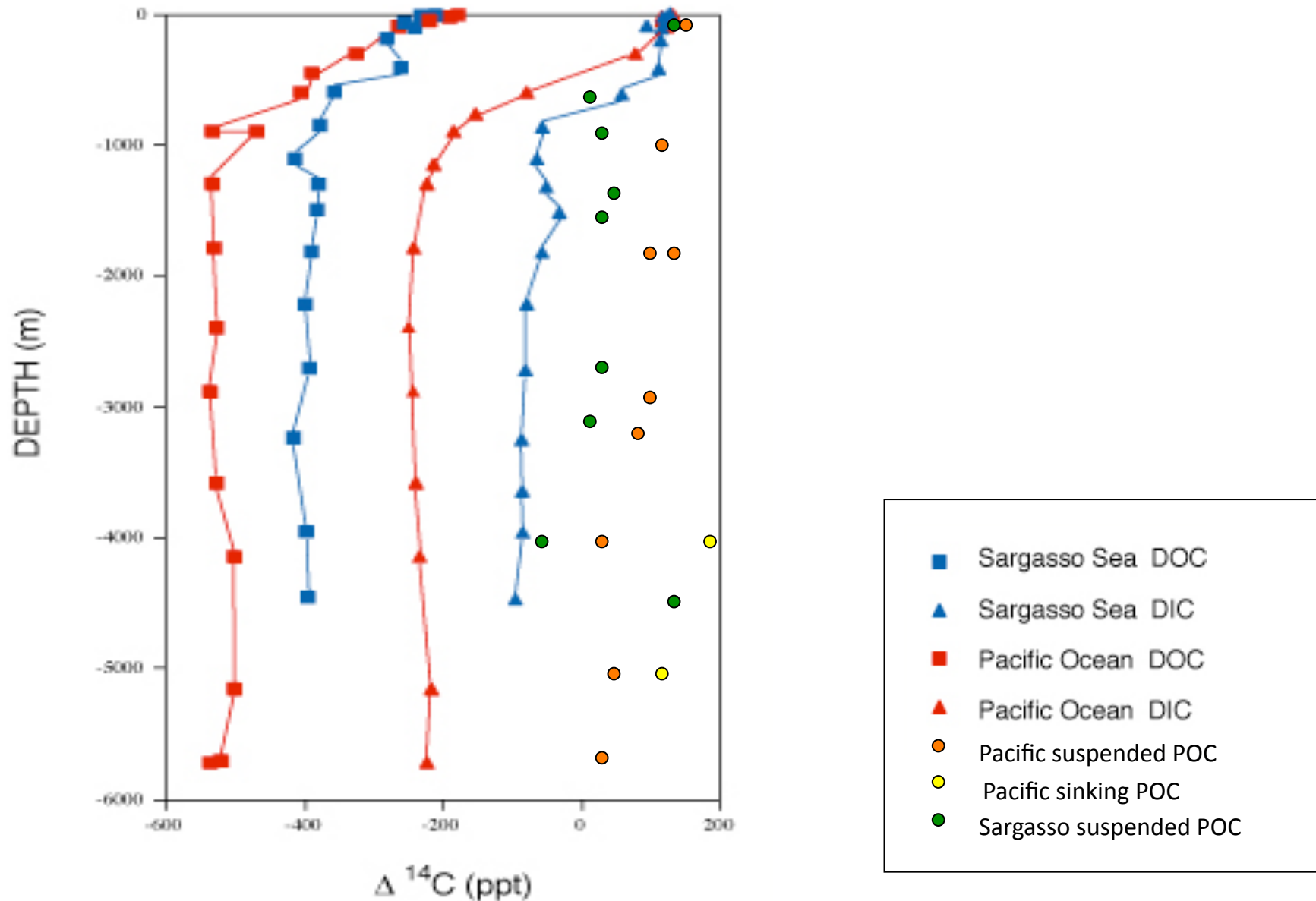
## UV photooxidation



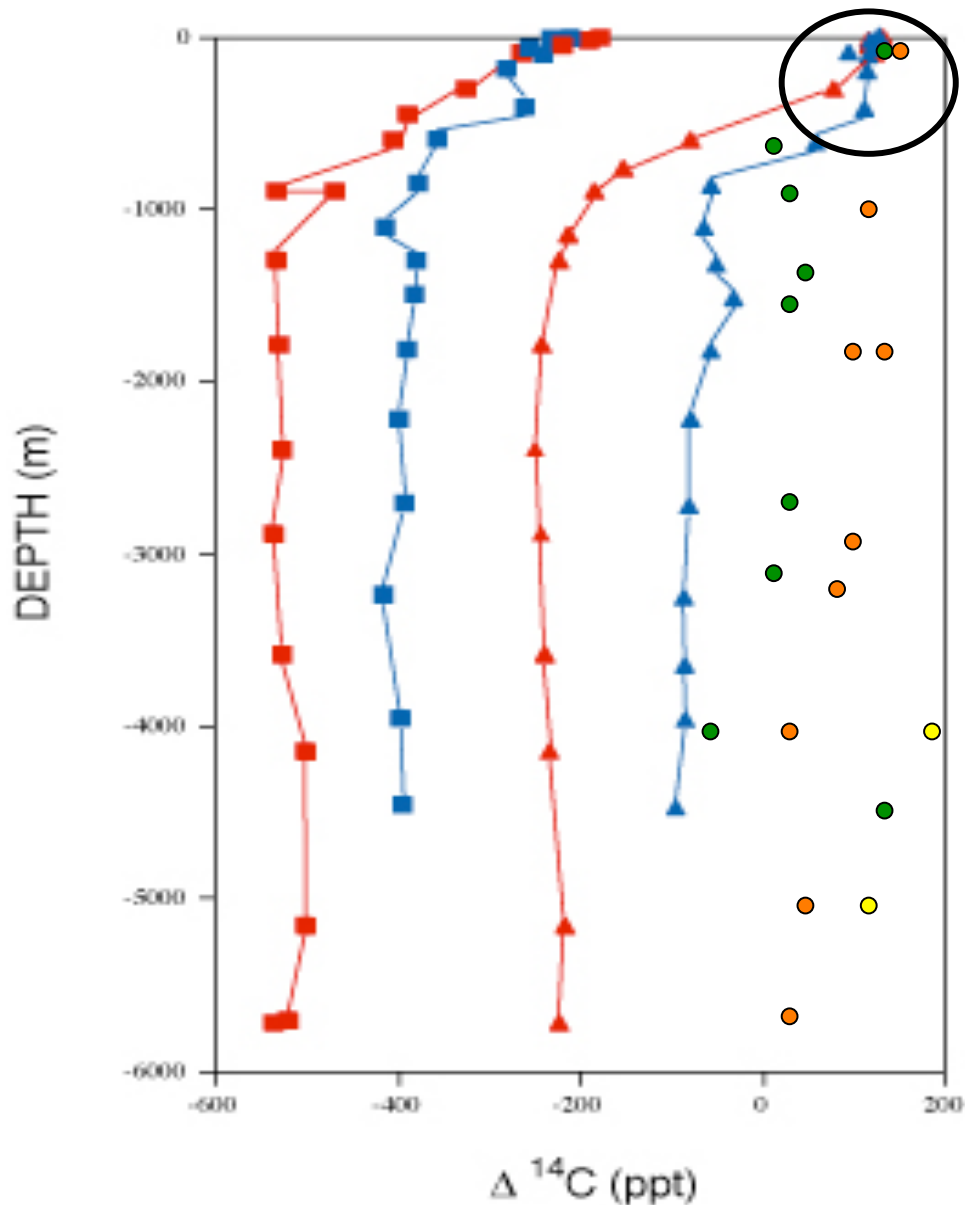
Depth	$\Delta^{14}\text{C}(\text{‰})$	Age
1880m	-351 ‰	-3470 $\pm$ 330 ybp
1920m	-341 ‰	-3350 $\pm$ 300 ybp

# Radiocarbon in the Atlantic and Pacific Oceans

Peter M. Williams and Ellen Druffel; Nature 1987, JGR 1992



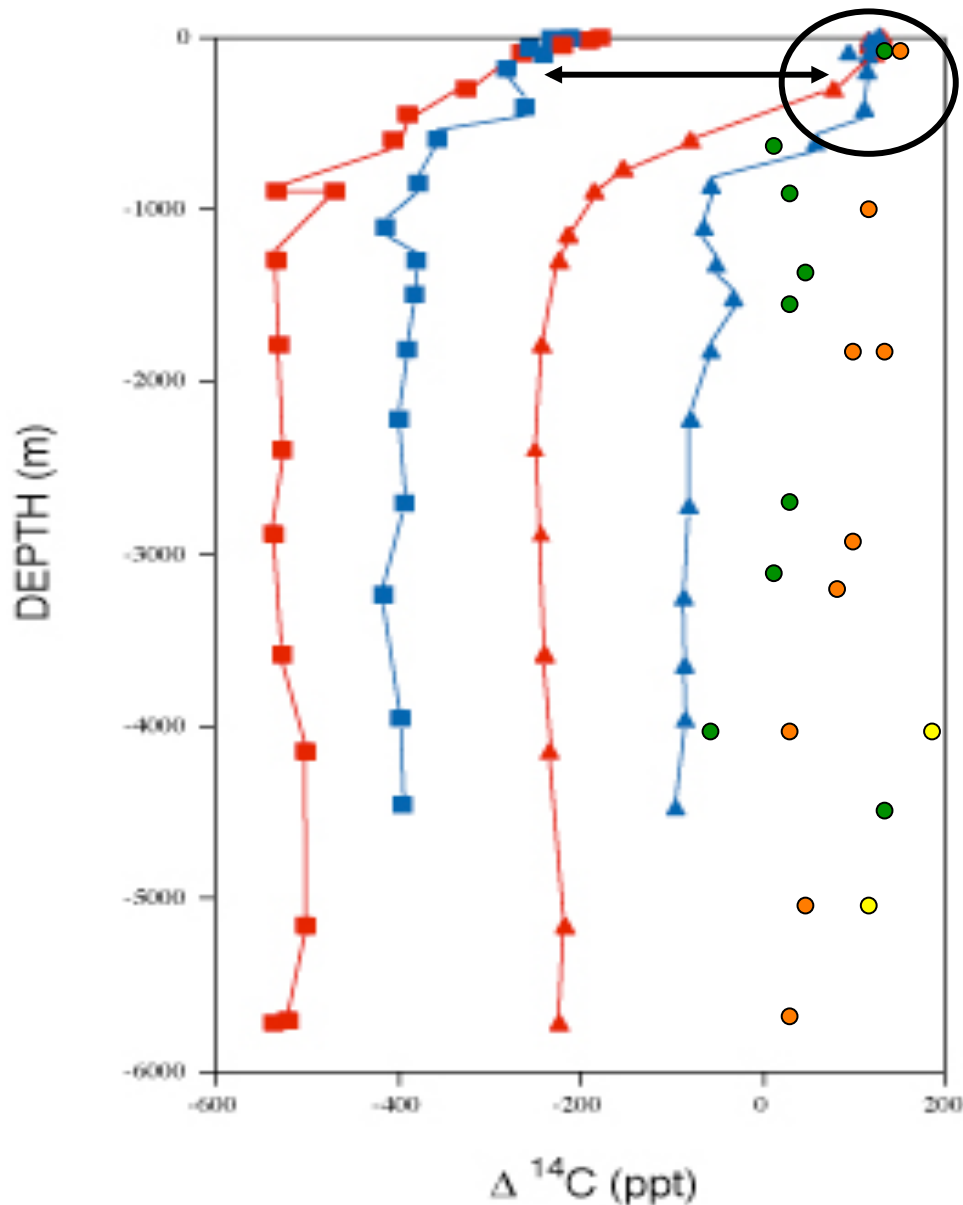
# Radiocarbon in the Atlantic and Pacific Oceans



DIC  $^{14}\text{C}$  in surface waters of the Atlantic and Pacific have similar isotopic values.

- Sargasso Sea DOC
- ▲ Sargasso Sea DIC
- Pacific Ocean DOC
- ▲ Pacific Ocean DIC
- Pacific suspended POC
- Pacific sinking POC
- Sargasso suspended POC

# Radiocarbon in the Atlantic and Pacific Oceans



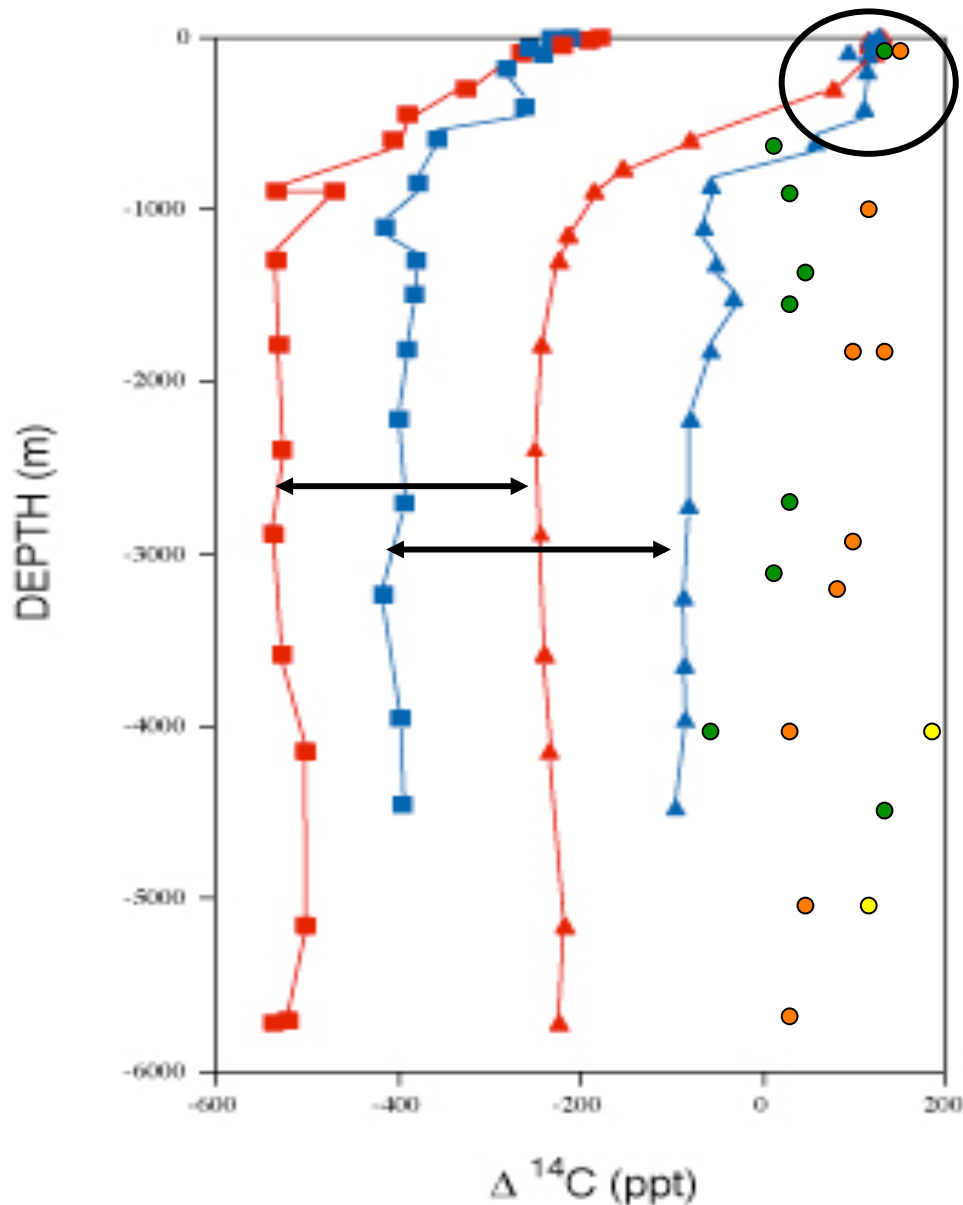
DIC  $^{14}\text{C}$  in surface waters of the Atlantic and Pacific have similar isotopic values.

DOC is always older than DIC (by 2-3 kyrs in surface water)

DIC  $\rightarrow$  POC  $\rightarrow$  DOC

- Sargasso Sea DOC
- ▲ Sargasso Sea DIC
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# Radiocarbon in the Atlantic and Pacific Oceans



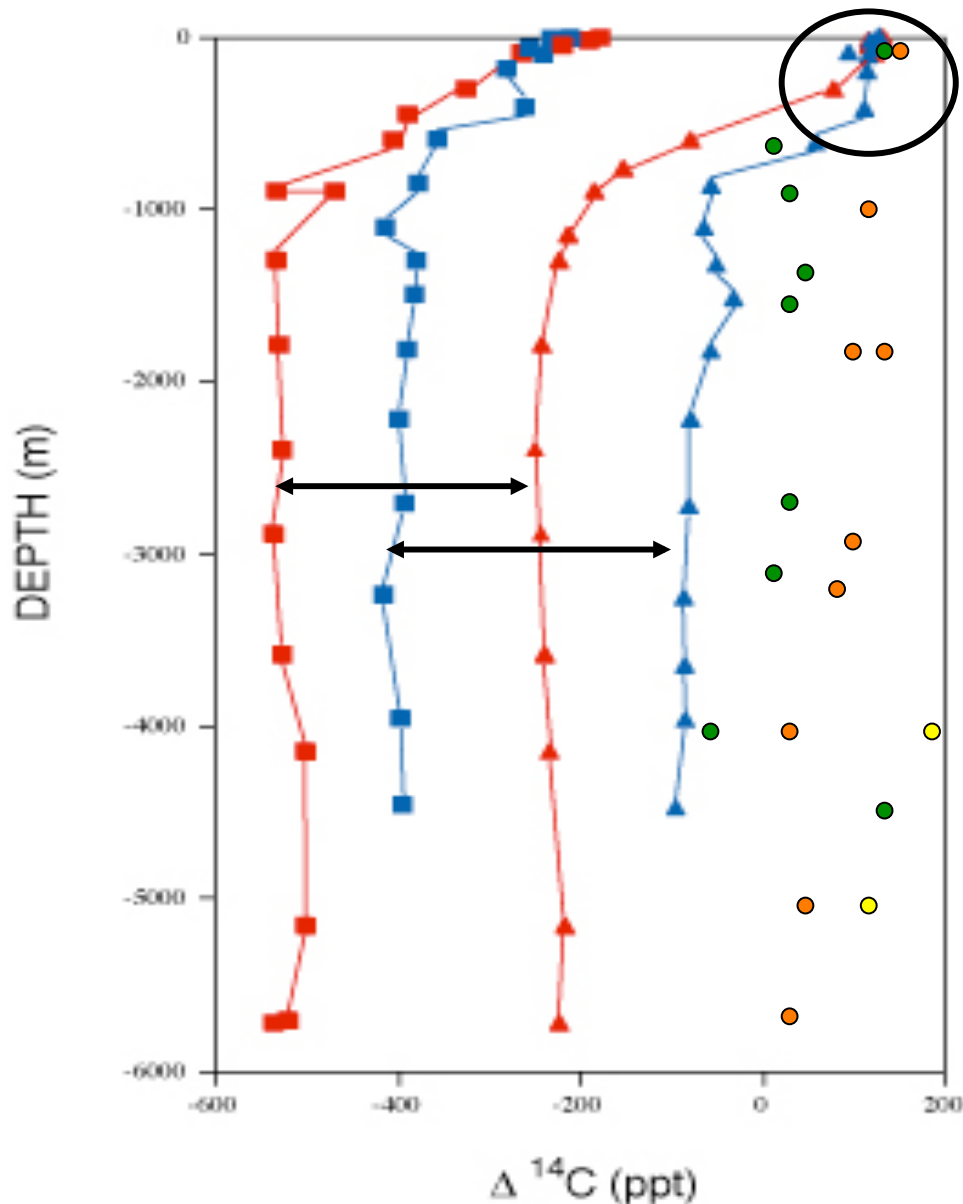
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- ▲ Sargasso Sea DIC
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# Radiocarbon in the Atlantic and Pacific Oceans



DIC  $^{14}\text{C}$  in surface waters of the Atlantic and Pacific have similar isotopic values.

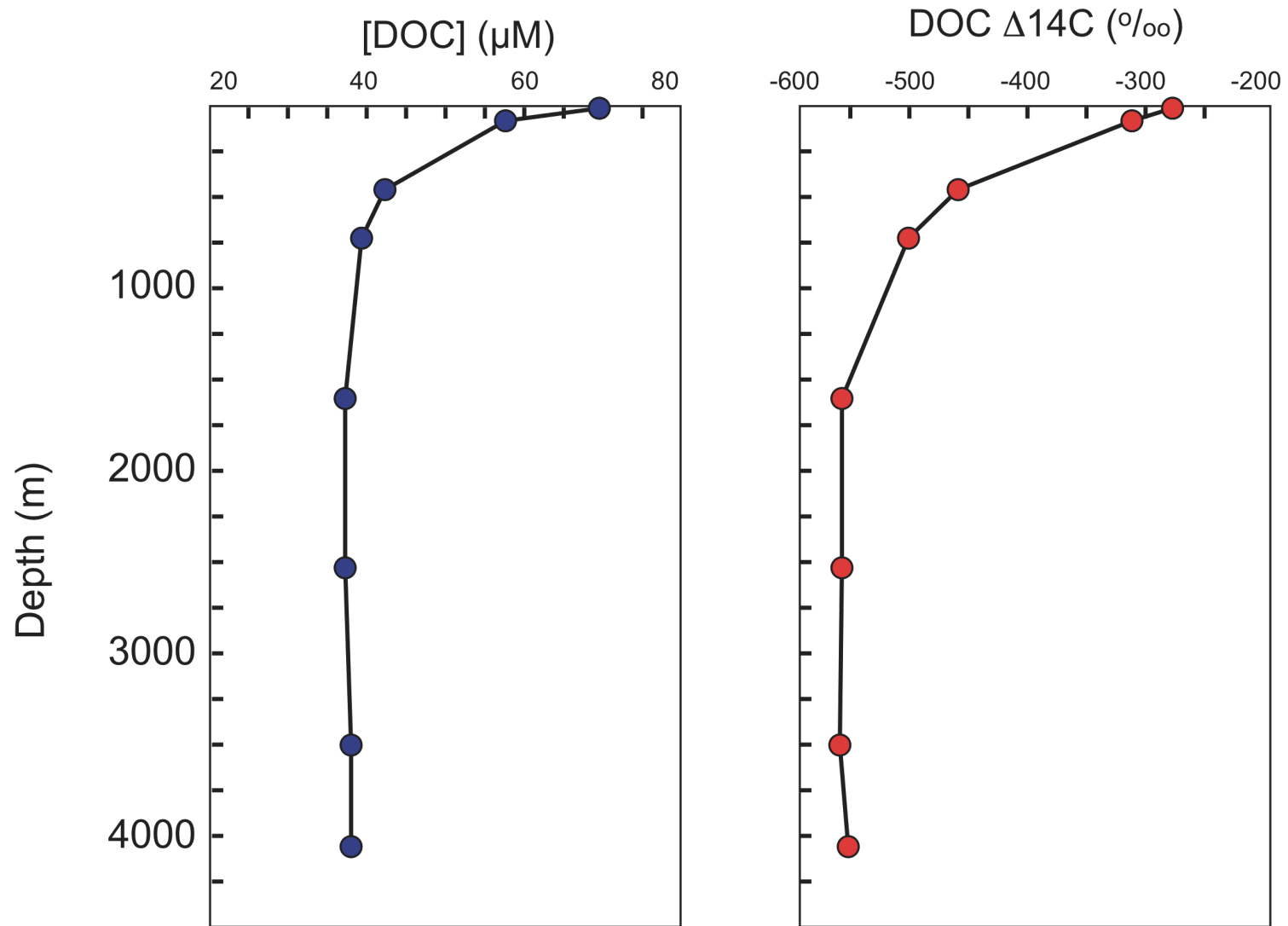
DOC is always older than DIC (by 2-3 kyrs in surface water)

$\Delta\Delta^{14}\text{C}$  of DIC and DOC is about the same in the deep Atlantic and Pacific

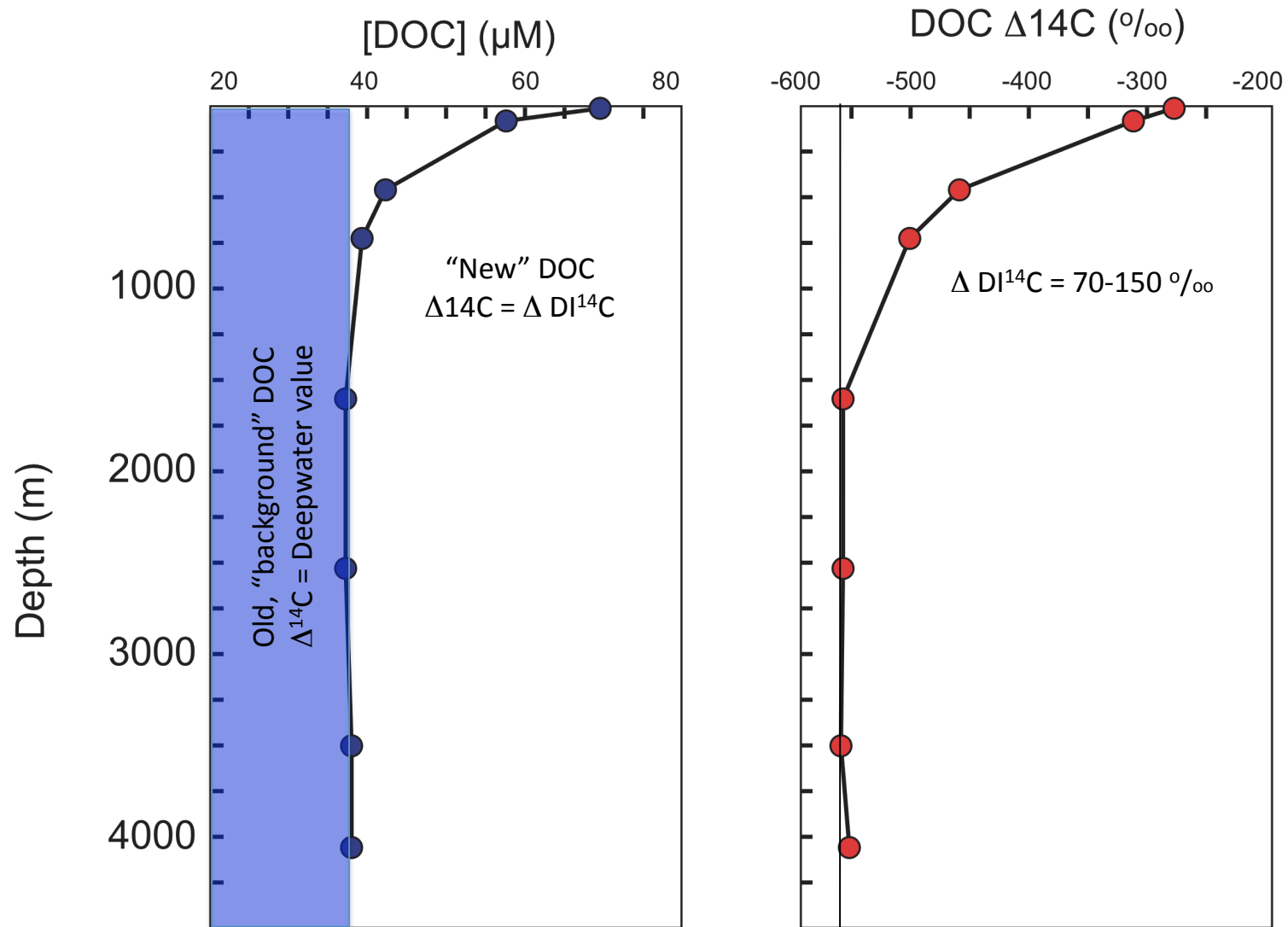
Deep ocean values of DOC are equal to a radiocarbon age of 4-6 kyrs

Either there is a source of "old" DOC, or DOC persists for several ocean mixing cycles

## Radiocarbon based models of DOC cycling in the water column



## Radiocarbon based models of DOC cycling in the water column



Williams and Druffel proposed a two component model to explain DOC cycling in the Water column.

In their model the old radiocarbon age of deep DOC implies a nonreactive reservoir of Carbon with a stable concentration and fixed radiocarbon value

Surface water DOC is a mixture of old, deep DOC and new DOC that has a radiocarbon value of equal to DIC. The new DOC is considered to be excess carbon that accumulates in the upper ocean over timescales of upper ocean mixing.

They assume that the origin of the new DOC in the ocean is photosynthesis:

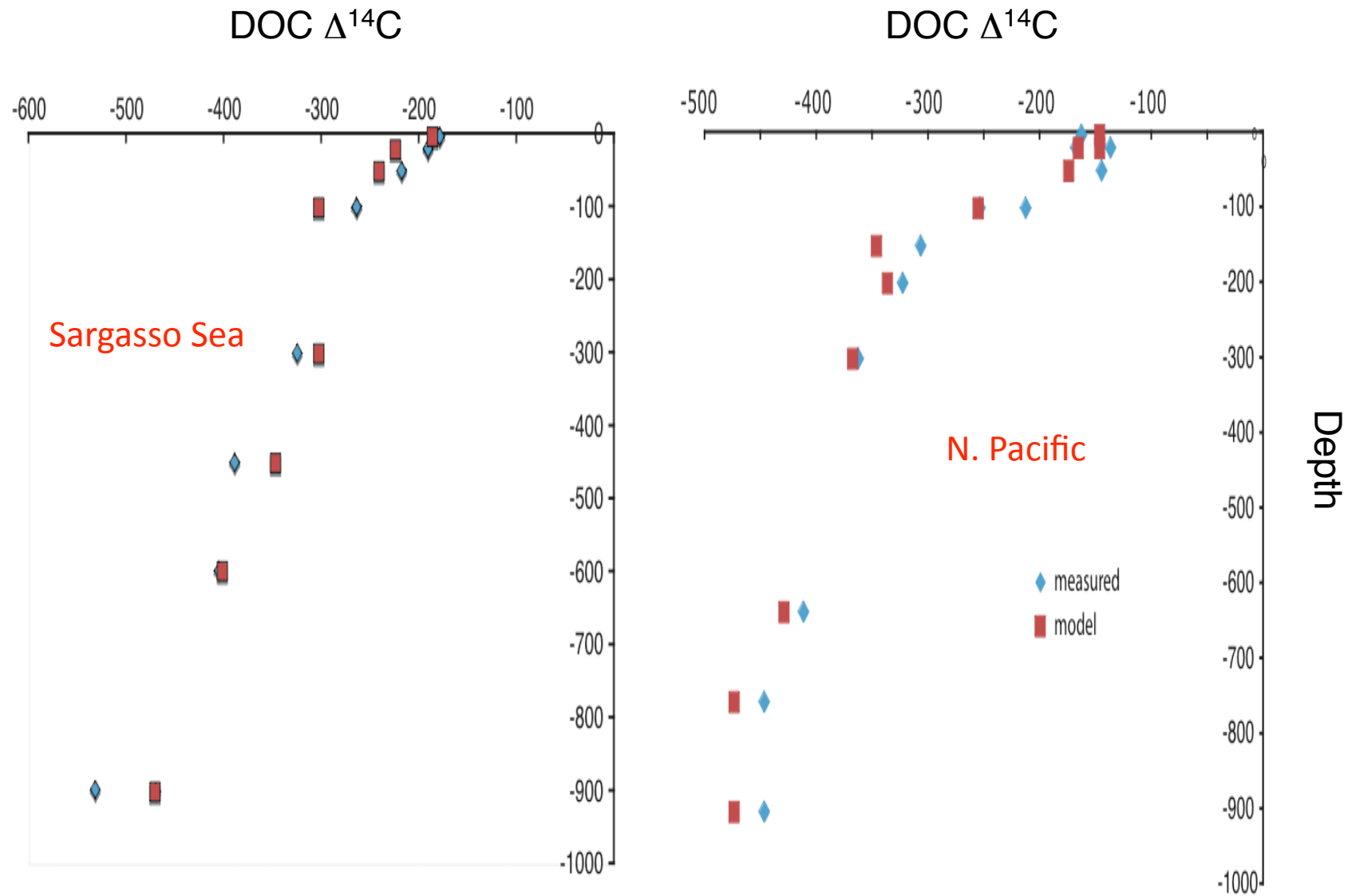
DIC -> POC-> DOC

Mass and isotopic balance can be expressed as:

$$[\text{DOC}]_{\text{sur}} = [\text{DOC}]_{\text{deep}} + [\text{DOC}]_{\text{xs}}$$

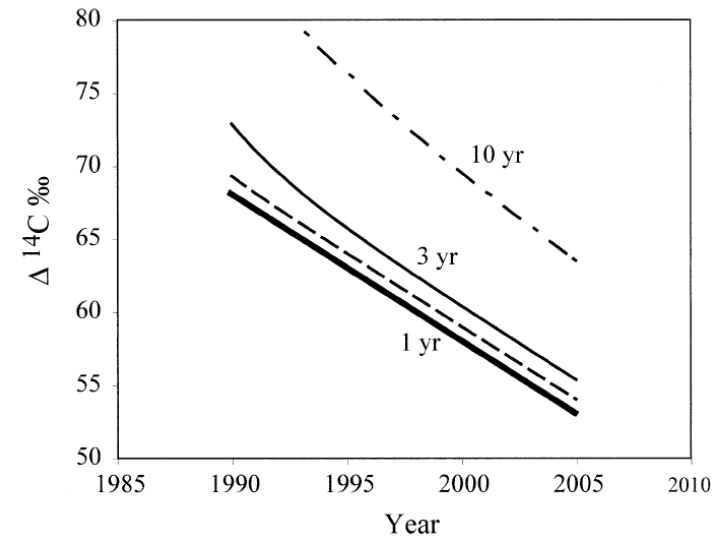
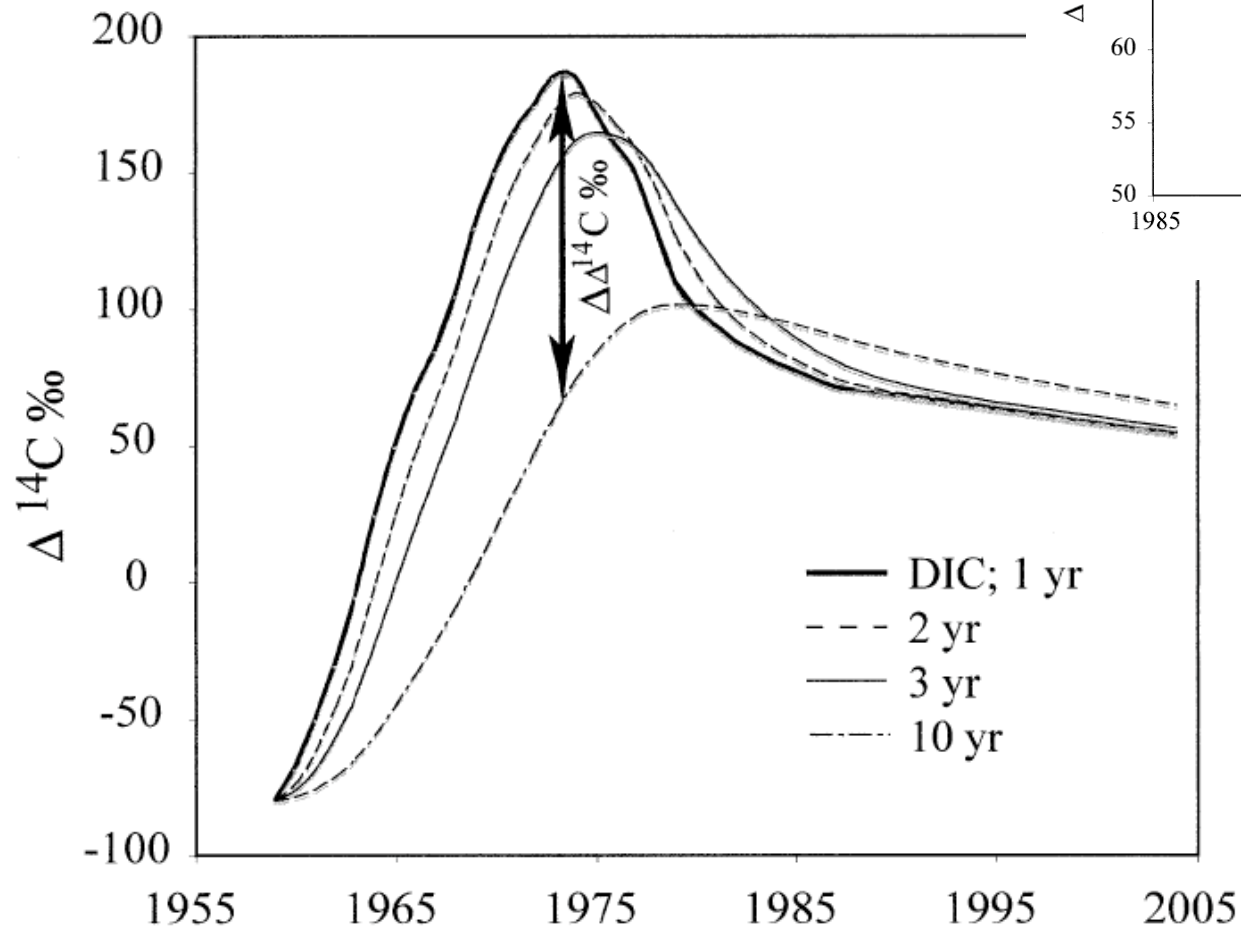
$$\Delta^{14}\text{C}_{\text{sur}} [\text{DOC}]_{\text{sur}} = \Delta^{14}\text{C}_{\text{deep}} [\text{DOC}]_{\text{deep}} + \Delta^{14}\text{C}_{\text{xs}} [\text{DOC}]_{\text{xs}}$$

The Williams and Druffel model allows us to predict what the Isotopic value of surface water should be based on deep water and DIC radiocarbon values.

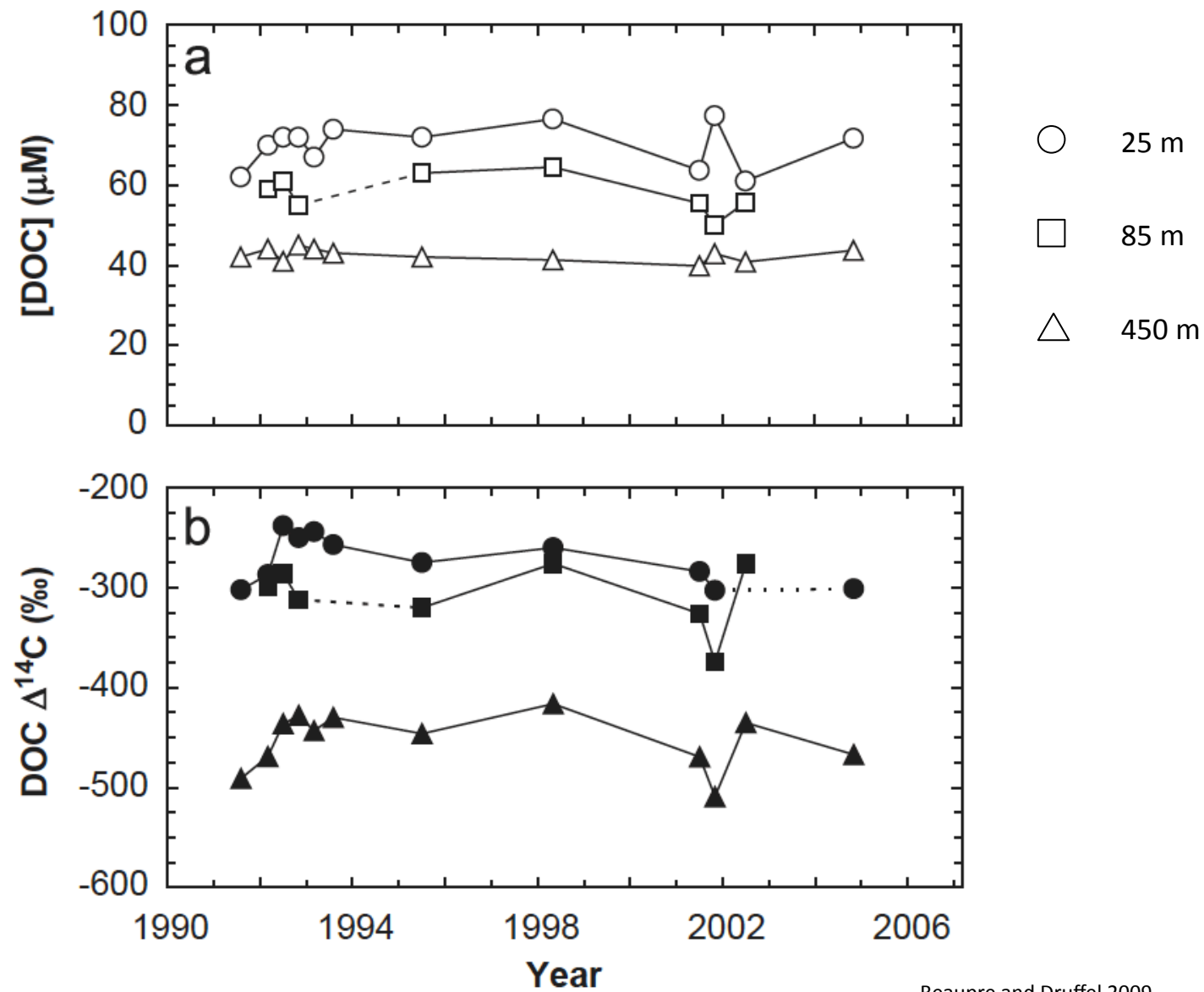


Williams and Druffel, 1987; Druffel et al. 1992

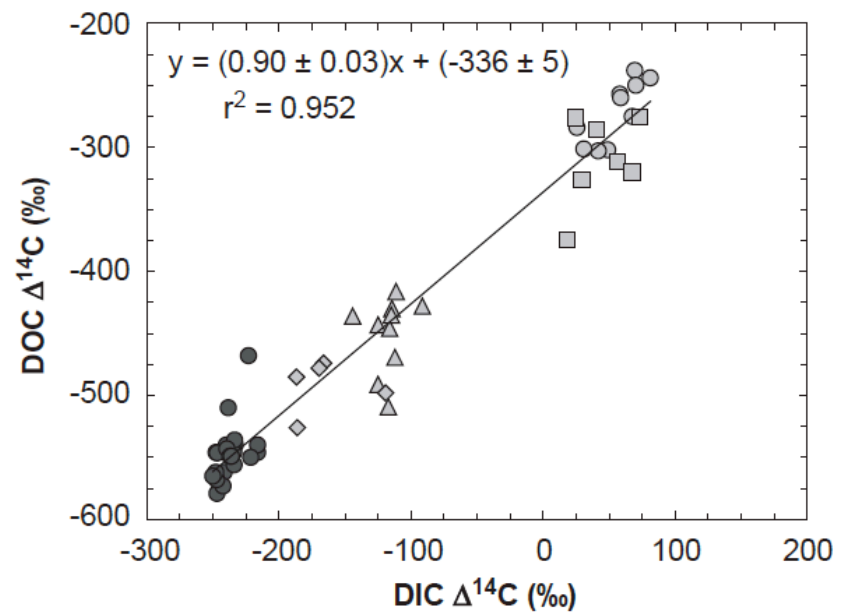
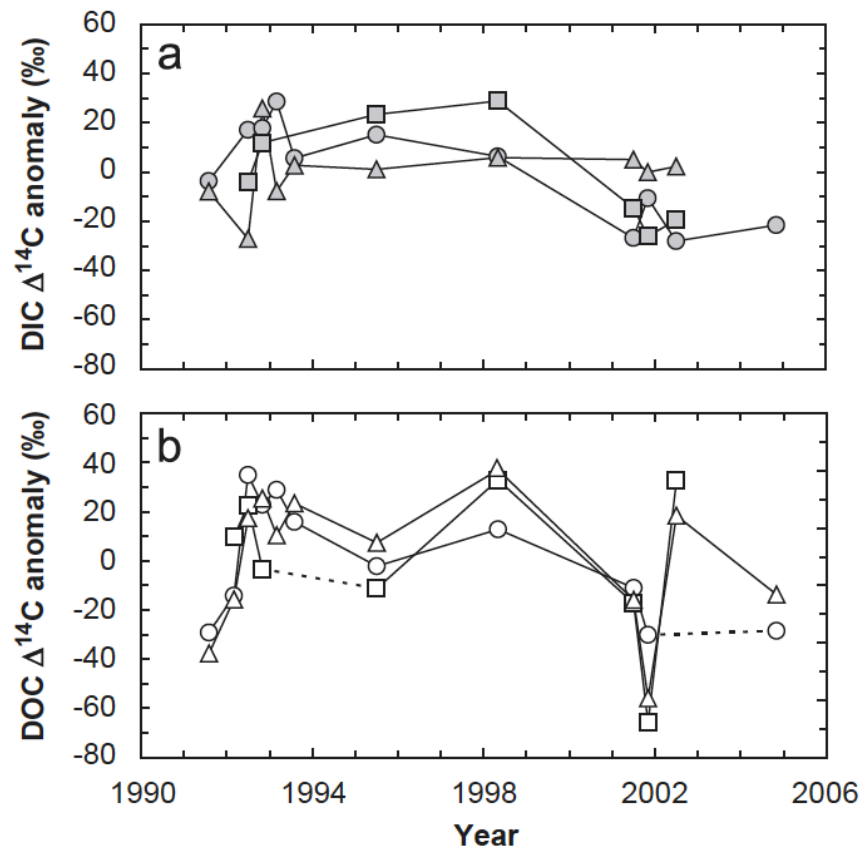
One of the major assumptions of the Williams and Druffel model is that DOC Rapidly equilibrates with POC. If this were true Why does DOC accumulate in the upper ocean?



# Time-series measurements of [DOC] and $\text{DOC } \Delta^{14}\text{C}$ at Station M



# What drives the changes in [DOC] and DOD<sup>14</sup>C values At Station M?



Mortazani and Chanton (2004) express the conservation of mass and isotope balance relations to formulate a Keeling plot. This solves the issue of the radiocarbon value of  $\text{DOC}_{\text{xs}}$

$$[\text{DOC}]_Z = [\text{DOC}]_{\text{deep}} + [\text{DOC}]_{\text{xs}}$$

$$\Delta^{14}\text{C}_Z [\text{DOC}]_Z = \Delta^{14}\text{C}_{\text{deep}} [\text{DOC}]_{\text{deep}} + \Delta^{14}\text{C}_{\text{xs}} [\text{DOC}]_{\text{xs}}$$

*substituting for  $[\text{DOC}]_{\text{xs}}$*

$$\Delta^{14}\text{C}_Z [\text{DOC}]_Z = \Delta^{14}\text{C}_{\text{deep}} [\text{DOC}]_{\text{deep}} + \Delta^{14}\text{C}_{\text{xs}} ([\text{DOC}]_Z - [\text{DOC}]_{\text{deep}})$$

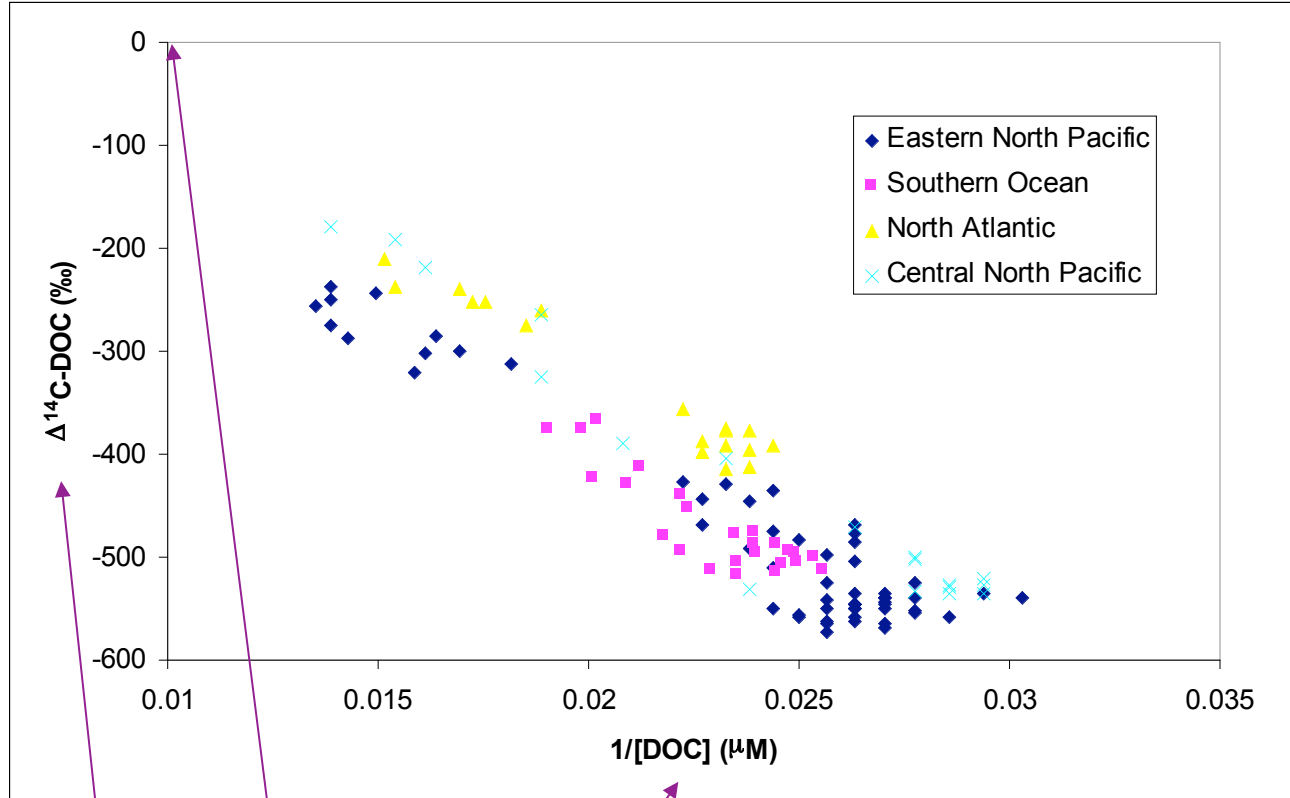
*and rearranging*

$$\Delta^{14}\text{C}_Z = \Delta^{14}\text{C}_{\text{xs}} + (1/[\text{DOC}]_Z) (\Delta^{14}\text{C}_{\text{deep}} [\text{DOC}]_{\text{deep}} - \Delta^{14}\text{C}_{\text{xs}} [\text{DOC}]_{\text{deep}})$$

*A plot of  $\Delta^{14}\text{C}_Z$  vs  $1/[\text{DOC}]_Z$  will yield an intercept of  $\Delta^{14}\text{C}_{\text{xs}}$  and a slope of  $(\Delta^{14}\text{C}_{\text{deep}} [\text{DOC}]_{\text{deep}} - \Delta^{14}\text{C}_{\text{xs}} [\text{DOC}]_{\text{deep}})$*

Can we derive the radiocarbon value of DOC xs independently?

(Mortazani and Chanton, 2004)



$\Delta^{14}\text{C}_{xs}$

$73 \pm 23\text{‰}$  ('91-'95)

$105 \pm 62\text{‰}$  ('95/'96)

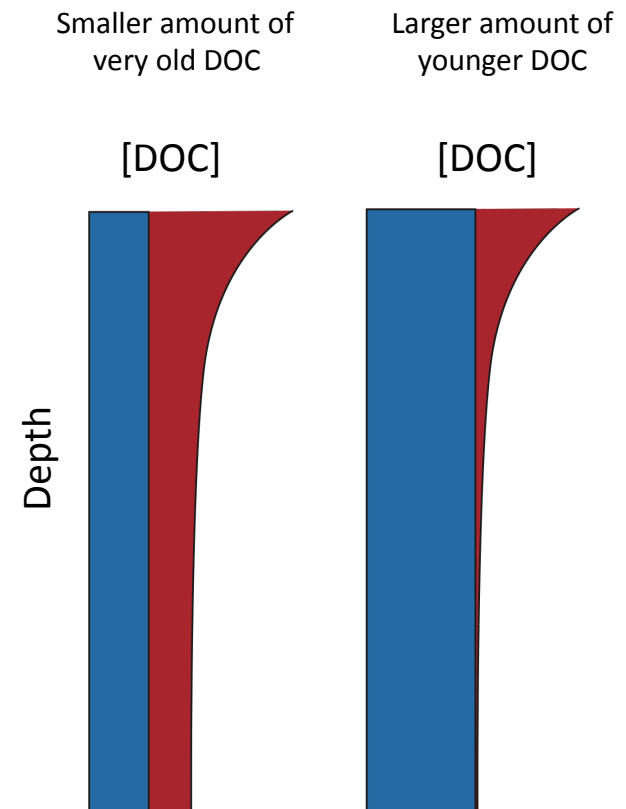
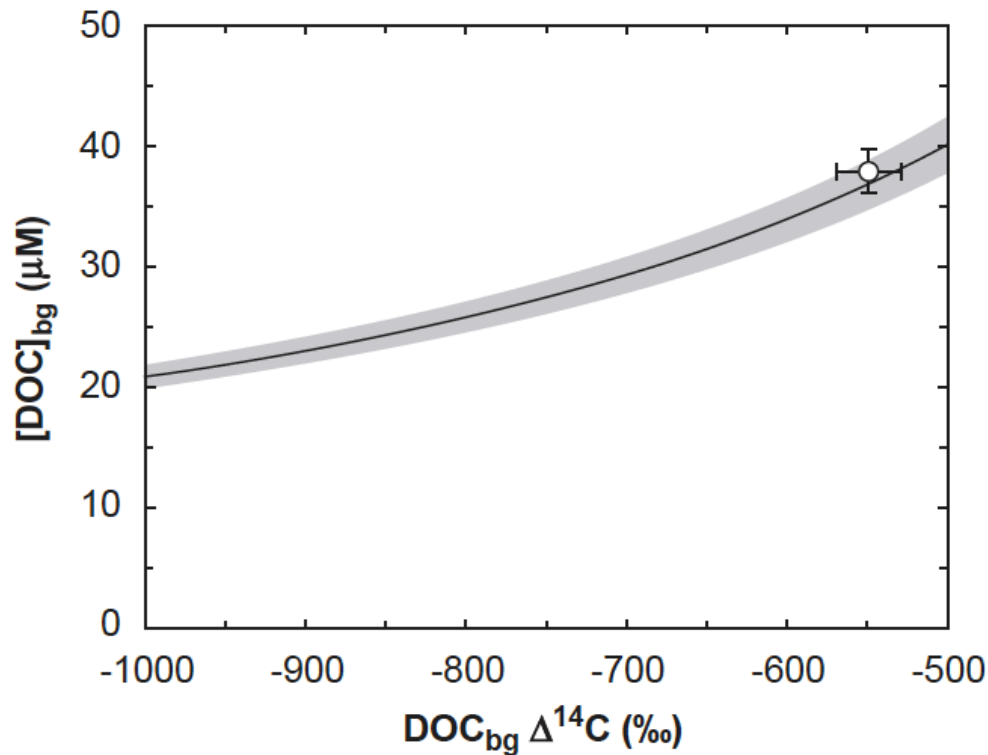
$135 \pm 26\text{‰}$  ('89)

$162 \pm 39\text{‰}$  ('87)

$$\Delta^{14}\text{C}_z = \Delta^{14}\text{C}_{xs} + \left( \frac{1}{\text{DOC}_z} \right) (\text{DOC}_b \Delta^{14}\text{C}_b - \text{DOC}_b \Delta^{14}\text{C}_{xs})$$

## Is there a transfer of carbon from the surface water into the deep ocean ?

The Keeling relationship only requires a conservation of mass, but does not stipulate what the isotopic/mass distribution of DOC is within the old (deep) fraction of DOC. A number of mass/isotope mixes can constitute the old fraction of DOC.



## Summary

DOC is the largest reservoir of “reactive” organic carbon in the ocean, about 680 GT C compared to a few GT C of microbial biomass. About 99% of water column marine organic matter is nonliving, and about 95-98% of total organic carbon is in DOC.

Carbon cycling on land and in the ocean is VERY efficient!

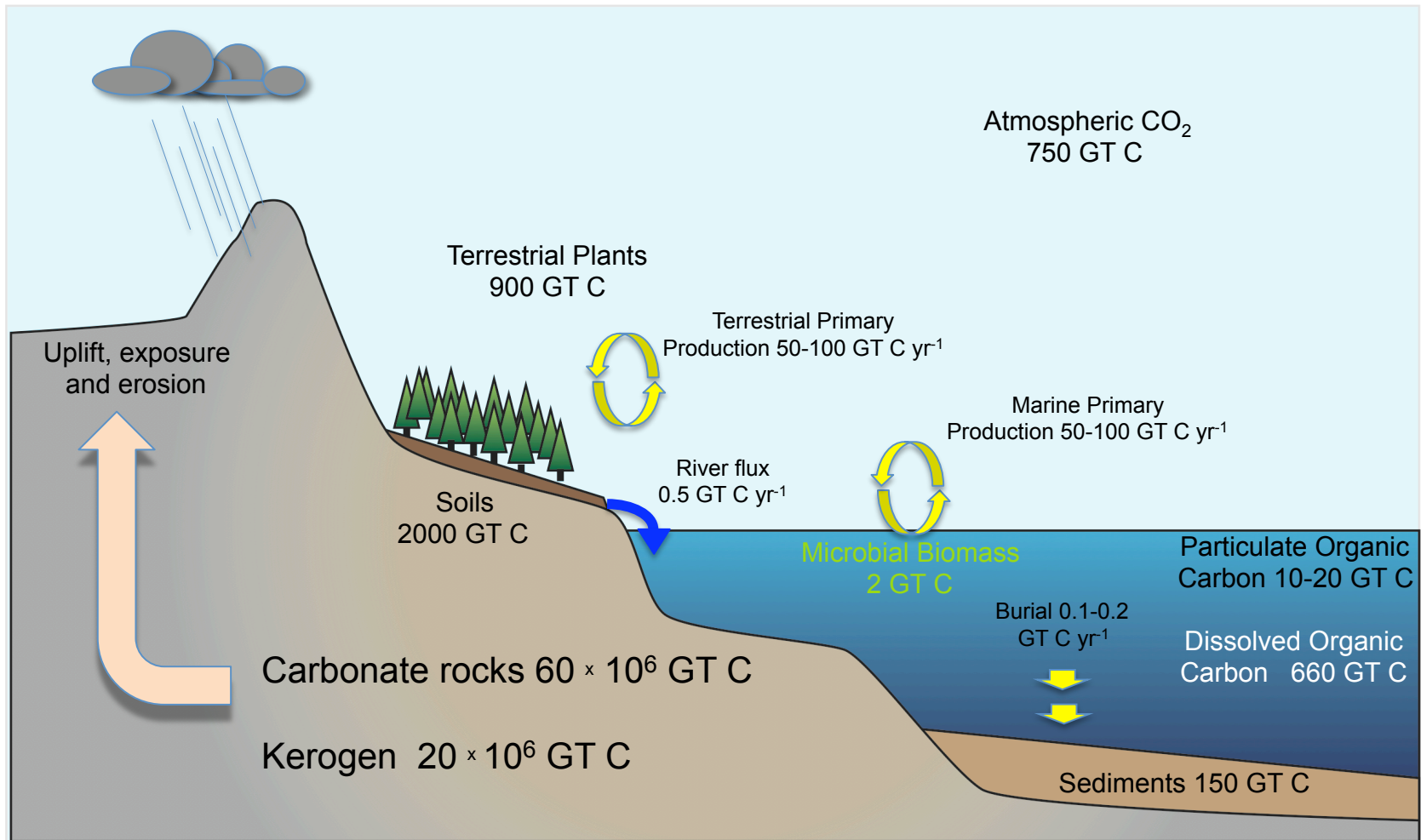
DOC has high concentrations in the euphotic zone indicating input or net production.

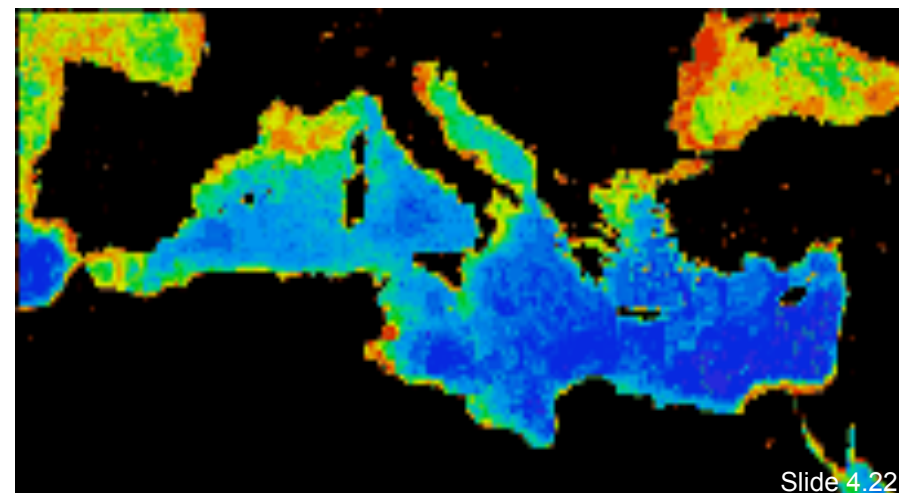
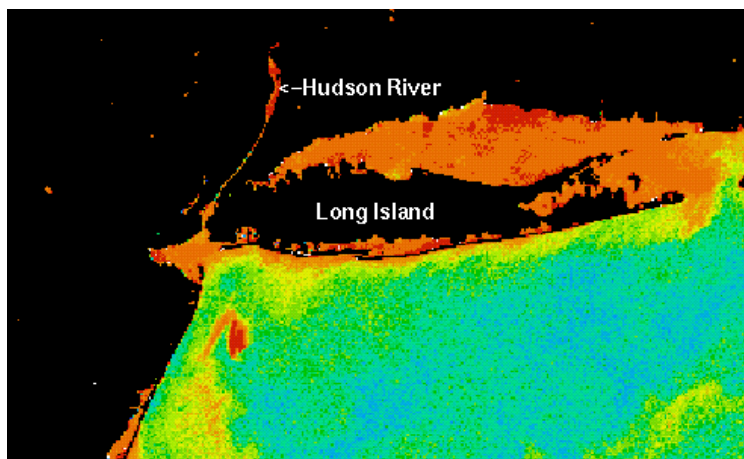
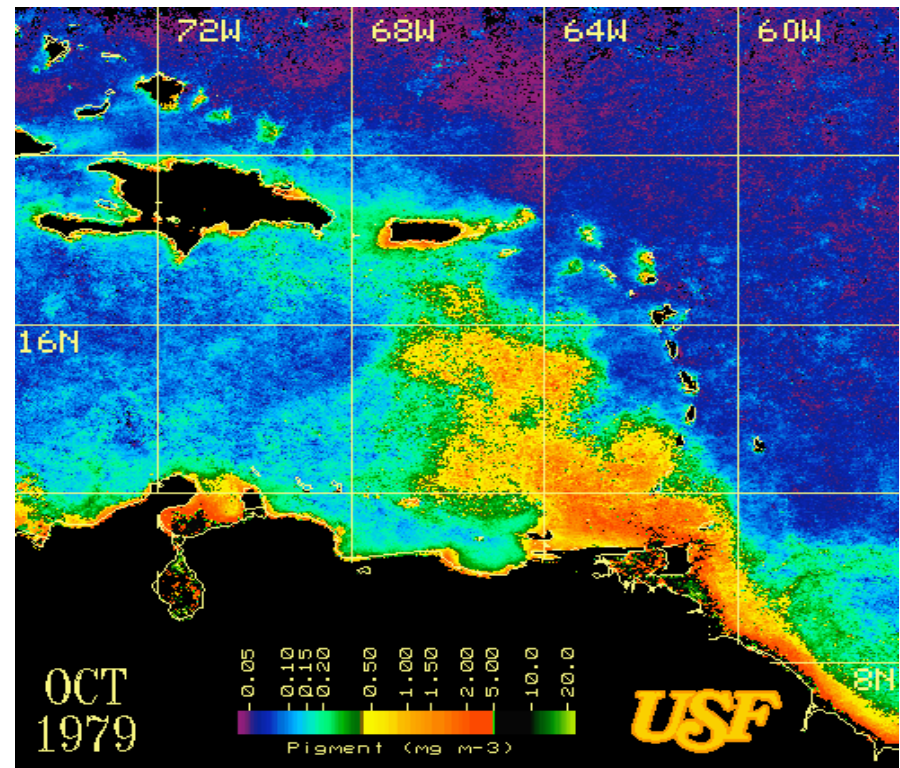
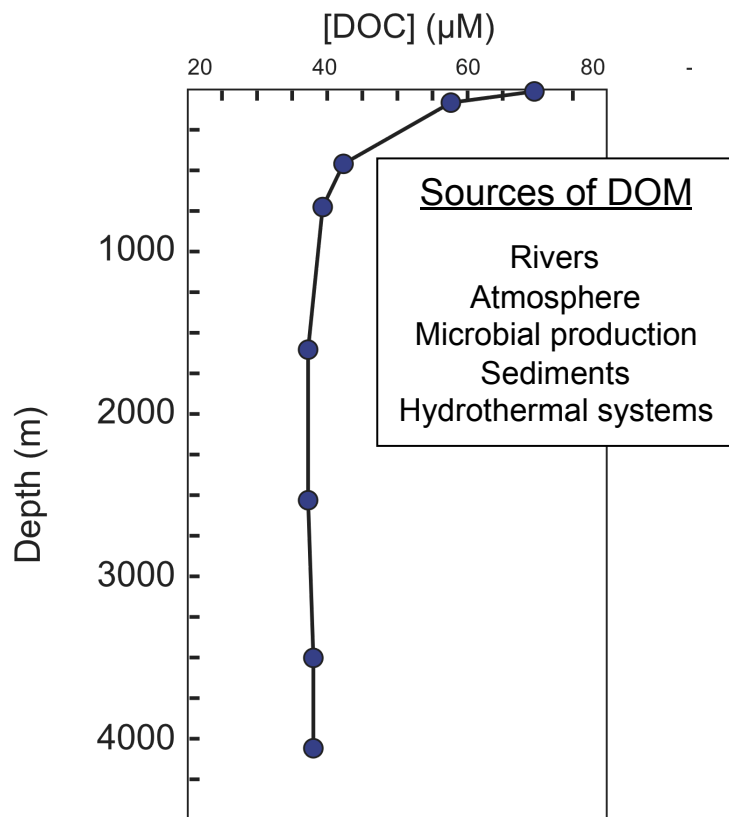
DOC concentrations are lower at depth (about half surface water values) and nearly constant throughout much of the deep ocean. High precision measurements show a removal of DOC from the deep ocean between the Atlantic and Pacific (-30%).

Radiocarbon values of DOC enriched in surface waters but highly depleted at depth. Radiocarbon values in surface water provide an age of 2000 years, and a deep sea average residence time of 5000-6000 years. Several ocean mixing cycles!!!

DOC radiocarbon values have been modeled as a two component system. The Model fits the data well, but includes a number of assumptions about DOC distributions and isotopic values that may be incorrect.

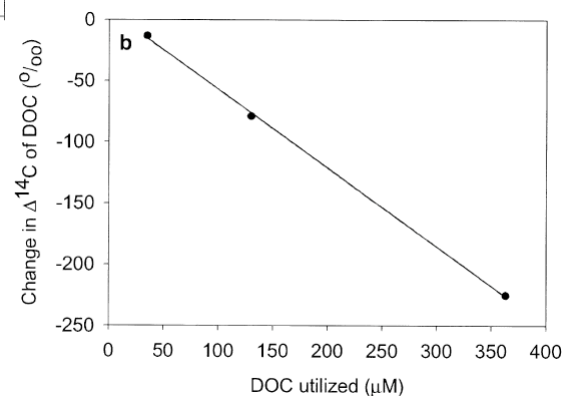
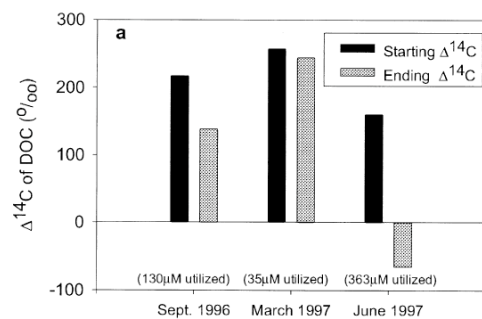
## What are the sources of DOC ?



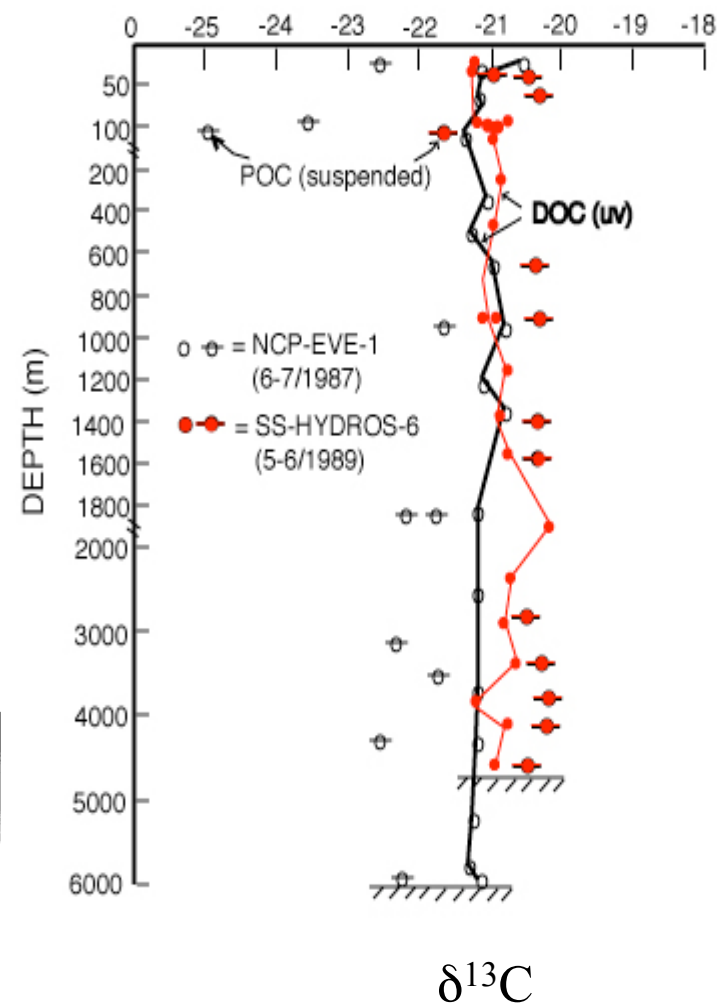


## The importance of terrestrial DOC depends on flux and isotopic value

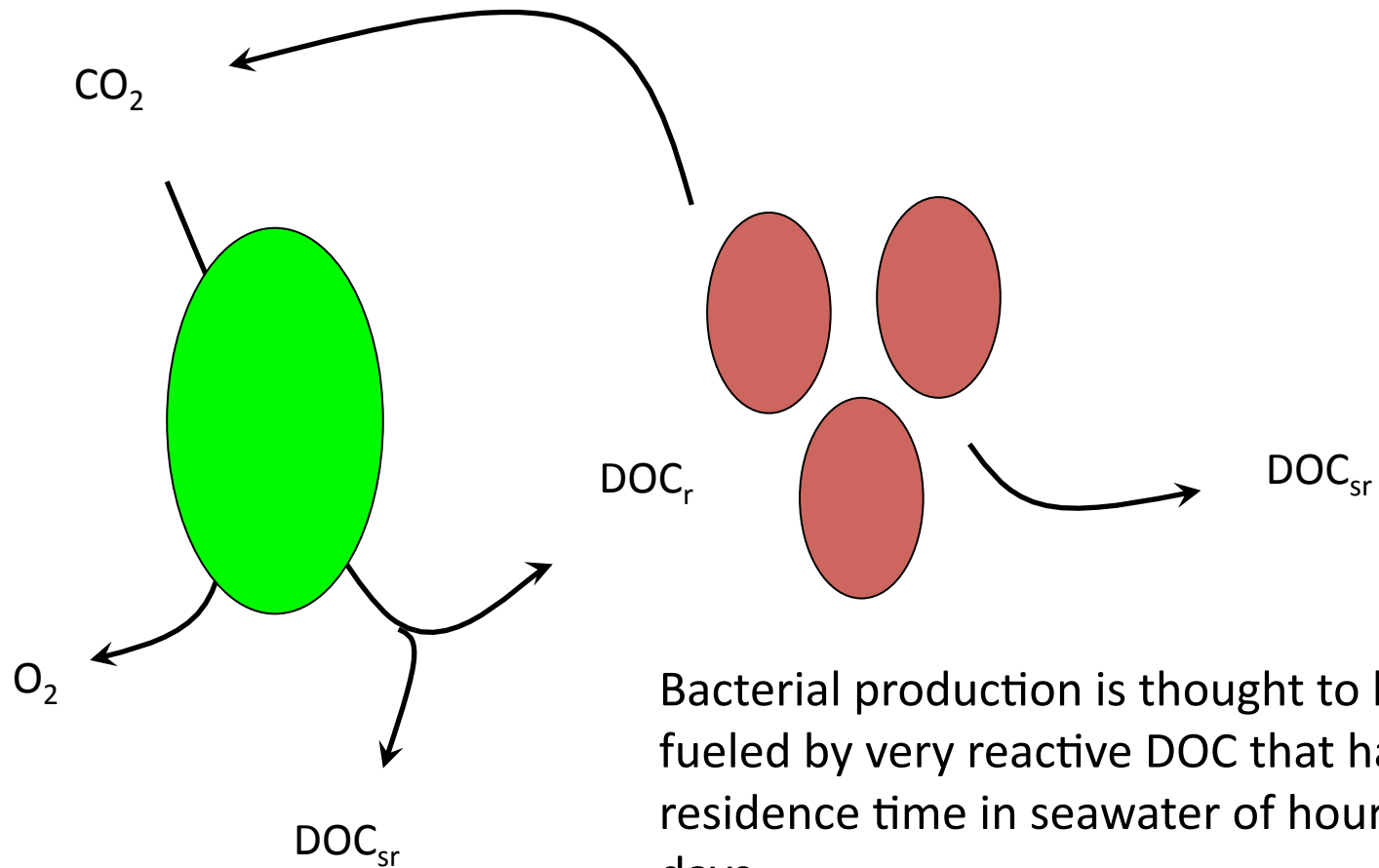
River	$\Delta^{14}\text{C}$ range (‰)	$\delta^{13}\text{C}$ range (‰)
DOC		
Amazon	28	-28.0
Amazon (total humics)	283	n.d.
Chesapeake Bay tributaries		
York (VA)	159 to 257	-28.8 to -27.9
Potomac (D.C.)	30 to 364	-29.9 to -32.4
Rappahannock (VA)	-83	-31.9
Susquehanna (MD)	-81	n.d.
James (VA)	43	-28.0
West (MD)	-25 to 170	-24.6 to -29.0
Parker (MA)	97 to 109	-28.3 to -29.0
Hudson (NY)	-158 to 31	-25.5 to -27.0
Sacramento (CA)	-31	n.d.



Stable carbon ( $^{13}\text{C}$ ) isotopes suggest a marine source



Production of very reactive and reactive DOC by  
phytoplankton and bacteria



Bacterial production is thought to be fueled by very reactive DOC that has a residence time in seawater of hour to days.

## What is bacterial production?

*gross production* = total carbon taken up by bacteria, it is used in the synthesis of new biomass, and includes both the new biomass and carbon respired during biomass production.

*net production* = new bacterial biomass over a set period of time.  
Bacterial production measurements almost always measure net production.

$$\textbf{Gross production} = \textbf{net production} + \textbf{respiration}$$

Gross production is also referred to as bacterial carbon demand (BCD) and is related to net production through the growth efficiency or fractional growth yield:

$$\textbf{Gross production} = (\textbf{net production}) \times (\textbf{growth yield})$$

## How is bacterial production measured?

- 1) Increase in the number of cells over time
- 2)  $^3\text{H}$ -adenine incorporation (DNA synthesis)
- 3)  $^3\text{H}$ -thymidine incorporation (DNA synthesis)
- 4)  $^3\text{H}$ -leucine incorporation (protein synthesis)

All methods measure net production only (!!!) and require empirically derived conversion factors. Need bacterial growth efficiencies to determine gross production (BCD)

## Comparison of bacterial and primary production in different ocean basins

Property	N Atlantic <sup>b</sup>	Eq Pac–Spr <sup>c</sup>	Eq Pac–Fall <sup>d</sup>	Sub N Pac <sup>e</sup>	Arabian <sup>f</sup>	Hawaii <sup>g</sup>	Bermuda <sup>h</sup>	Ross Sea <sup>i</sup>
Euphotic zone m	50	120	120	80	74	175	140	45
Biomass, mg C m <sup>-2</sup>								
Bacteria	1000	1200	1467	1142	1448	1500	1317	217
Phytoplankton	4500	1700	1940	1274	1248	447	573	11450
B:P	0.2	0.7	0.75	0.9	1.2	3.6	2.7	0.02
Production, mg C m <sup>-2</sup> d <sup>-1</sup>								
Bacteria	275	285	176	56	257	nd	70	5.5
Phytoplankton	1083	1083	1548	629	1165	486 <sup>j</sup>	465	1248
B:P	0.25	0.26	0.11	0.09	0.22	nd	0.18	0.04
Growth Rates, d <sup>-1</sup>								
Bacteria	0.3	0.13	0.12	0.05	0.18	nd	0.05	0.25
Phytoplankton	0.3	0.64	0.8	0.50	0.93	1.1	0.81	0.11
B:P	1	0.2	0.15	0.1	0.19	nd	0.06	2.3

<sup>a</sup>All stock estimates based on 20 fg C cell<sup>-1</sup>. Data may overestimate actual heterotrophic bacterial biomass as a consequence of lower C contents and/or interference by *Prochlorococcus* and *Archaea*. Production estimated from 3000 g C mol<sup>-1</sup> leucine incorporation.

<sup>b</sup>Eastern North Atlantic spring phytoplankton bloom, 47°N, 20°W; May, 1989, *n* = 13 (Ducklow et al. 1993).

<sup>c</sup>Equatorial Pacific, 0°N, 140°W; March–April 1992, *n* = 18 (Ducklow et al. 1995).

<sup>d</sup>Equatorial Pacific, 0°N, 140°W; September–October 1992, *n* = 19 (Ducklow et al. 1995).

<sup>e</sup>Subarctic North Pacific, 45°N, Kirchman et al. (1993).

<sup>f</sup>Northwest Arabian Sea, 10–20°N, 165°E, January–December 1995, *n* = 21 (Ducklow et al. in press).

<sup>g</sup>Hawaiian Ocean Time Series (HOT); 1995–1997; *n* = 21; (<http://hahana.soest.hawaii.edu/hot/methods/pprod.html>).

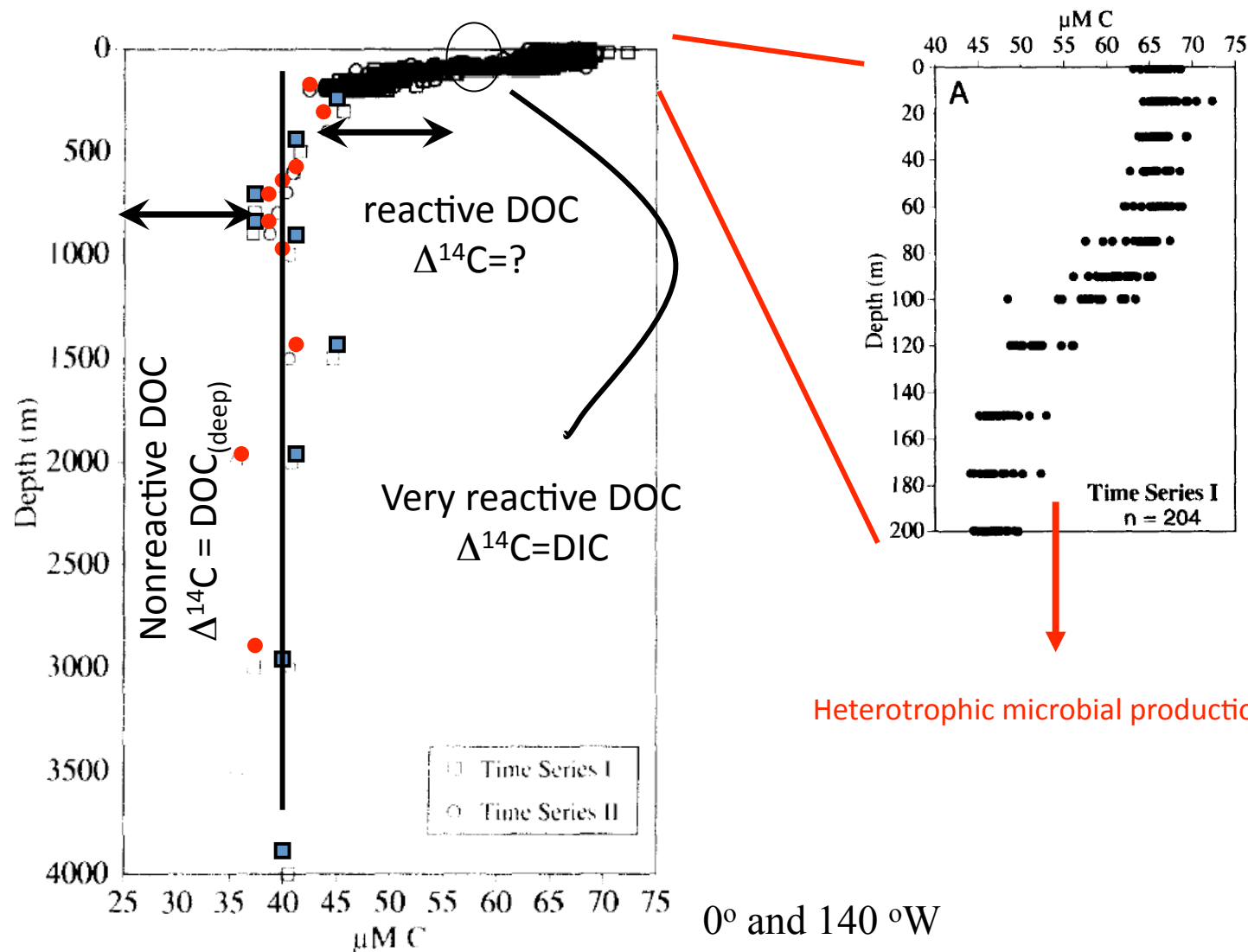
<sup>h</sup>Bermuda Atlantic Time Series (BATS); 1991–1998, *n* = 106 paired comparisons; for BP and phytoplankton biomass calculations, see Carlson et al. (1996).

The ratios are means of the ratios, not ratios of the means. BP calculated from TdR (1.6 × 10<sup>18</sup> cells mol<sup>-1</sup>).

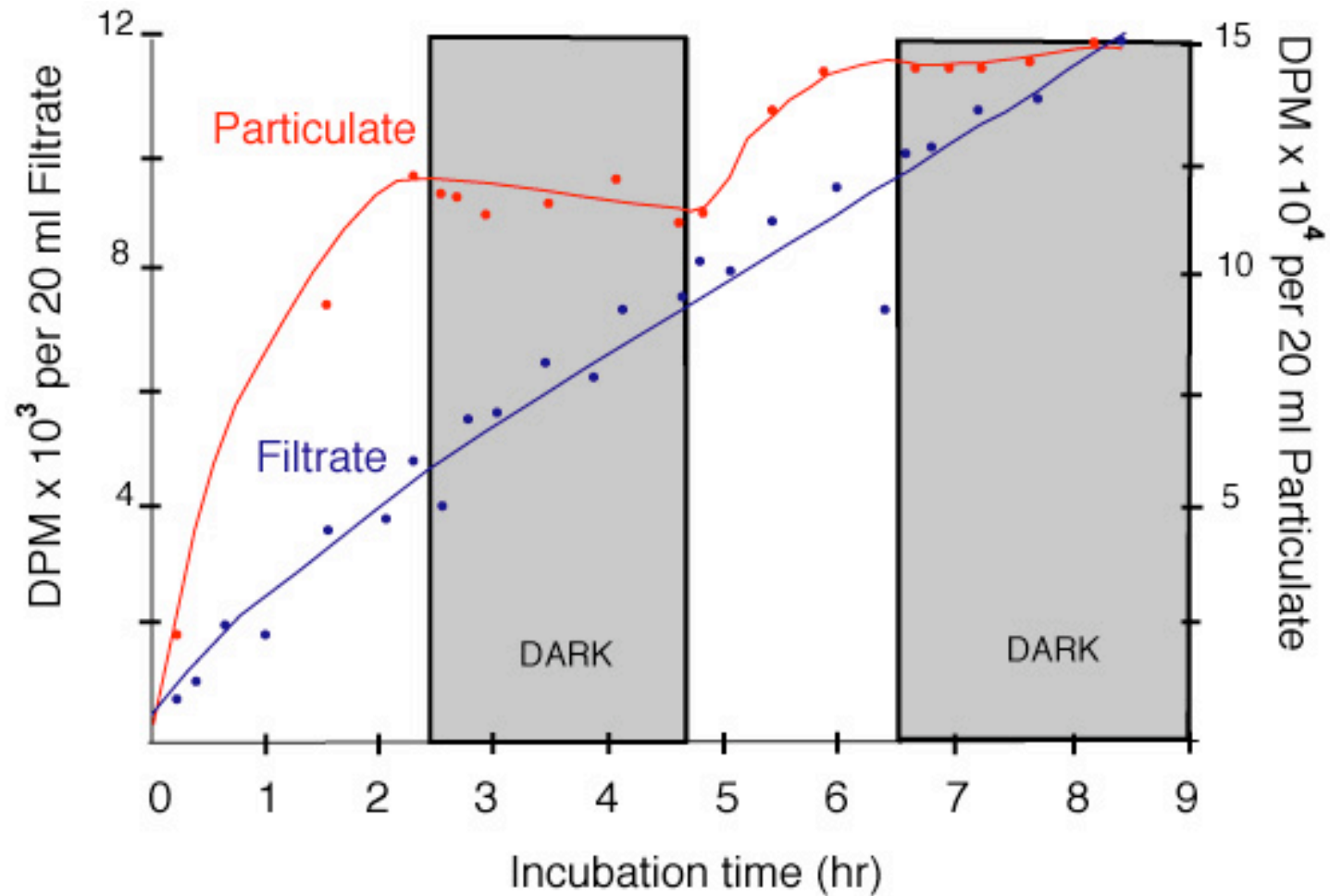
<sup>i</sup>Ross Sea, Antarctica; 76°S, 180°W; 1994–1997; Carlson et al. (1998); Ducklow, unpublished data.

<sup>j</sup>1989–1996; *n* = 64. Data source as for note *g*.

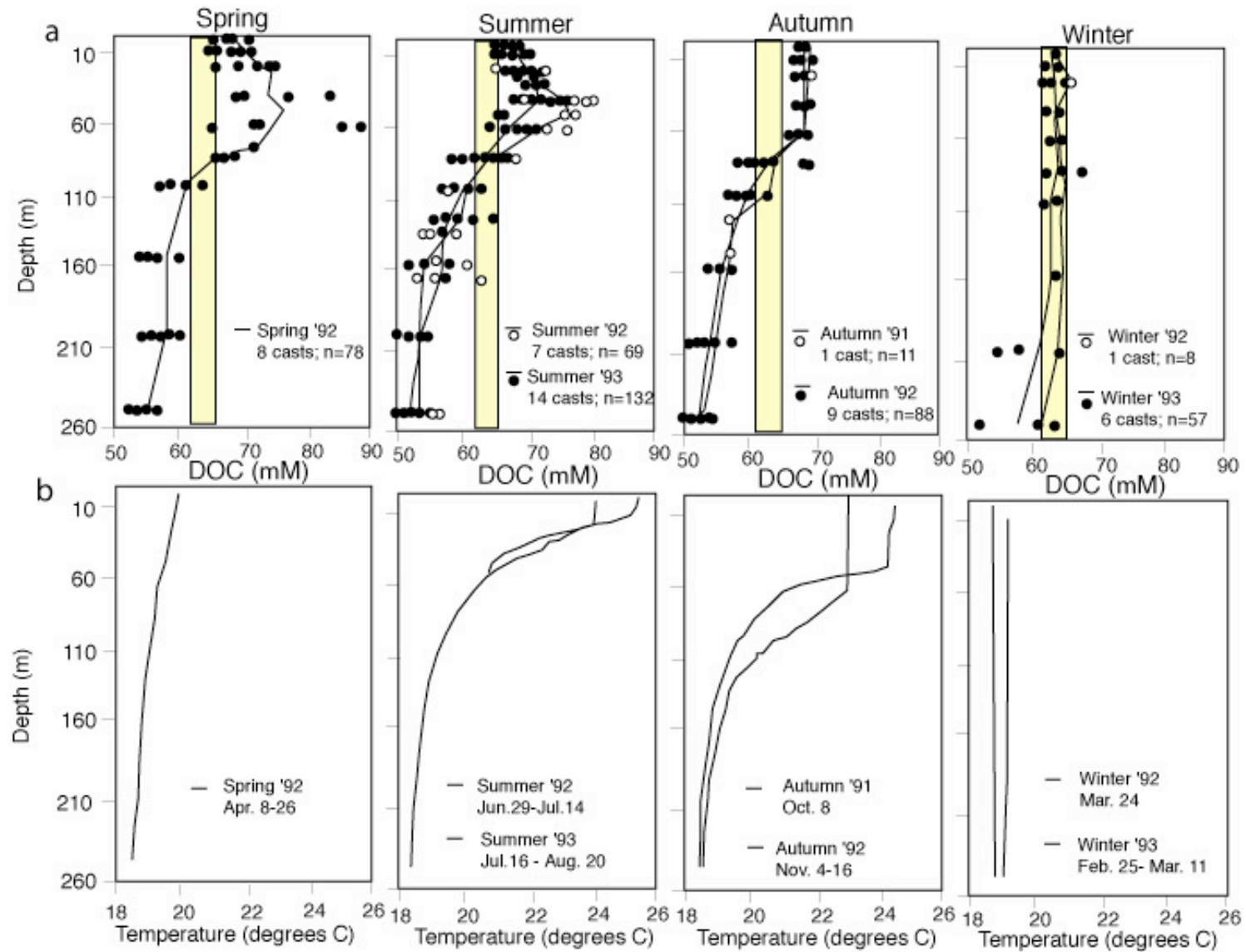
Reactivity and the cycling of DOC in seawater. There is probably a continuum of Reactive DOC, but conventionally considered to be three fractions depending on How fast the DOC cycles- very reactive, reactive, non reactive.



Production of DOC by phytoplankton in  
axenic laboratory culture\*



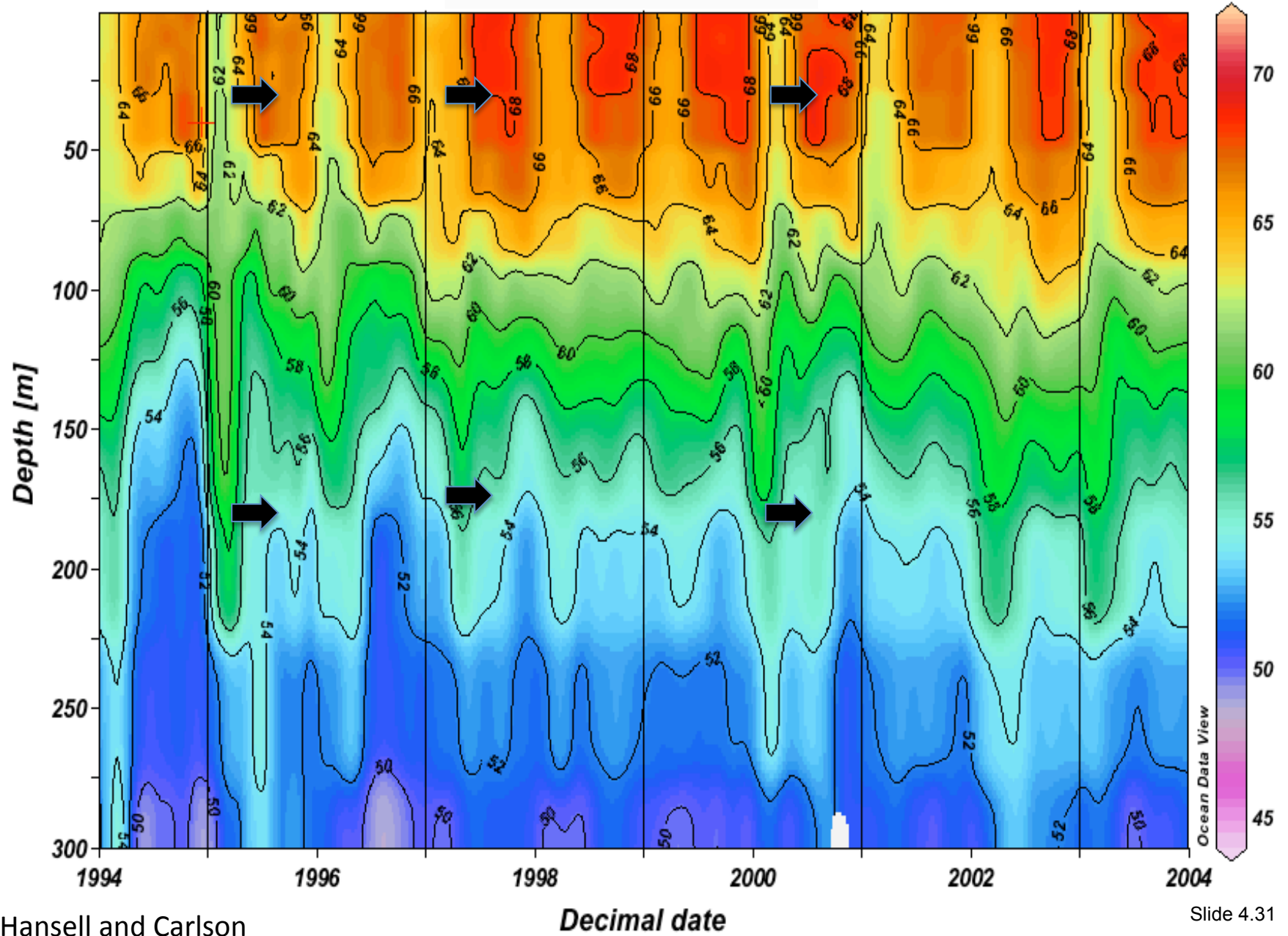
## Annual cycle of DOC production in the mixed layer at BATS\*



\*Bermuda Atlantic Time Series, a JGOFS LTEM site

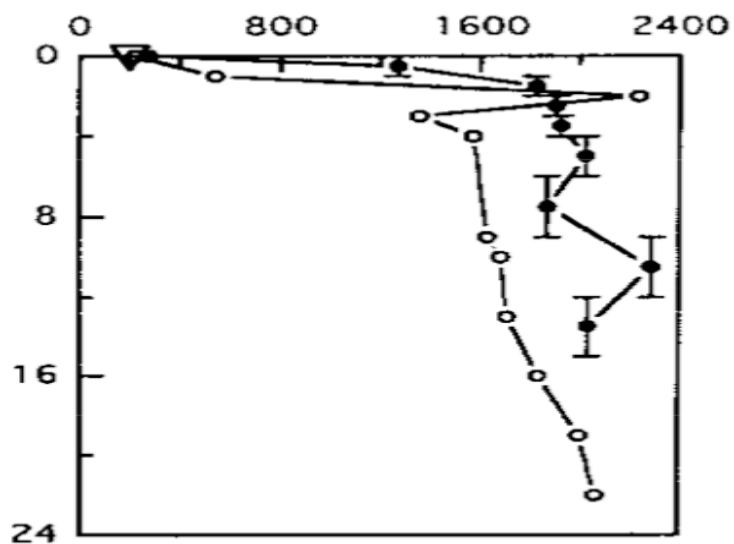
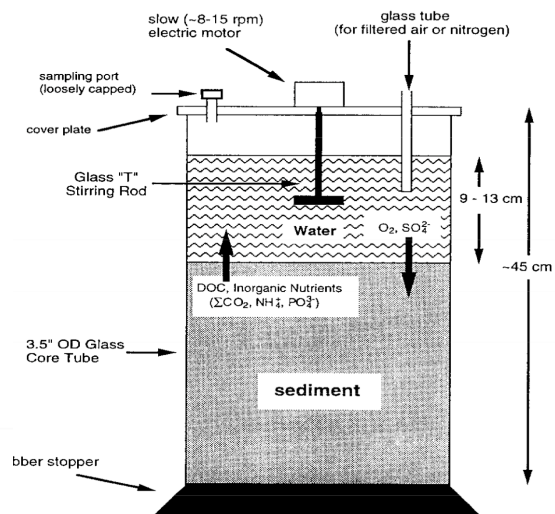
Carlson et al.1994; Nature

## BATS DOC ( $\mu\text{M C}$ )

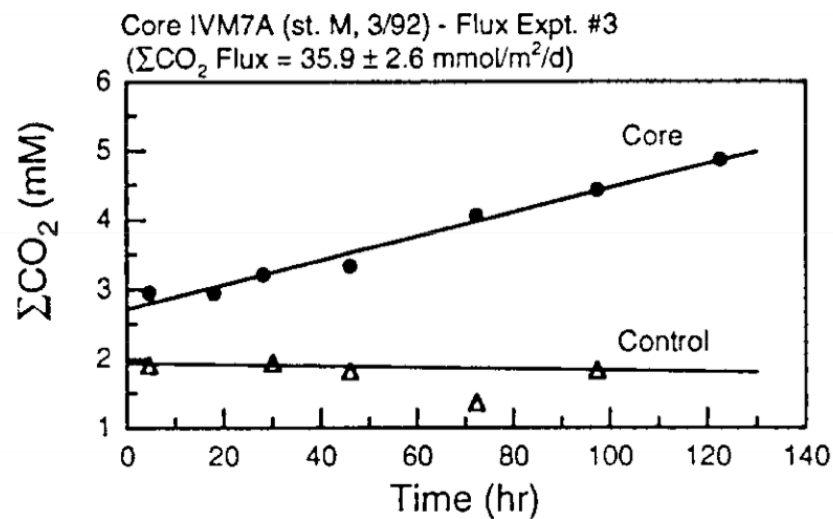
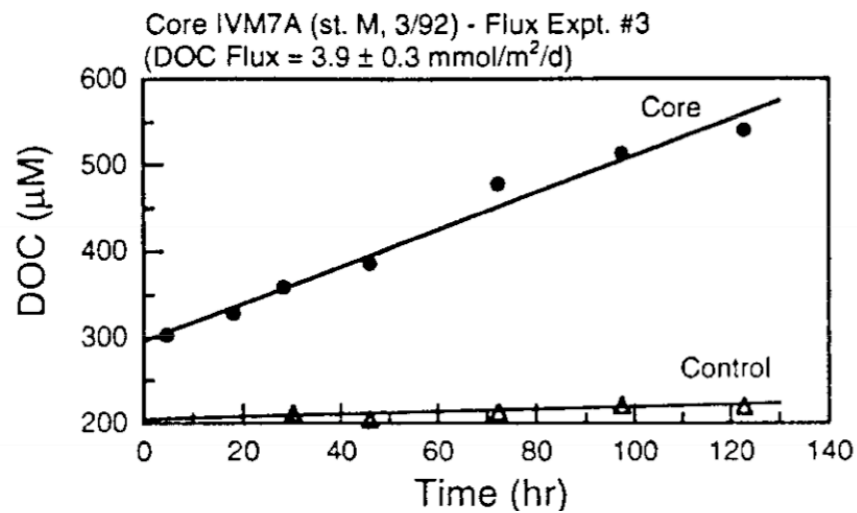


# What are the sources of DOC ?

## Release of DOC from marine sediments



[DOC] μM



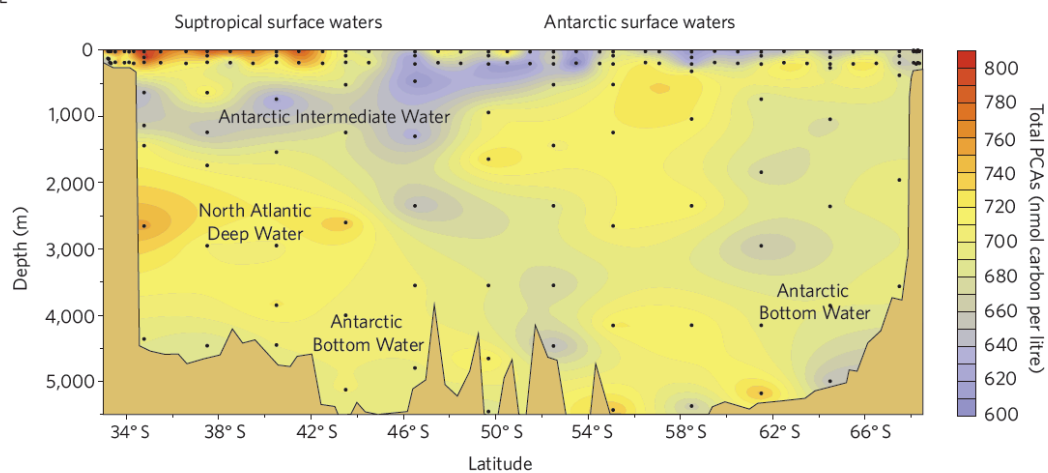
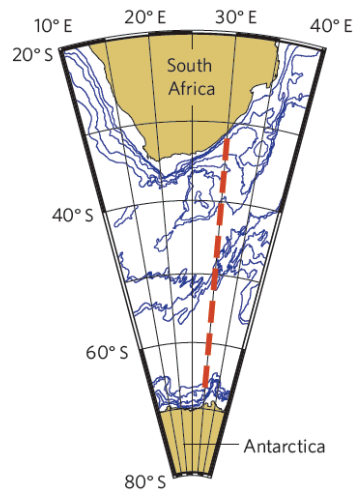
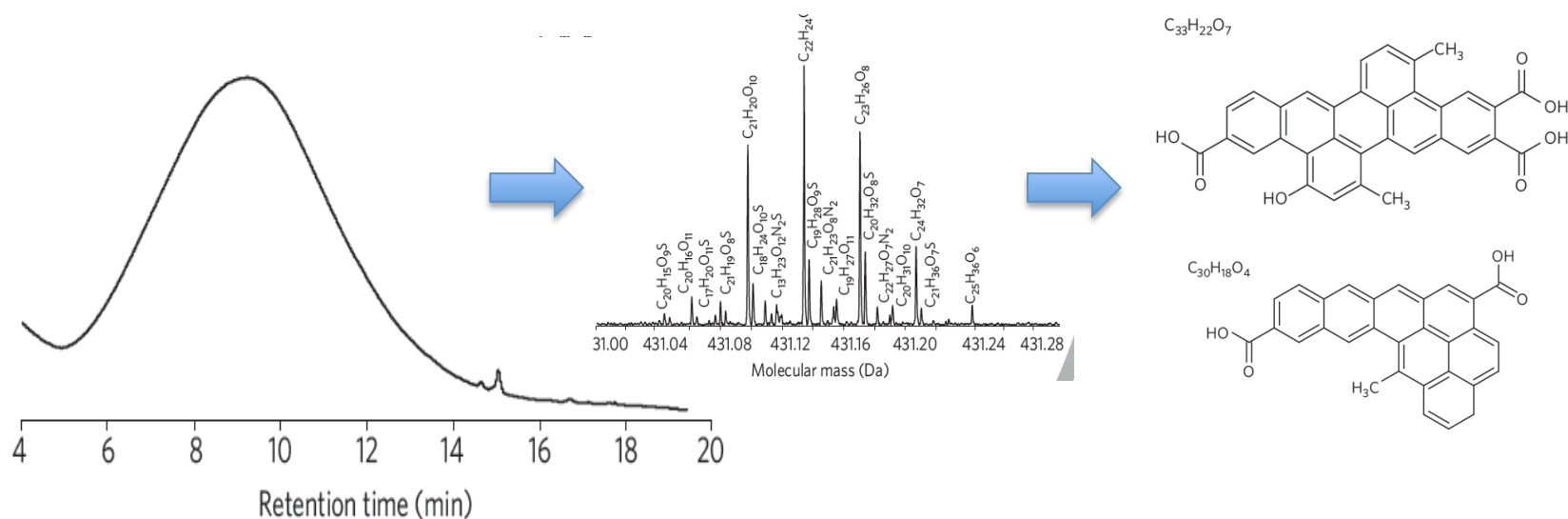
## What are the sources of DOC ?

Sediments are a source for DOC- sediment pore-water concentrations of C are higher than seawater, and there is a flux out of sediments into the water column. Only a few measurements have been made, and the global flux is estimated to be small, but on the order of what is needed to maintain DOC stocks.

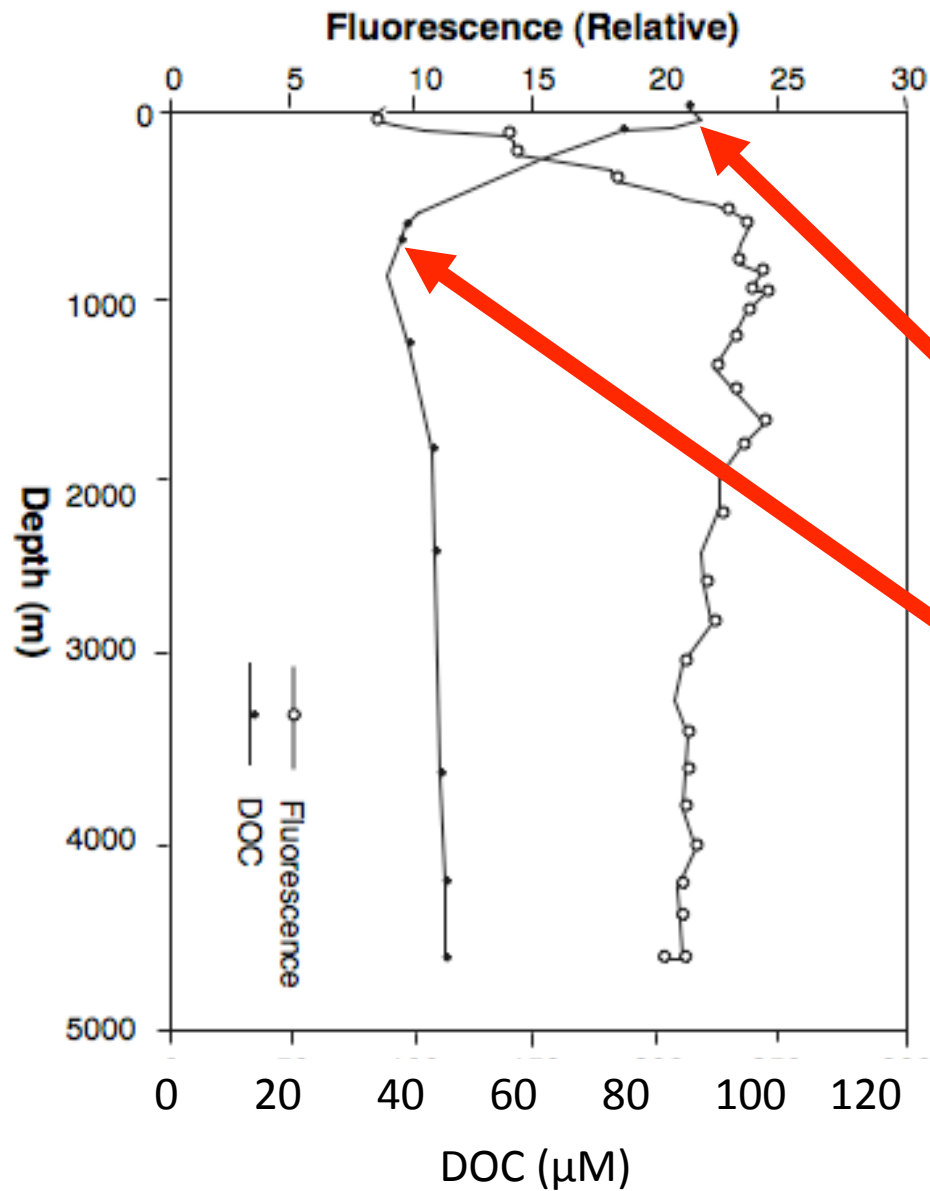
Table 2. Integrated benthic DOC fluxes from coastal and continental margin sediments.\*

Sediment regime <sup>a</sup>	Sediment Carbon Oxidation (C <sub>ox</sub> )		Benthic DOC Flux		
	Integrated <sup>b</sup> (Tg C/yr) <sup>†</sup>	Average <sup>c</sup> (mmol/m <sup>2</sup> /d)	Average <sup>d</sup> (mmol/m <sup>2</sup> /d)	Integrated <sup>e</sup>	
				(Tg C/yr)	(% of C <sub>ox</sub> ) <sup>f</sup>
“Coastal” sediments (0–200 m; 9%)	1630 (52%)	14.7	0.91	88 ± 30	5.4%
“Margin” sediments (200–2,000 m; 7%)	940 (30%)	6.6	0.65	89 ± 25	9.5%
Coastal plus margin sediments (0–2,000 m)	2570 (82%)			177 ± 56	6.9%

# Thermal alteration of organic matter as a source of recalcitrant DOM



## Central North Pacific



What are the sinks for DOC?

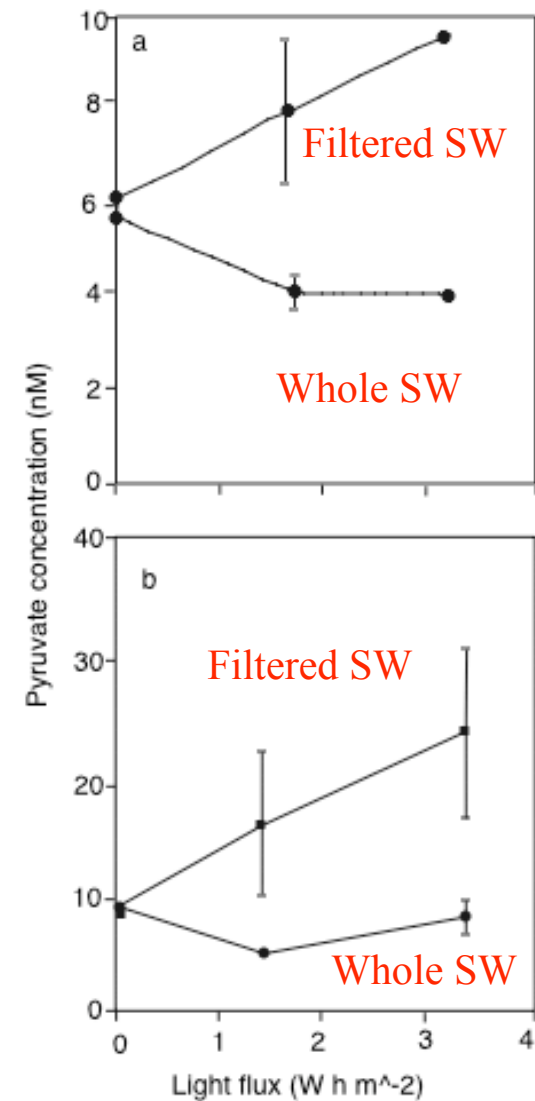
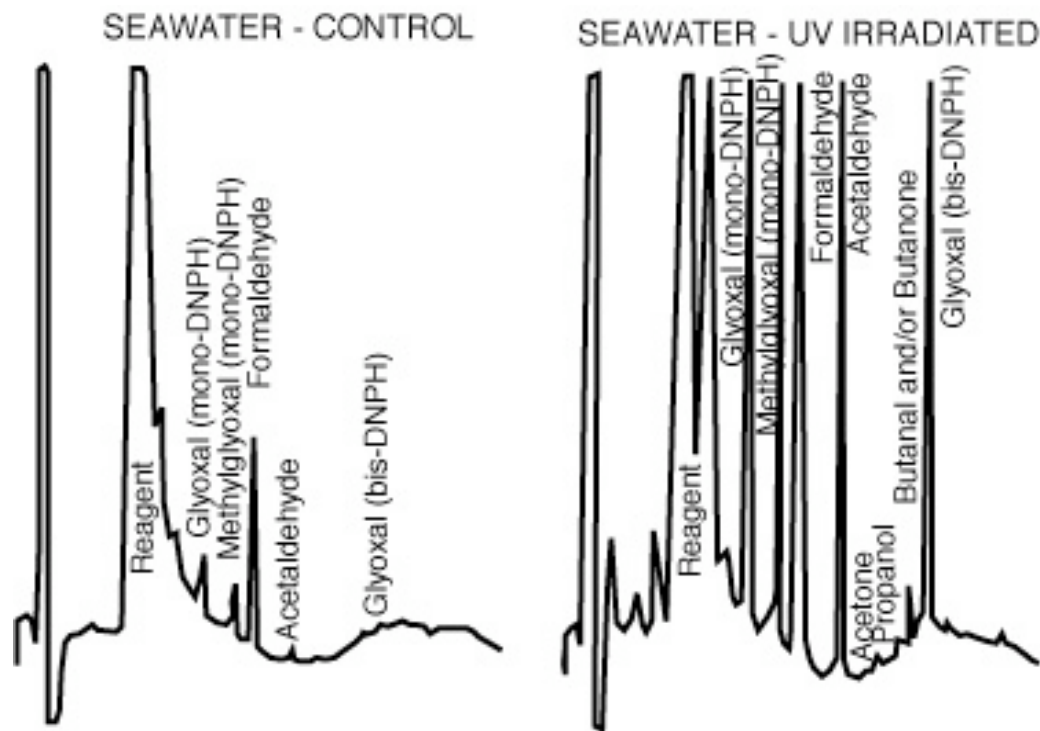
Photooxidation  
Microbial consumption  
Particle scavenging



DOM from surface and 900 m

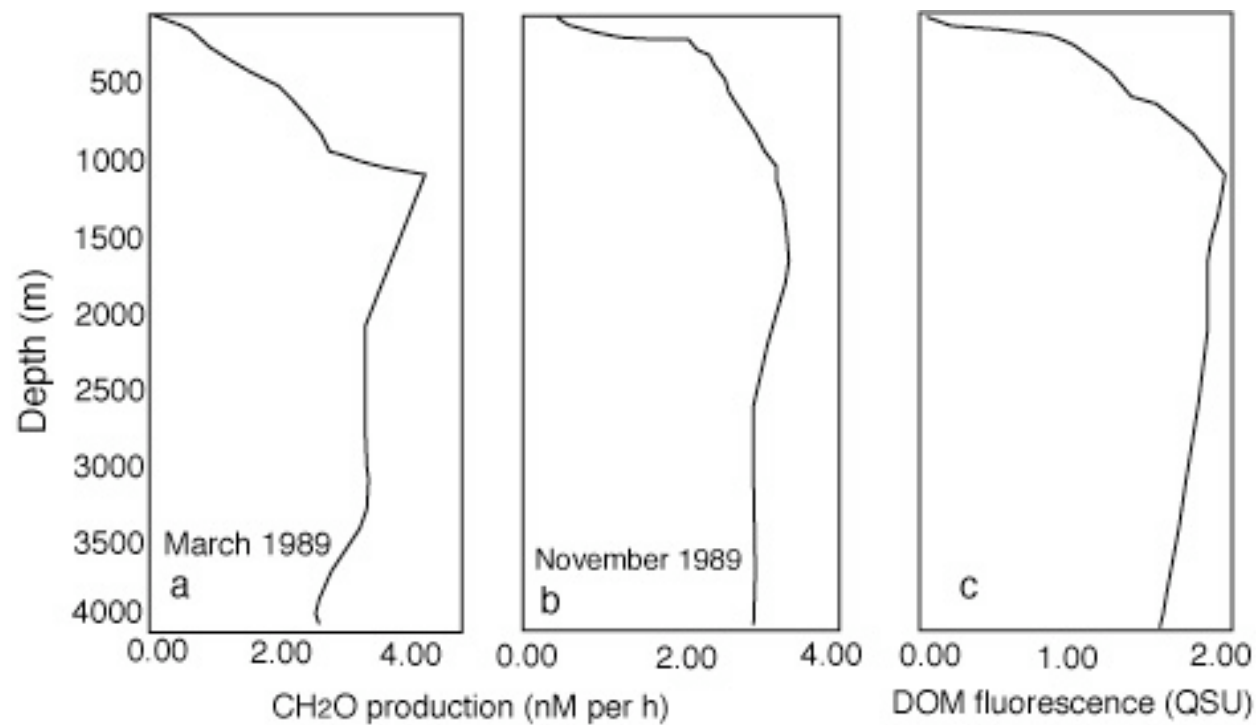
DOC + light  $\rightarrow$  LMW carbonyls (C=O)

C=O + fluorophore  $\rightarrow$  HPLC

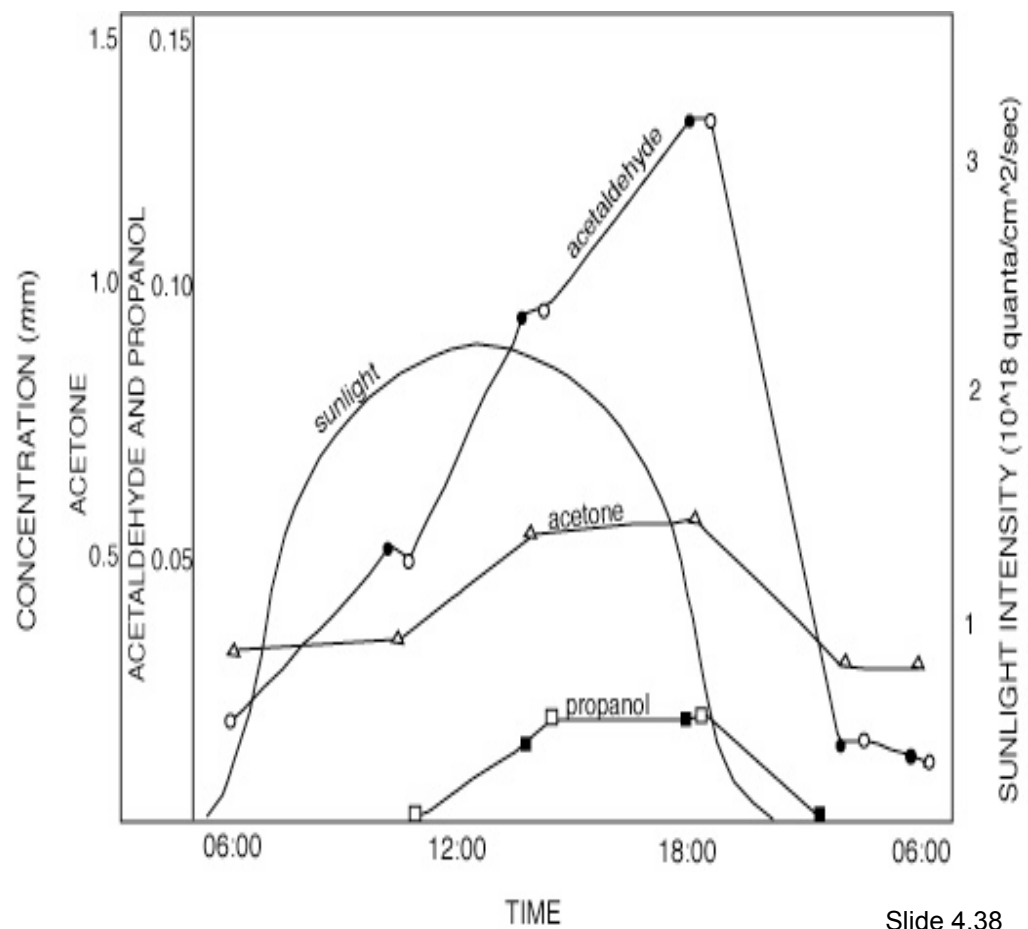
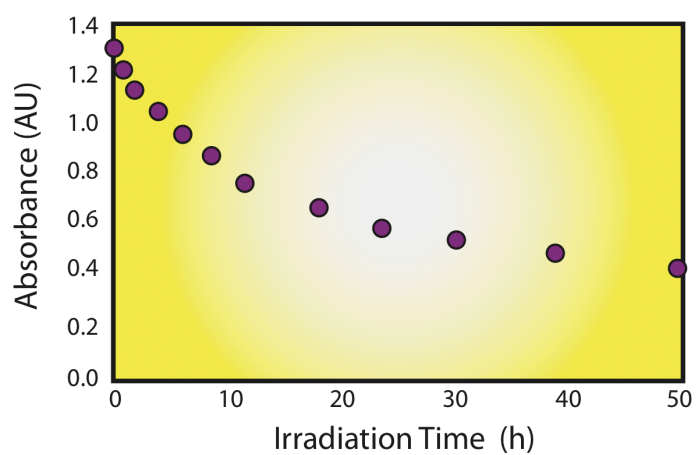
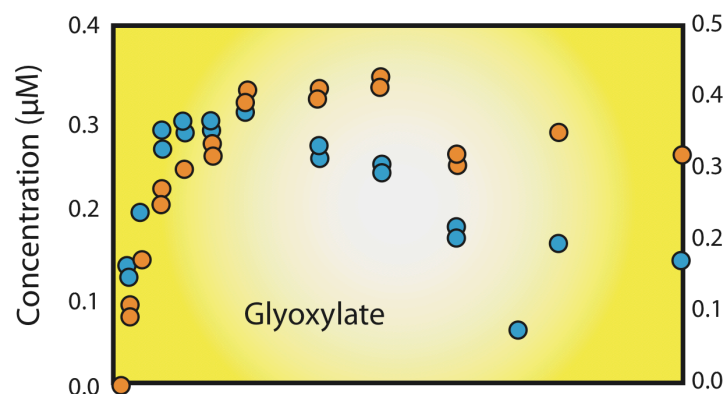
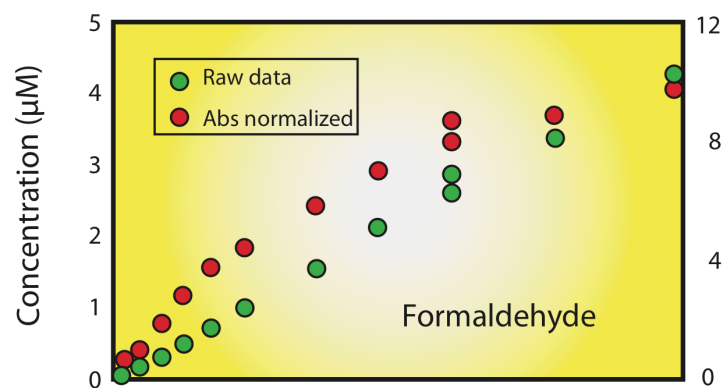


Not produced in dark controls, but are produced in sterile controls

Production of LMW highly oxidized DOC with depth in the ocean

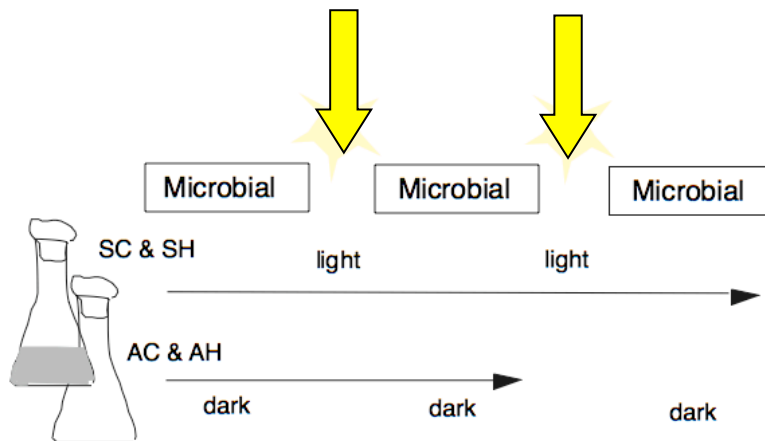


Is photochemical degradation the long term sink for recalcitrant DOM ???

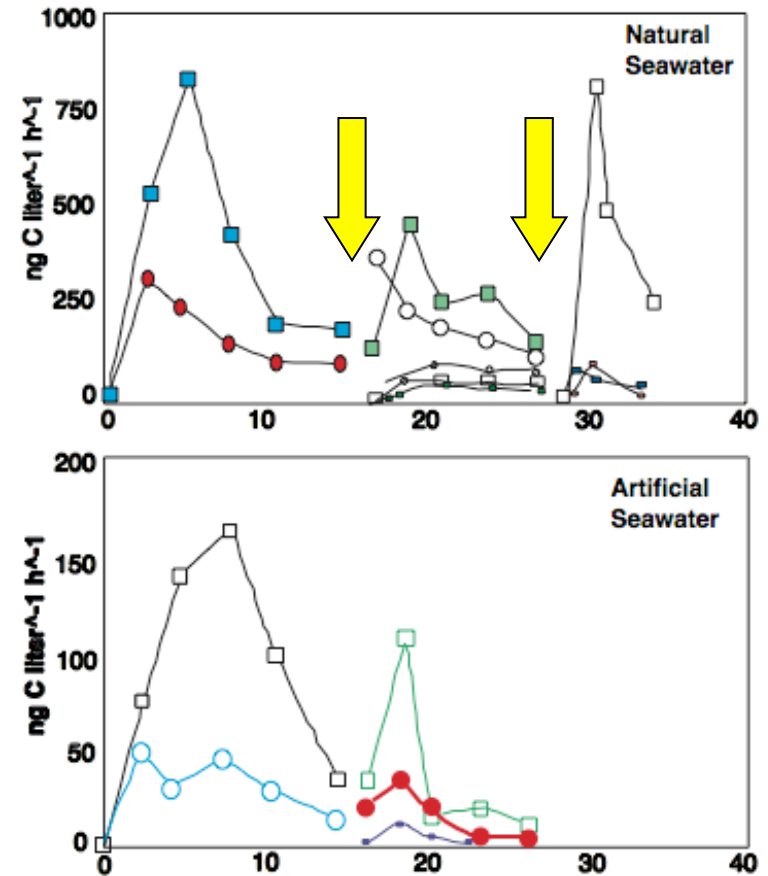


## Coupling of photooxidation and microbial oxidation of DOM

Photooxidation yields a large number of low molecular weight, oxidized products that are good substrates for Microbial uptake and utilization



Instantaneous uptake of  $^3\text{H}$  leucine

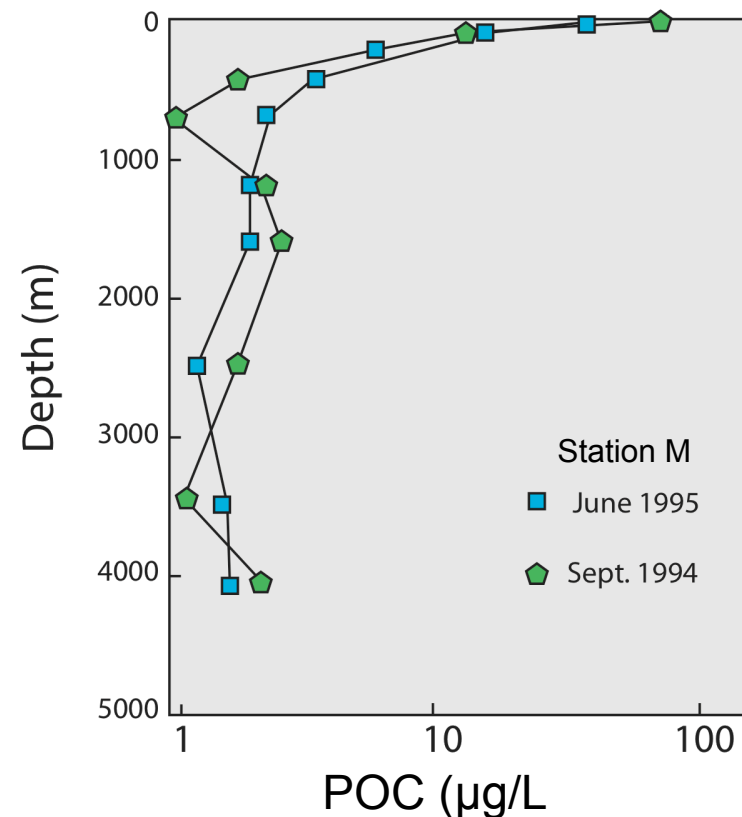
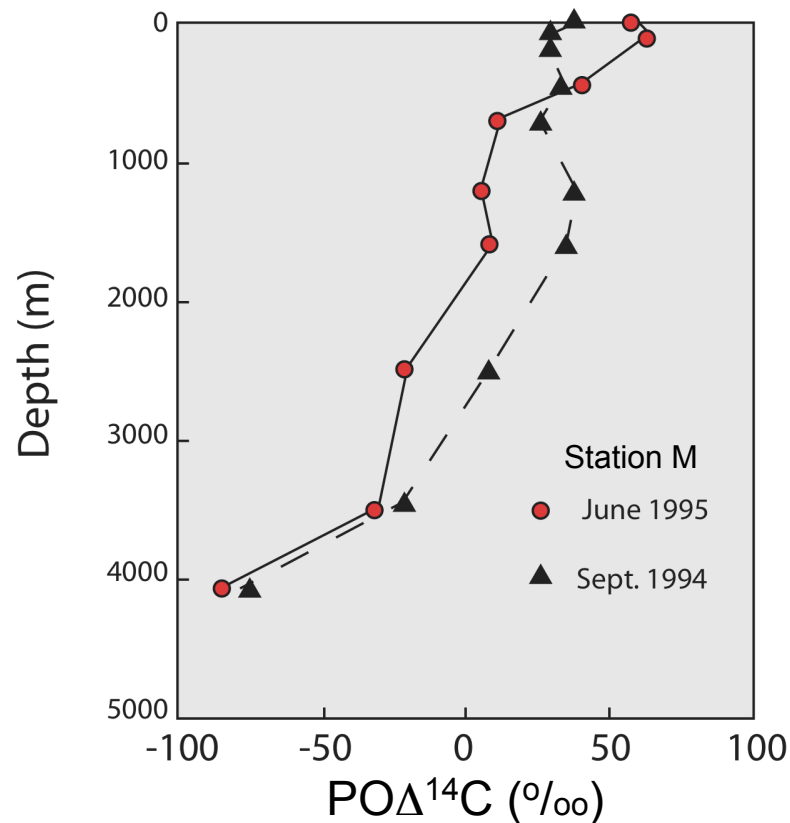


# Removal of old, recalcitrant DOC by particles sinking through the water column

The depletion of radiocarbon with depth in the water column cannot be explained by  $^{14}\text{C}$  decay. The particles sink too fast ( $< 10$  years based on Stokes settling velocity)

Since the particles are synthesized with a modern  $^{14}\text{C}$  value, Druffel concludes Old ( $^{14}\text{C}$  depleted radiocarbon must be added to the particles via adsorption

Sinking particles “strip” old DOC from the water column and act as a sink for nonreactive DOC



## Summary

A number of putative sources for DOM have been identified- continental organic matter from rivers, dust, and the atmosphere. Most DOC has an old apparent radiocarbon age, and therefore the calculated residence time of DOM is on the order of 4000-6000 years and a flux of 0.1-0.15 GT C/year.

In this context, almost any putative source can supply enough organic matter to support the reservoir of DOM. We need to look at other ways (profiles, composition, isotopes) to identify the important sources of DOM.

Measurements of bacterial carbon demand in the ocean suggest a much higher flux of DOM up to 15 GT C/year (100x the radiocarbon flux).

DOM probably has a range of reactivity and turnover times, but conventionally DOM is divided into three categories: nonreactive (large steady state concentration and old radiocarbon age), reactive (or semi-reactive) that has a moderately sized inventory and modern radiocarbon age, and very reactive DOM that has a very small inventory and modern radiocarbon age.

## Summary (*continued*)

Microbial oxidation is the largest sink for DOM, and is tremendously efficient; returning 99.9% of (photoautotrophic) microbially produced DOC to CO<sub>2</sub>.

Other sinks focus on the removal of nonreactive DOM. These include photochemical oxidation and adsorption onto sinking particles.