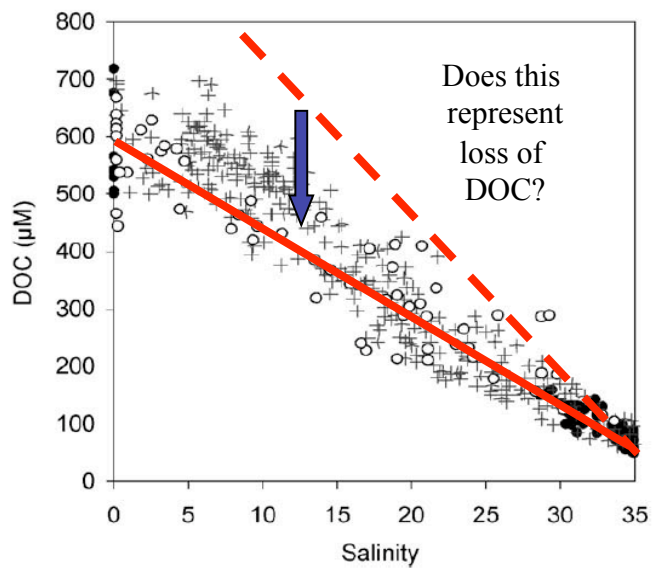
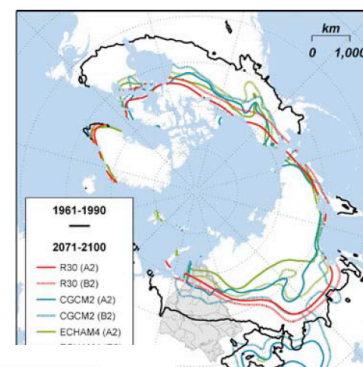
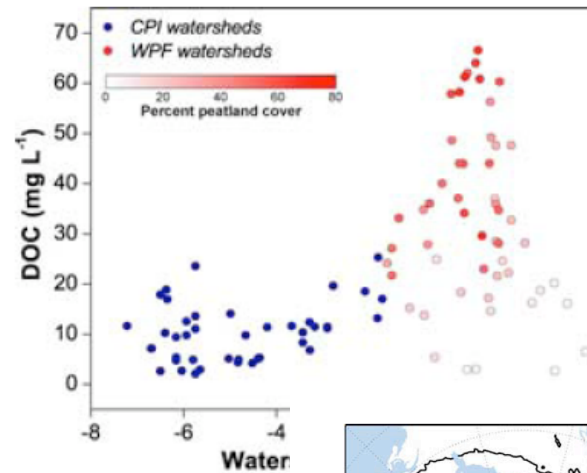


Fig. 4. Comparison of FW source anomalies and FW storage anomalies relative to 1965 (units are km^3). Black curve is cumulative N55B ocean FW storage. Colored areas represent cumulative FW contributions from P-E local (Subpolar plus Nordic Seas, dark green), P-E remote (Arctic Ocean, HBCA, and river discharge, light green), sea ice attrition (blue), and glacier melt (red). Source contributions are stacked to show total FW source input.

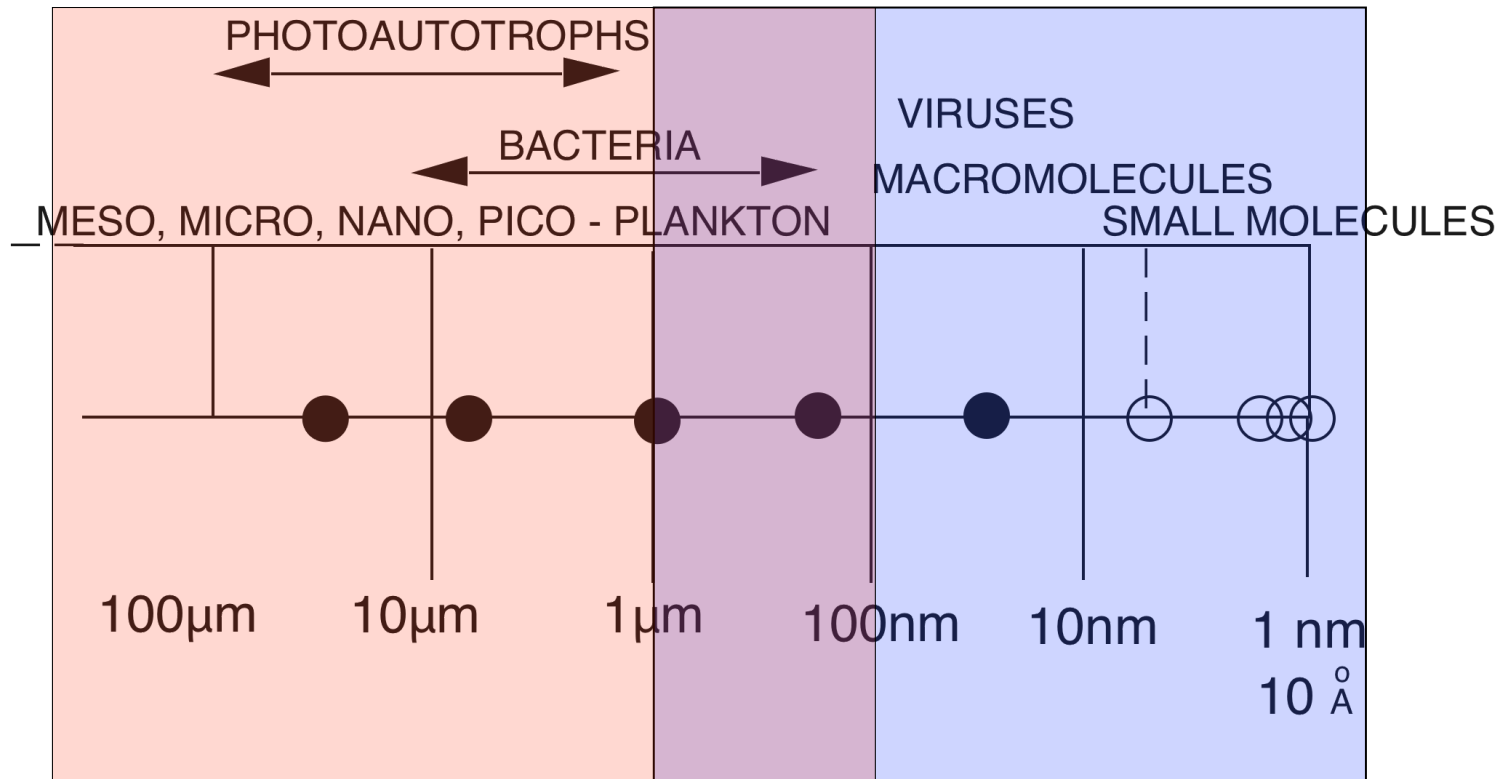


The possible consequences of massive carbon transfer from arctic soils to the ocean:

1. **Not much:** the carbon stored in arctic soils represents the end product of carbon cycling on land. The material is inert and cannot be oxidized in the ocean. It is transferred into the ocean and stays there.
2. **Some effect:** It would have been oxidized anyway in soils so the transfer just effects the location of oxidation, not the ultimate fate of the carbon.
3. **Large effect:** The carbon was effectively sequestered in soils and would not have been oxidized if it remained there. Different degradation processes are active in the sea, leading to a different long term fate of the carbon (and N and P).

The three scenarios will have different consequences for atmospheric CO₂ global climate and global carbon cycling!

What is “particulate” and what is “dissolved” carbon?



Particulate Organic Matter

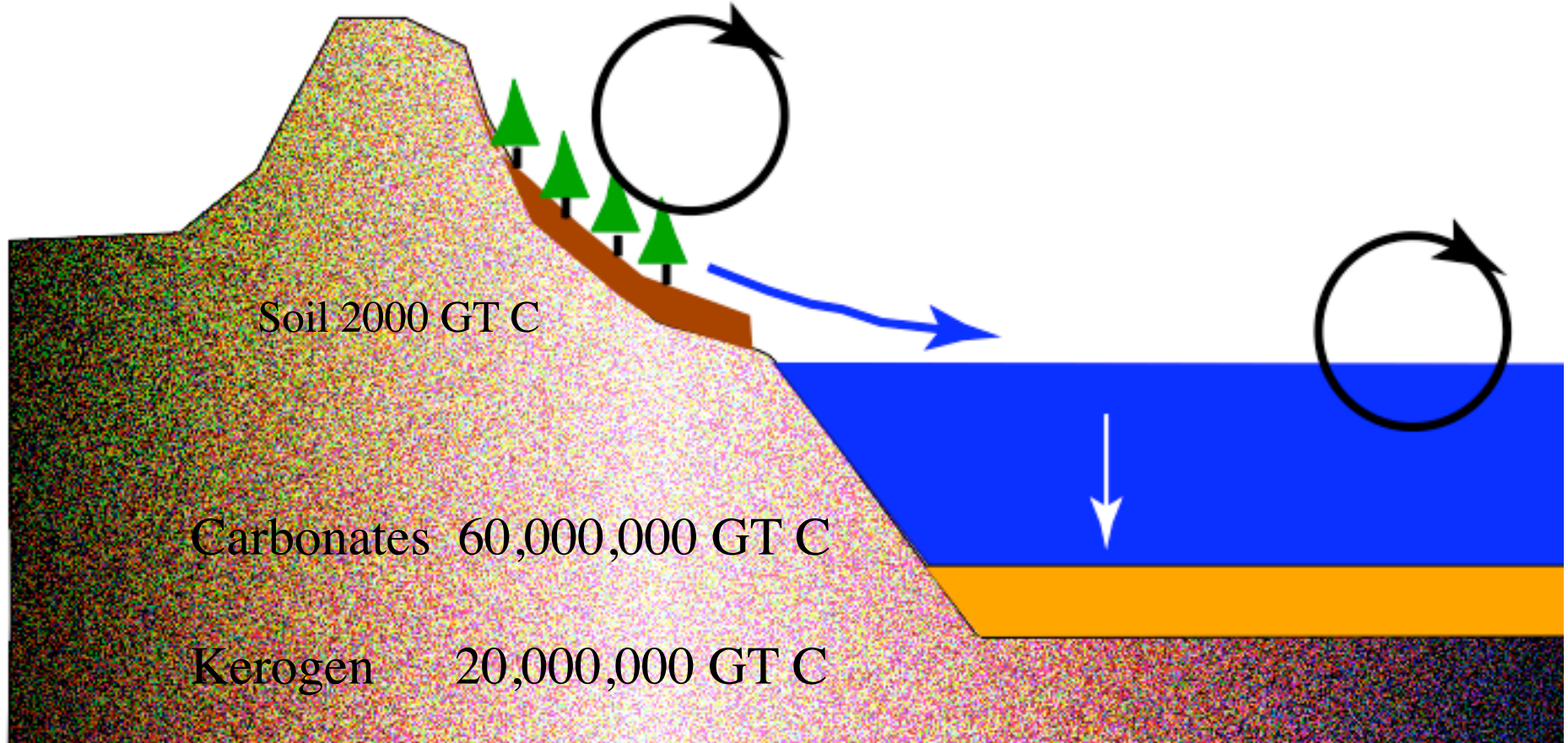
Dissolved Organic Matter

Organic matter is classified by size, as defined by filtration

DOC and major carbon reservoirs and fluxes

Terrestrial Plants
900 GT C

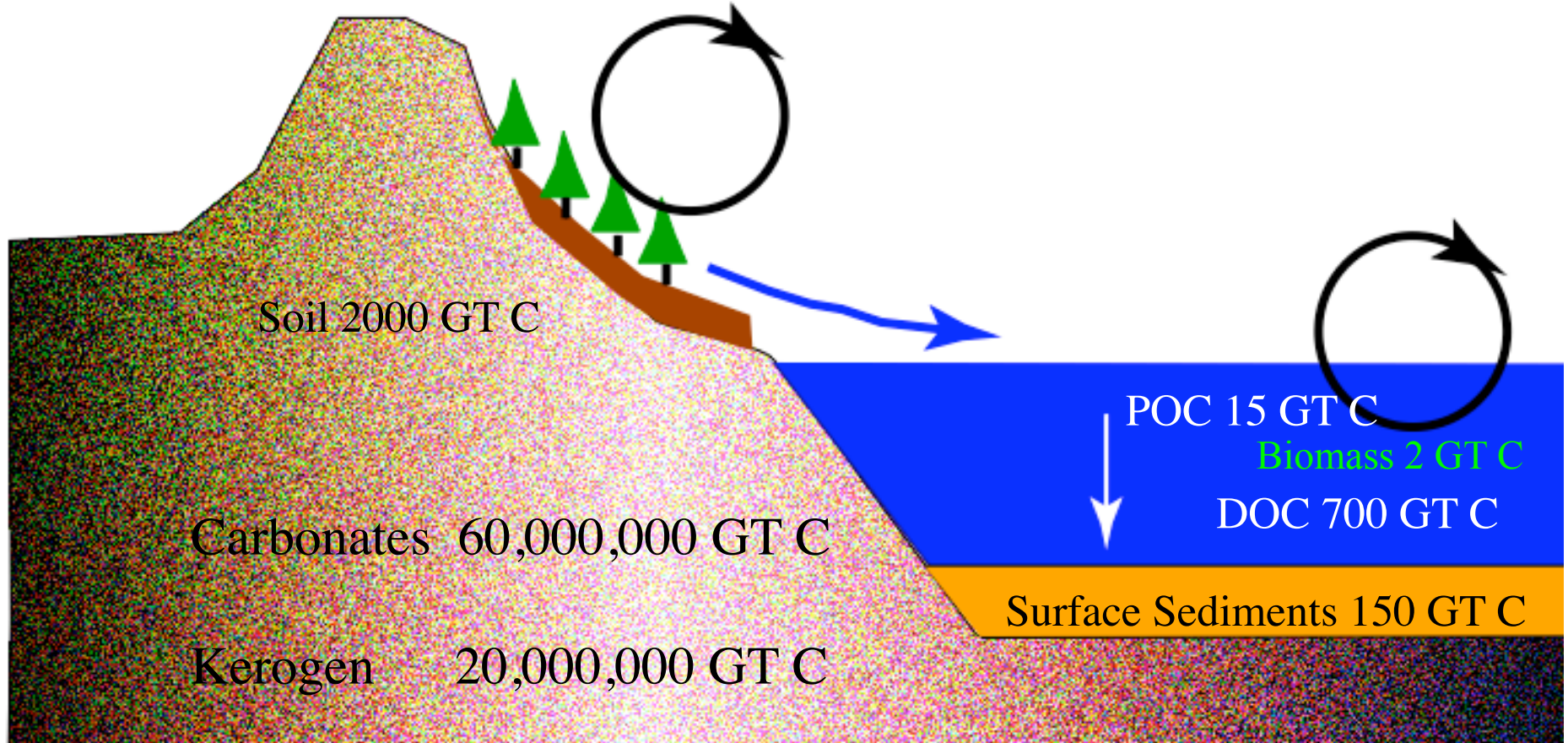
Atmosphere 750 GT (CO₂)



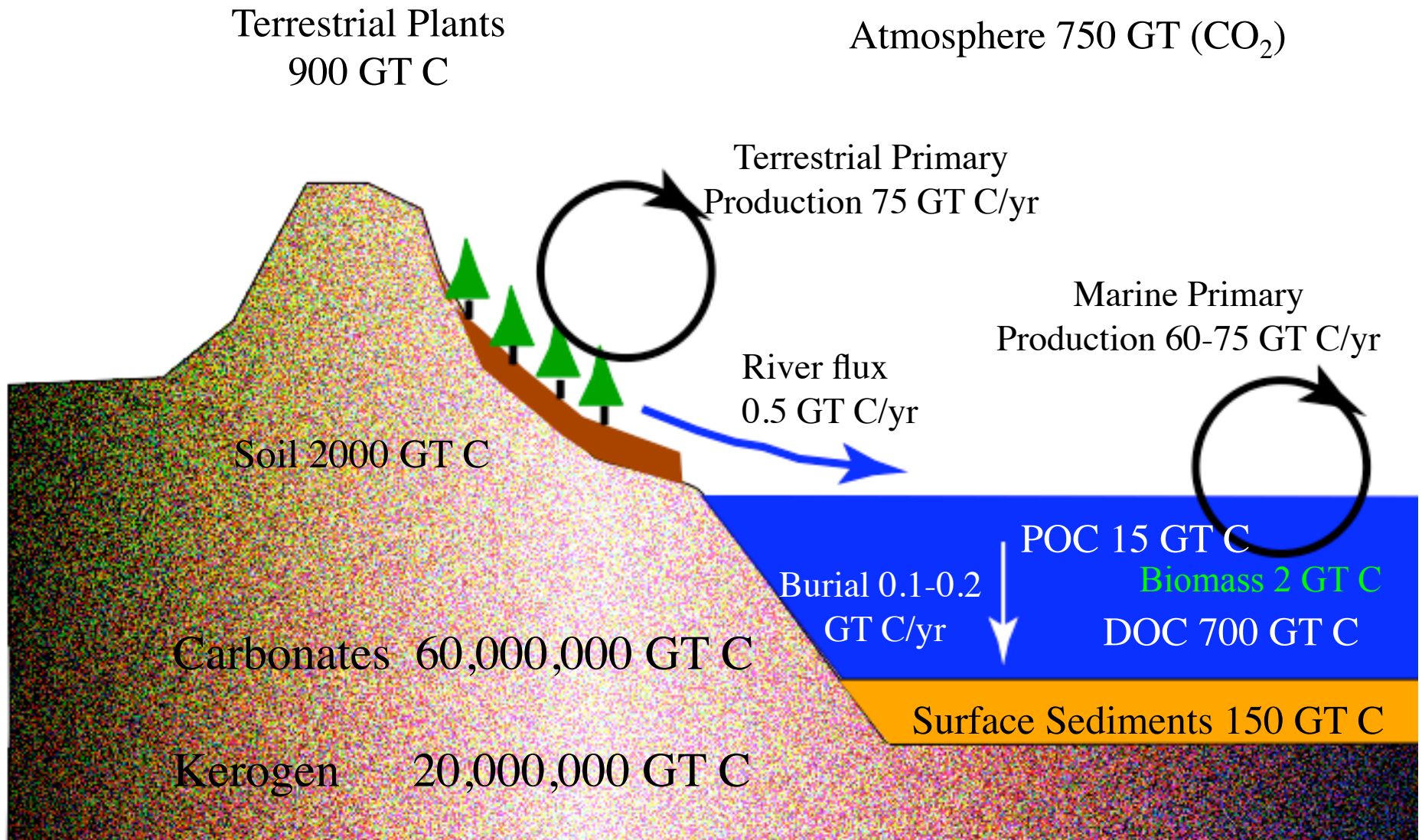
DOC and major carbon reservoirs and fluxes

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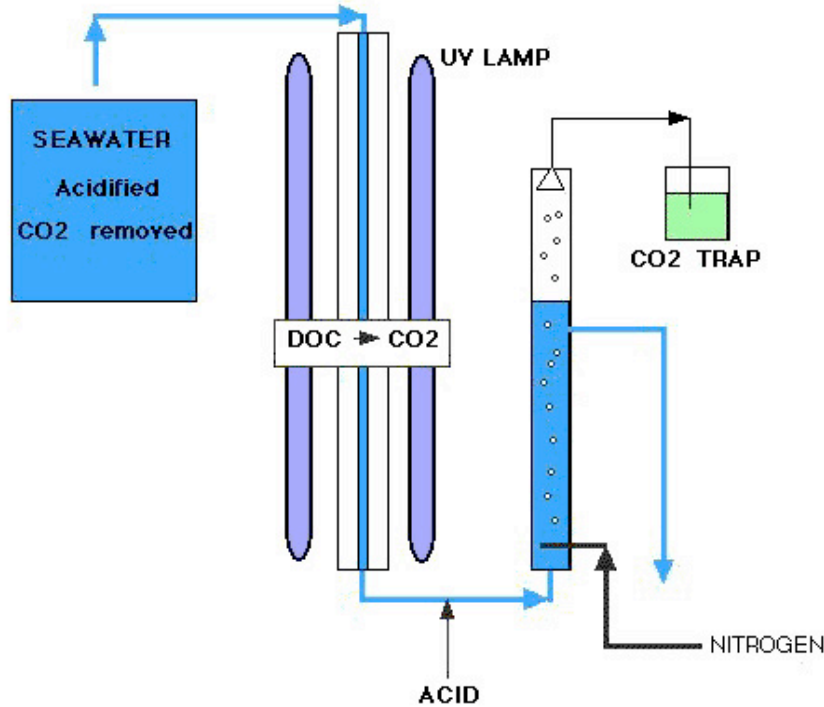


DOC and major carbon reservoirs and fluxes

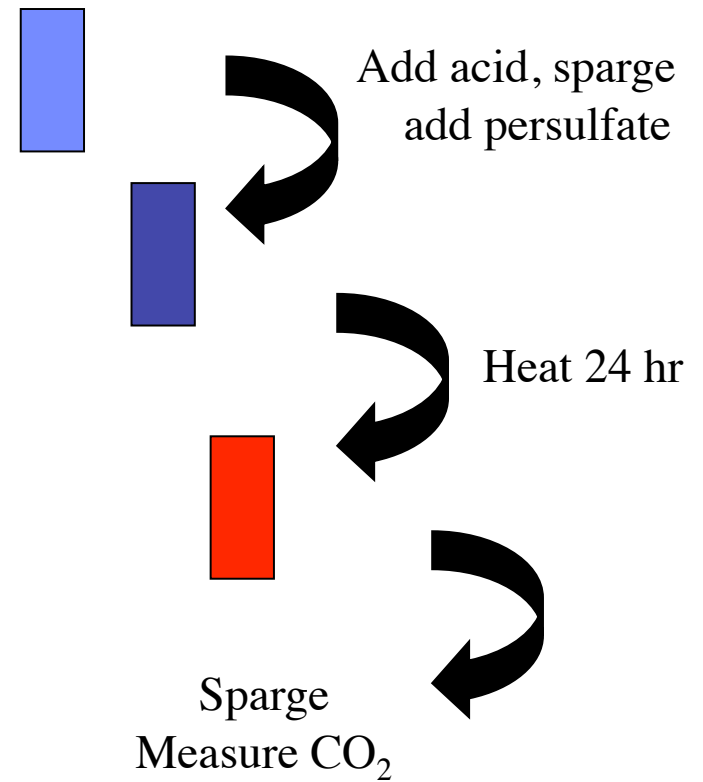


Analytical methods for measuring DOC

UV photooxidation

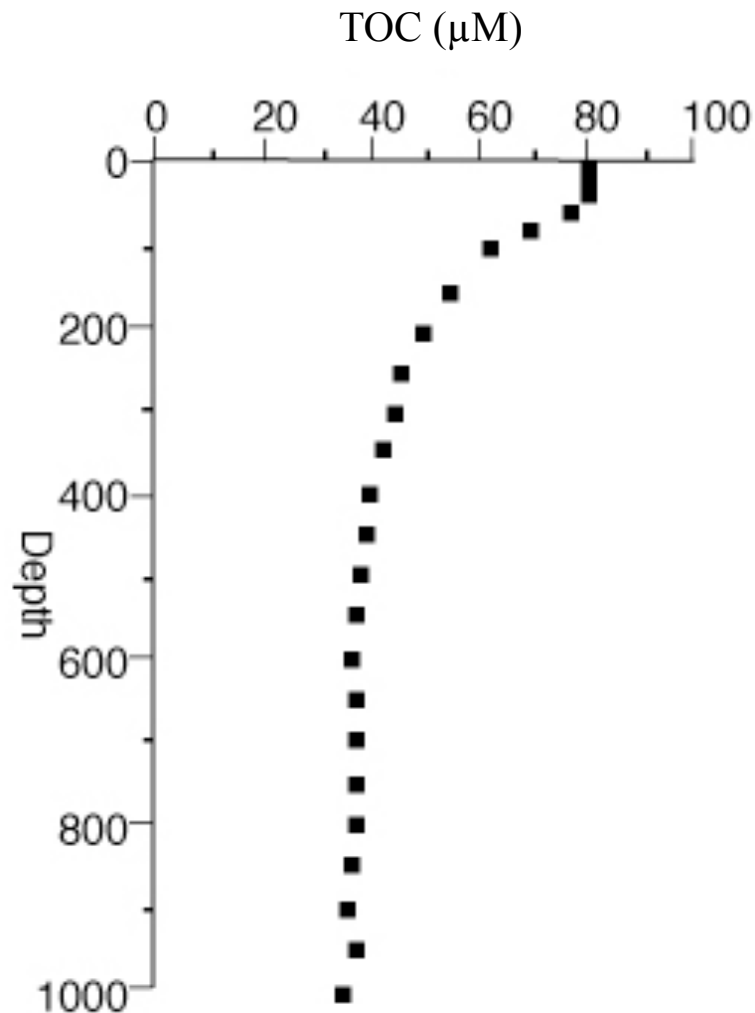


Chemical oxidation



Used for large volume samples (stable and radioisotope analyses)

Vertical profiles of dissolved organic carbon in the ocean



Often measured as TOC

Surface values typically 60-80 μM

Deep water values @ $40 \pm 1 \mu\text{M}$
(implies some unknown feedback/
control of DOC values)

Global inventory about 680 GT C

Data from Peltzer and Hayward (1996) DSR

Analytical methods for measuring DOC

High Temperature Catalytic Oxidation



100 μ L seawater

Inject directly onto
Pt or M column

Water vaporized and
trapped

DOC oxidized by Pt
to CO_2

LiCOR detector

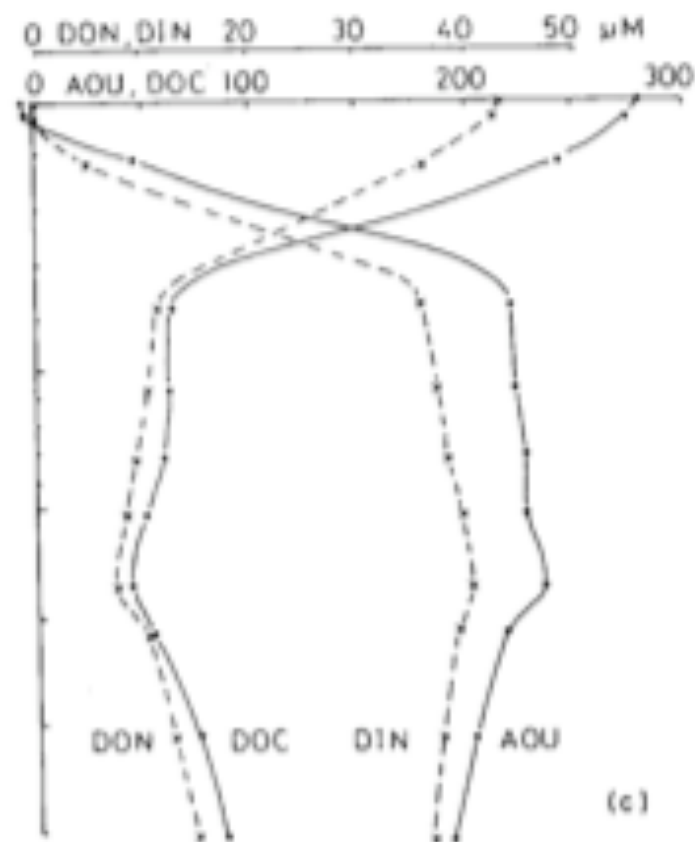
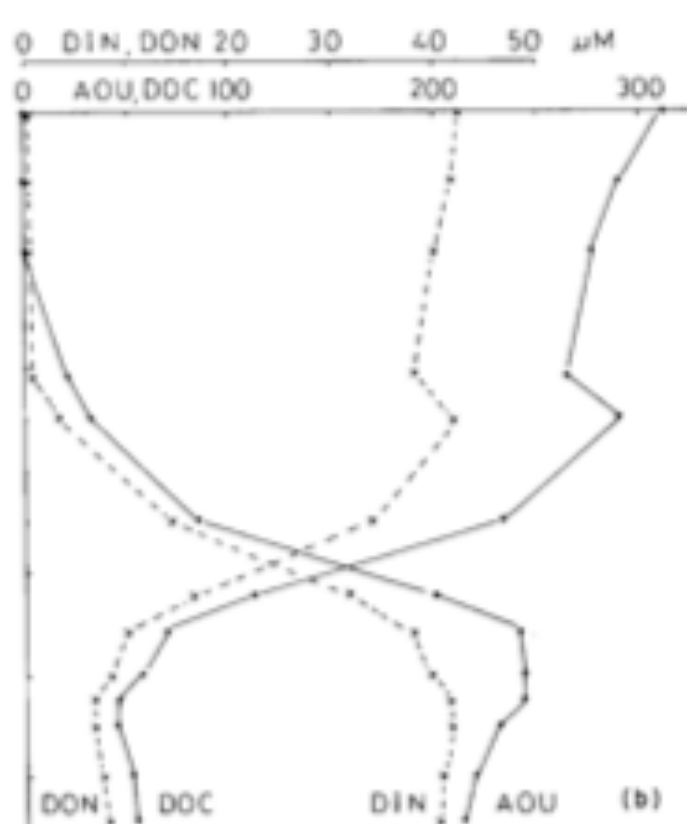
Precision + 0.5- 1 μ M

A High-Temperature Catalytic Oxidation Method for the Determination of Non-Volatile Dissolved Organic Carbon in Seawater by Direct Injection of a Liquid Sample

YUKIO SUGIMURA and YOSHIMI SUZUKI

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(Received May 26, 1986; revision accepted August 31, 1987)



Dissolved organic carbon in the Atlantic, Southern and Pacific oceans

John H. Martin & Steve E. Fitzwater

Moss Landing Marine Laboratories, Moss Landing, California 95039, USA

THE amount of dissolved organic carbon (DOC) in sea water is controversial^{1,2}. Using a high-temperature catalytic oxidation (HTCO) technique, Sugimura and Suzuki³ reported that surface waters contained 2–4 times as much DOC as that measured previously using wet chemistry and ultraviolet oxidation techniques^{4,5}. They also observed a relationship between DOC content and apparent oxygen utilization suggesting that the consumption of DOC is responsible for oxygen depletion in the deep sea. How to reconcile the apparent differences between these techniques has not been clear. Here we provide independent confirmation of the findings of Sugimura and Suzuki. We collected surface and deep waters from the equatorial Pacific Ocean, the Drake passage and the Atlantic Ocean south of Iceland, and analysed their DOC content using the HTCO methodology³. We found DOC concentrations 2–3 times higher than those measured previously. These results imply that the carbon content of the oceans has previously been underestimated by 10^{12} (1,000 billion) tonnes, and that the new estimated total of 1,800 billion tonnes represents one of the largest carbon reservoirs on Earth⁶. We found no evidence of a cause-and-effect relationship between DOC and apparent oxygen utilization.

Comparison of two methods for measuring dissolved organic carbon in sea water

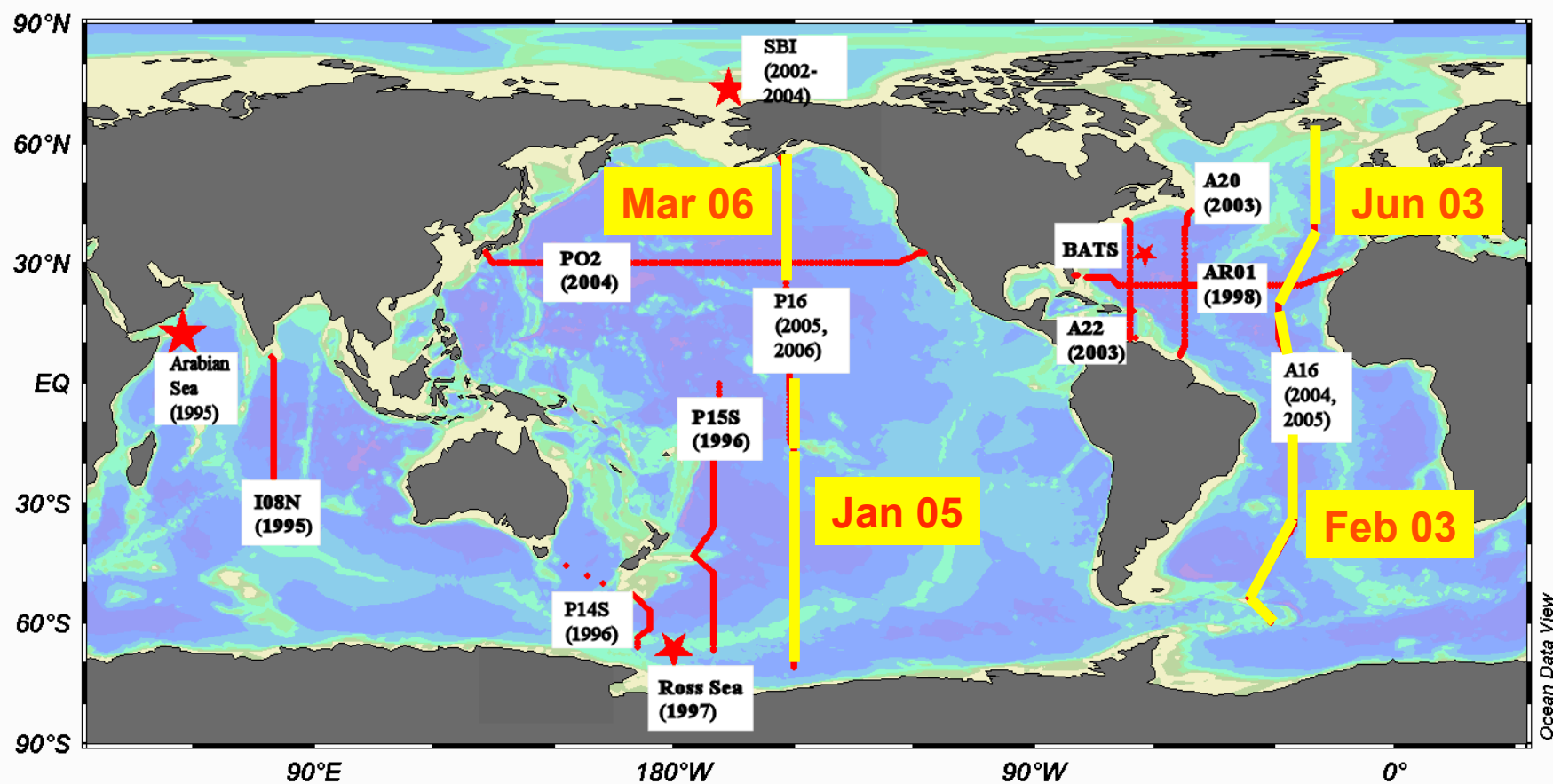
Hiroshi Ogawa & Norio Ogura

Department of Environmental Science and Conservation,
Faculty of Agriculture, Tokyo University of Agriculture and Technology,
3-5-8 Saiwaicho, Fuchu-shi, Tokyo 183, Japan

RECENT measurements³ of the amount of dissolved organic carbon (DOC) in sea water using a high-temperature catalytic oxidation (HTCO) method have generated intense interest because they indicated concentrations several times greater than those obtained from conventional wet chemical oxidation (WCO) methods^{2,4}. As dissolved organic matter in the oceans represents one of the major pools of organic matter in the biosphere^{5,6}, these findings of 'new' DOC have prompted important revisions to models of the oceanic carbon cycle^{7–9}. A satisfactory explanation for the origin of the 'new' DOC, however, which seems to be chemically refractory¹, biologically labile¹⁰ and of high molecular mass¹, has not been forthcoming. Here we present a comparison of measurements of seawater DOC using the HTCO and WCO methods. We obtain fairly good agreement between the two methods, with the HTCO results being considerably lower than those reported previously¹. Our data suggest that the WCO technique may not fail to detect so much DOC as had been previously supposed, and that any carbon that is missed by this method may be in the low- rather than the high-molecular-mass fraction.

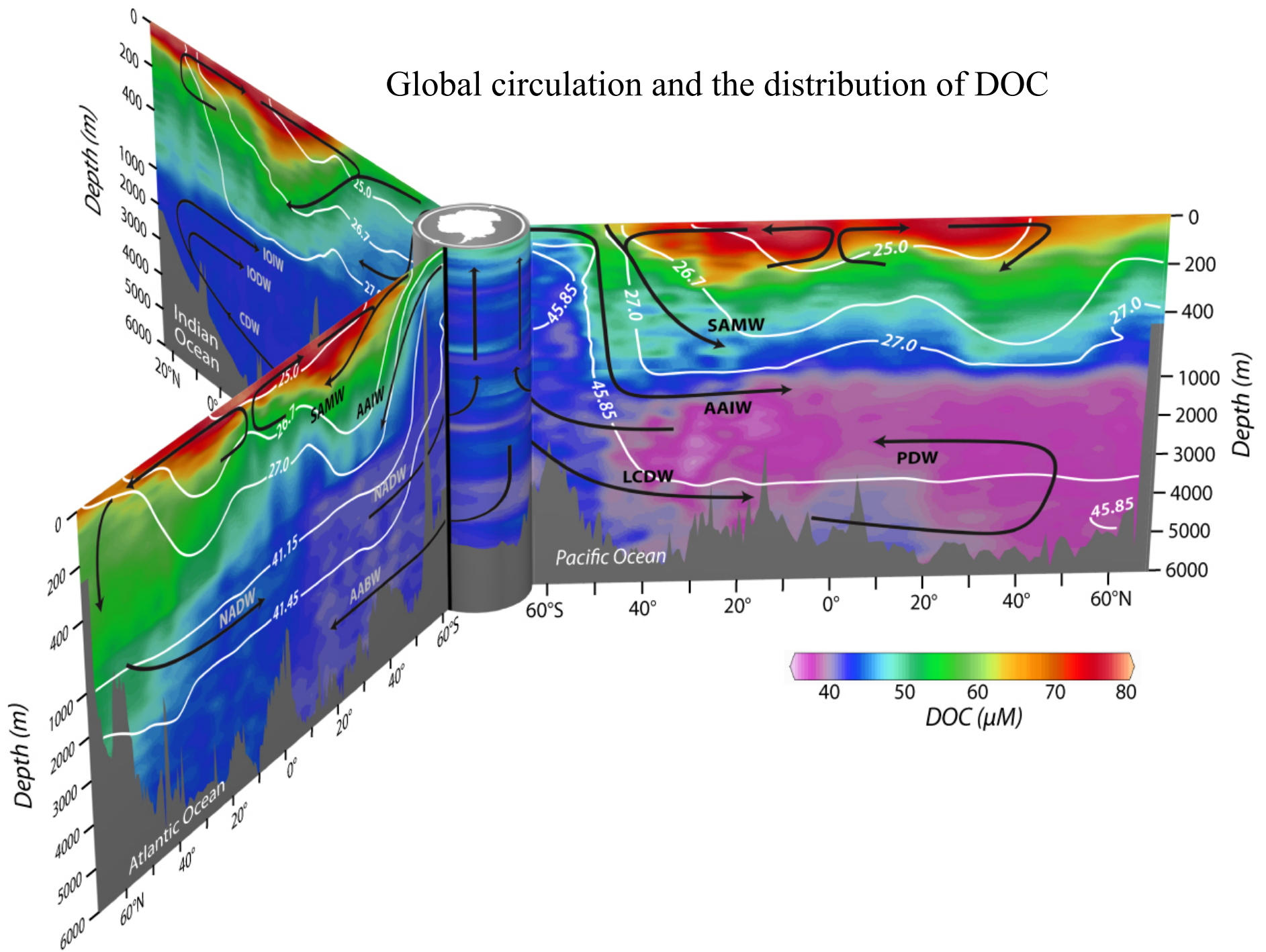
Nature v 356,(1992) p 696-698 (Ogawa) and p 699-700 (Martin)

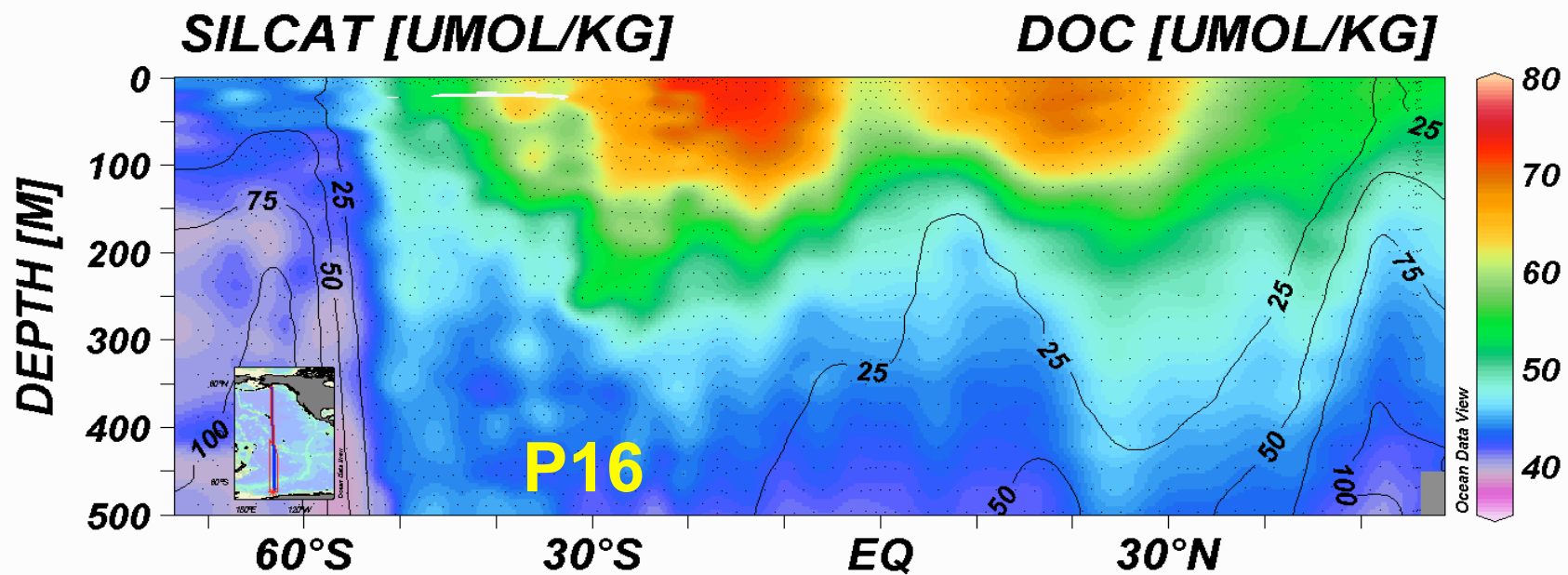
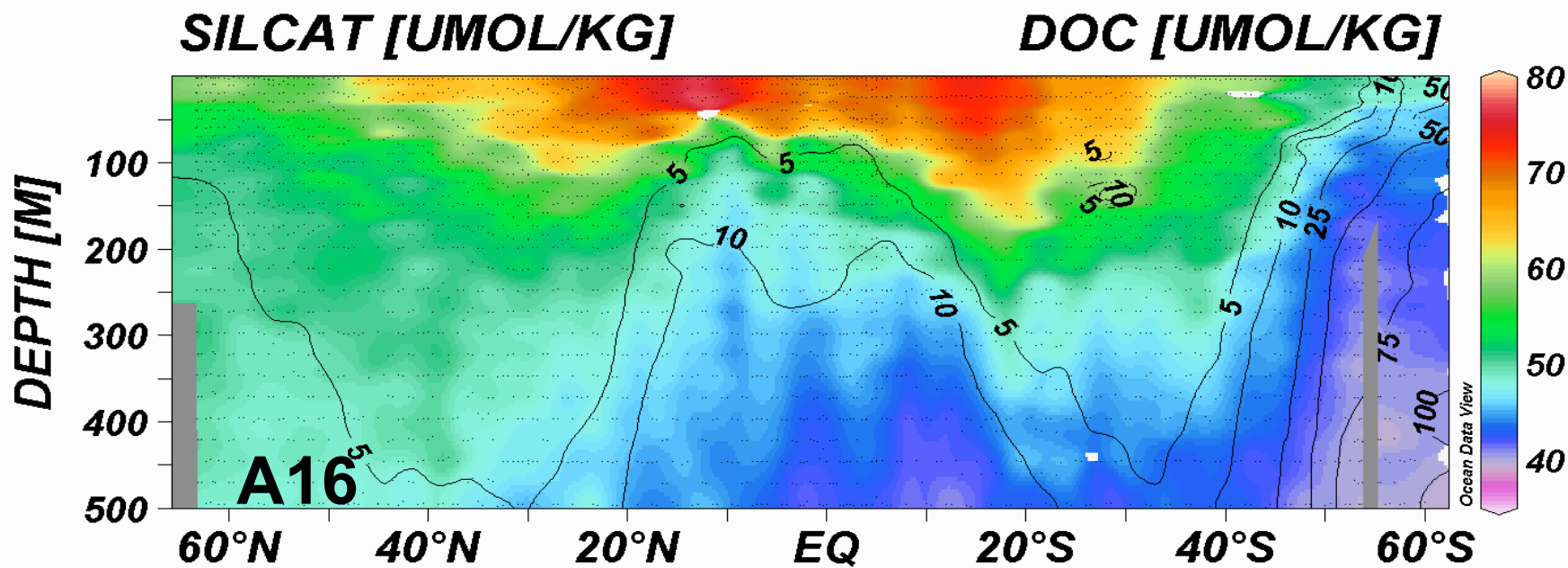
Distribution of DOC in the Pacific and Atlantic Basins

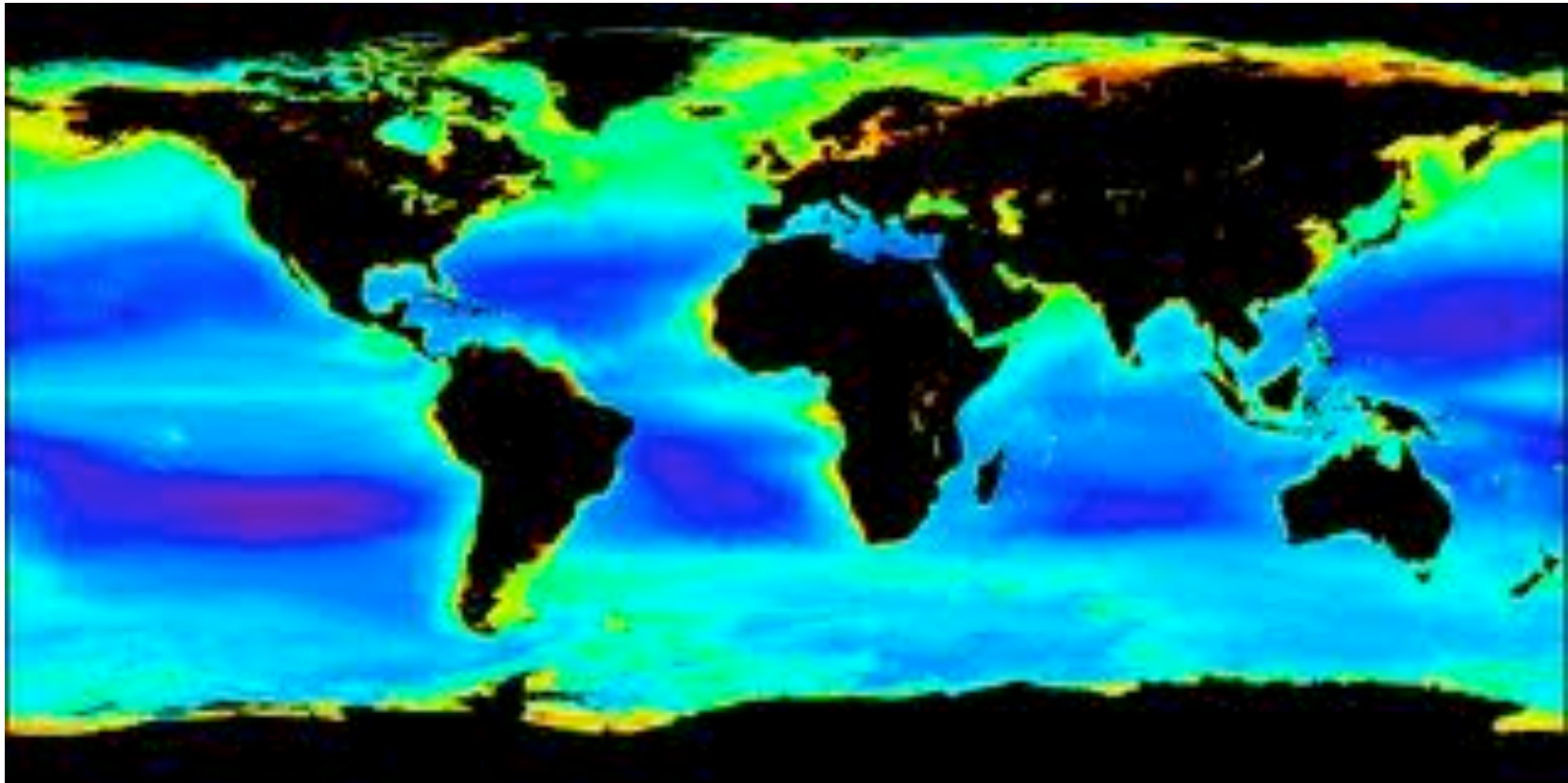


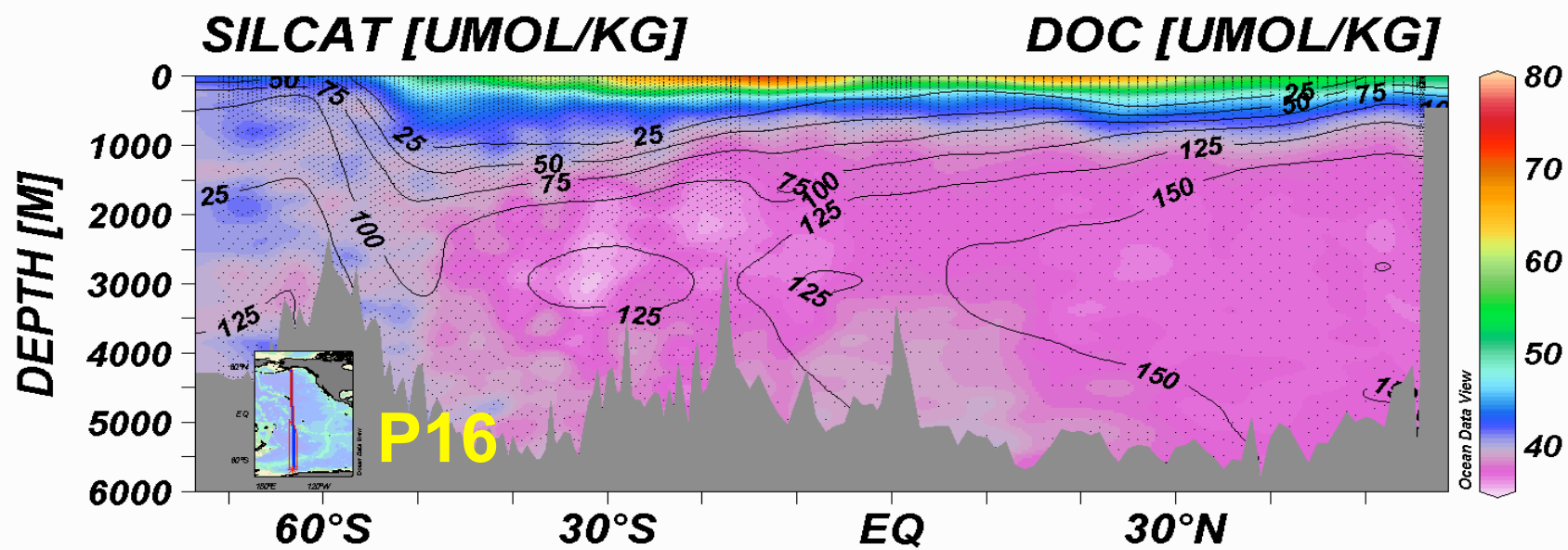
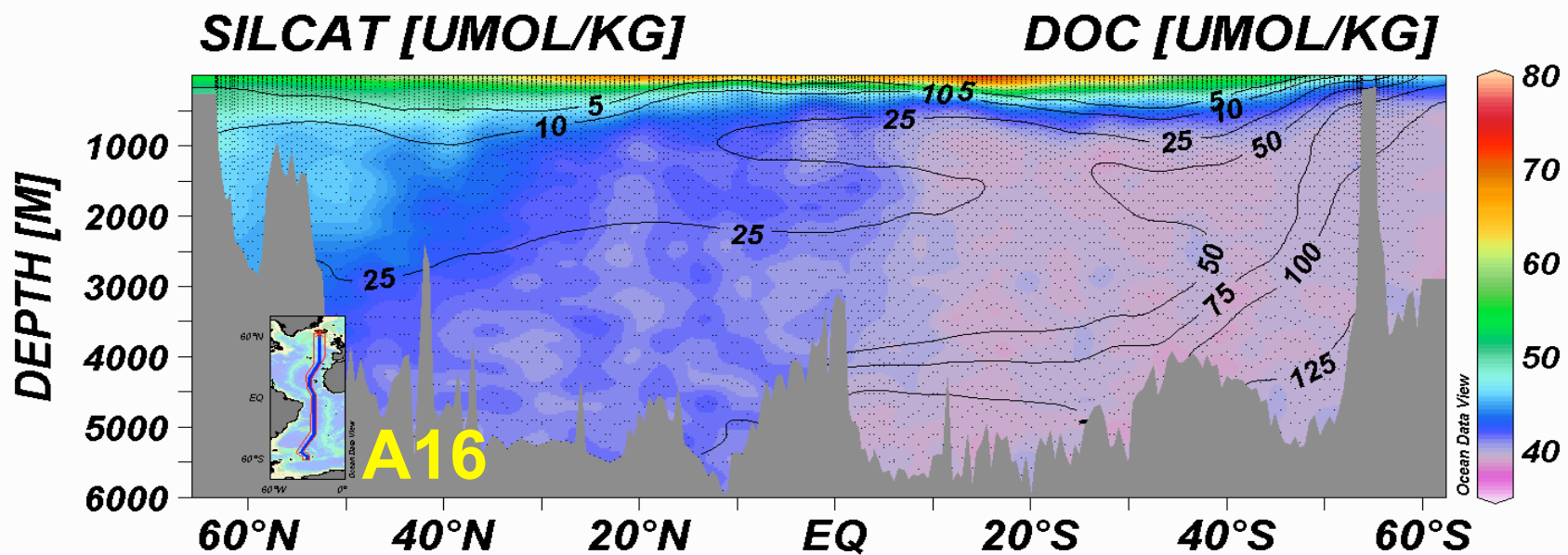
Data from Dennis Hansell (www.rsmas.miami.edu/groups/biogeochem/Data.htm)

Global circulation and the distribution of DOC

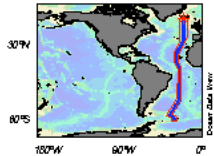
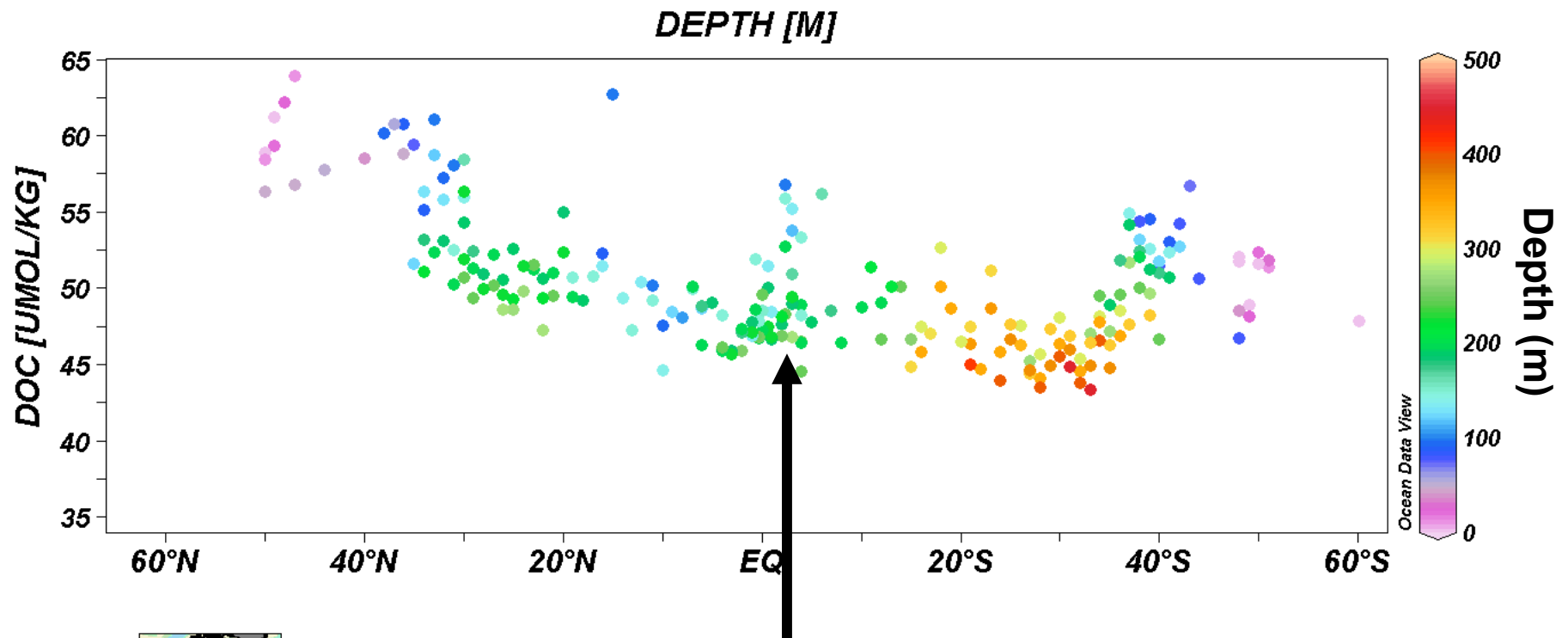








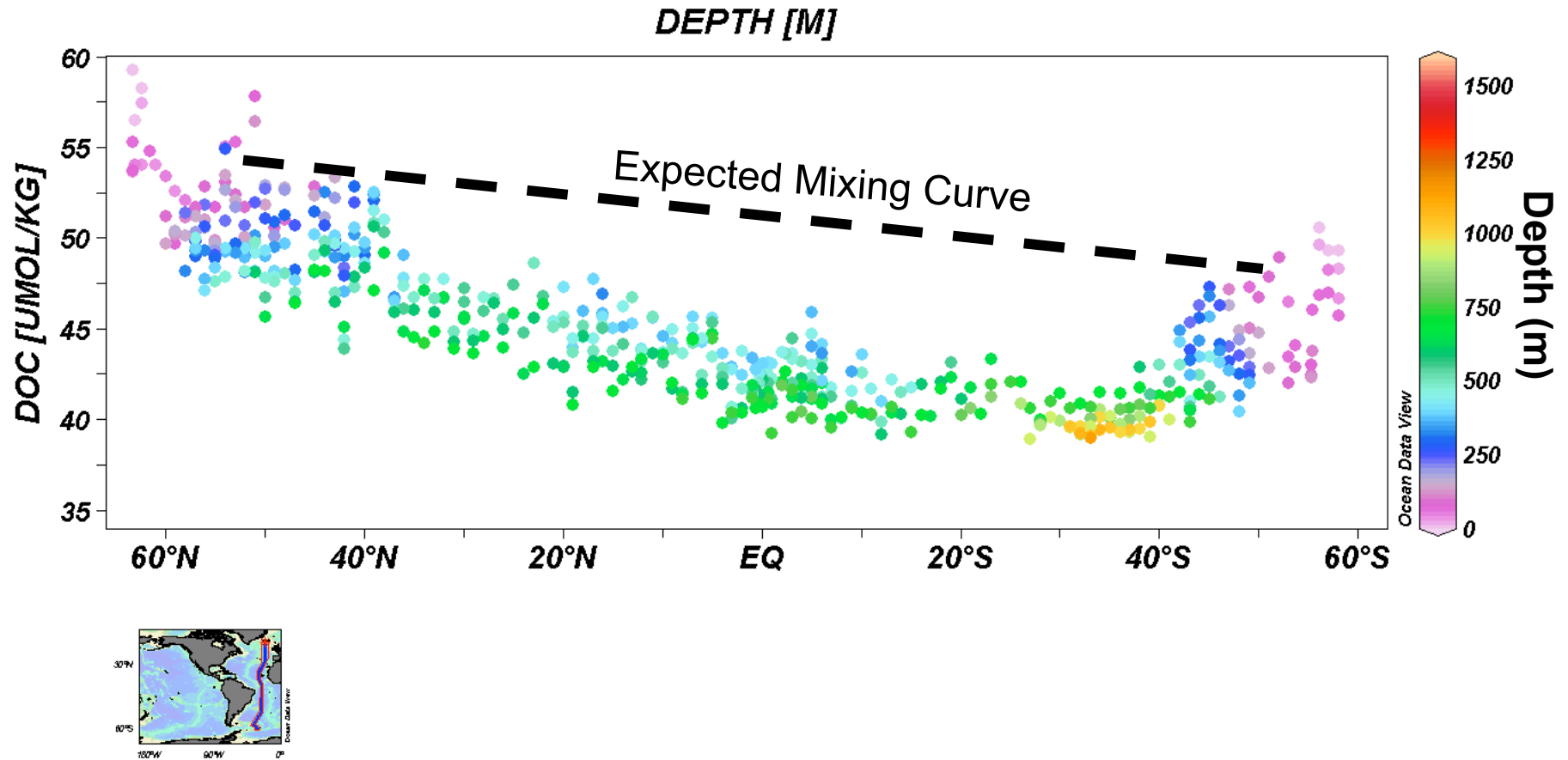
A16: DOC on δ_θ 26.4 – 26.7



**Input on the Equator
(solubilization of sinking particles
or advective input?)**

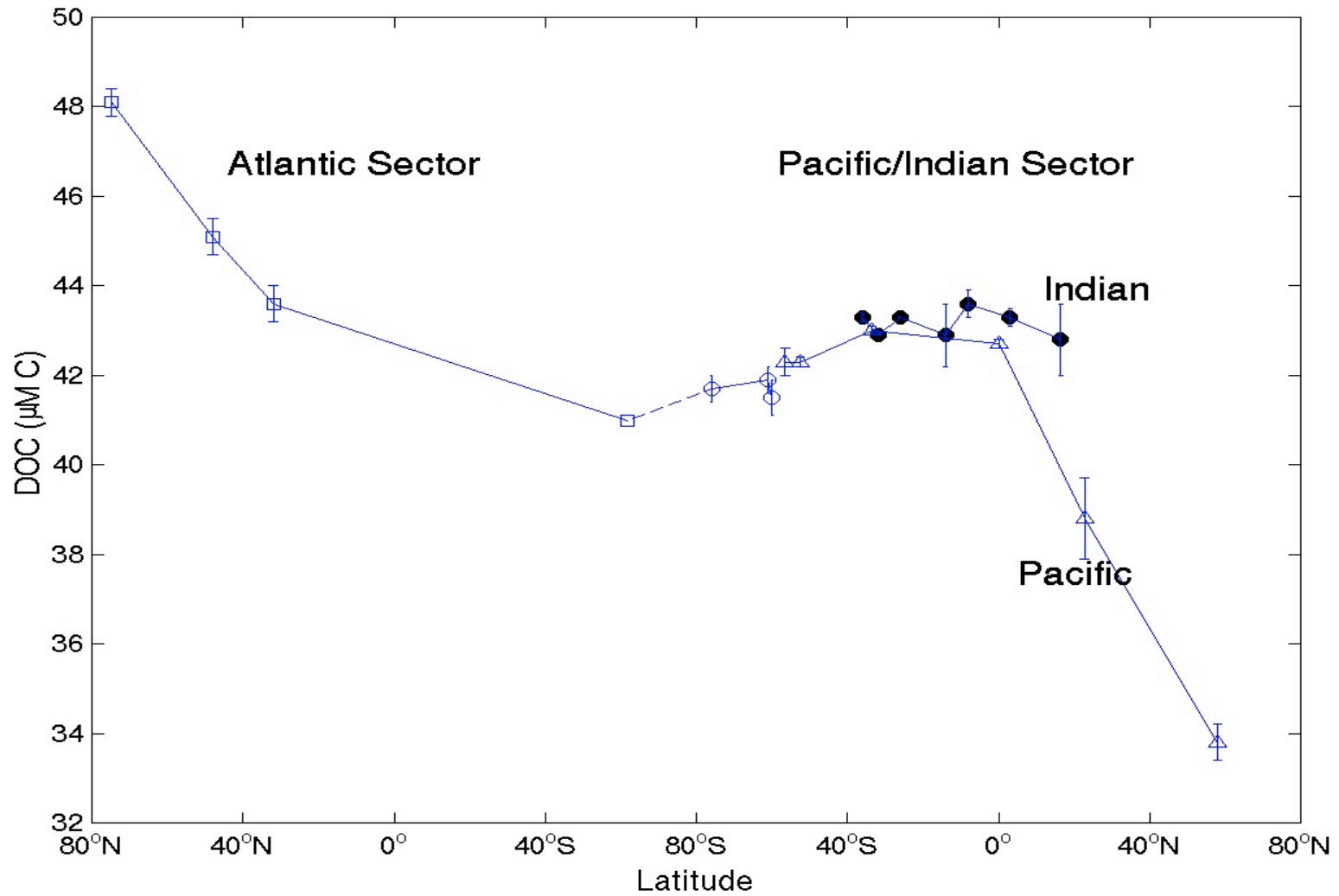
Data from Dennis Hansell (www.rsmas.miami.edu/groups/biogeochem/Data.htm)

A16: DOC on δ_θ 27.0 – 27.3

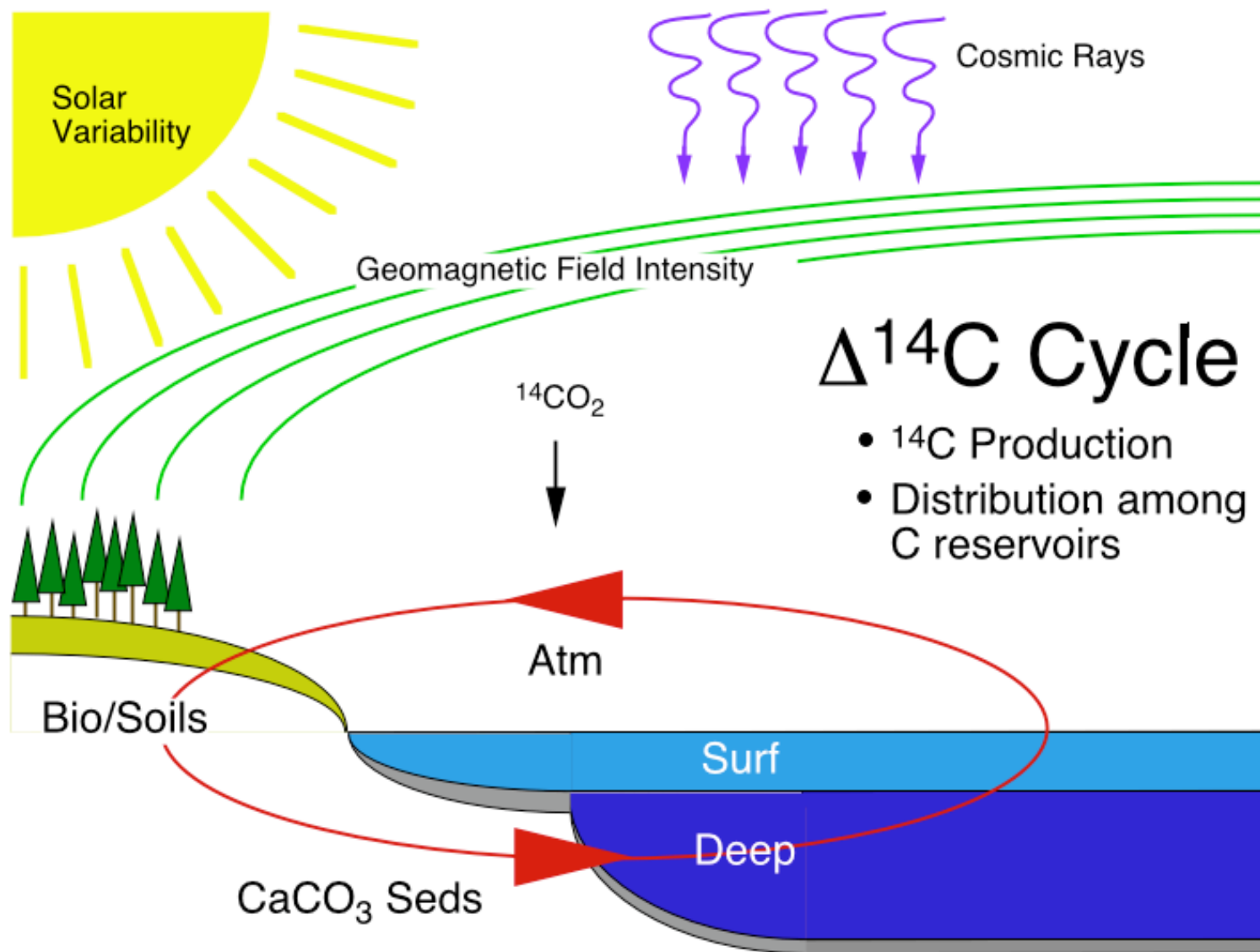


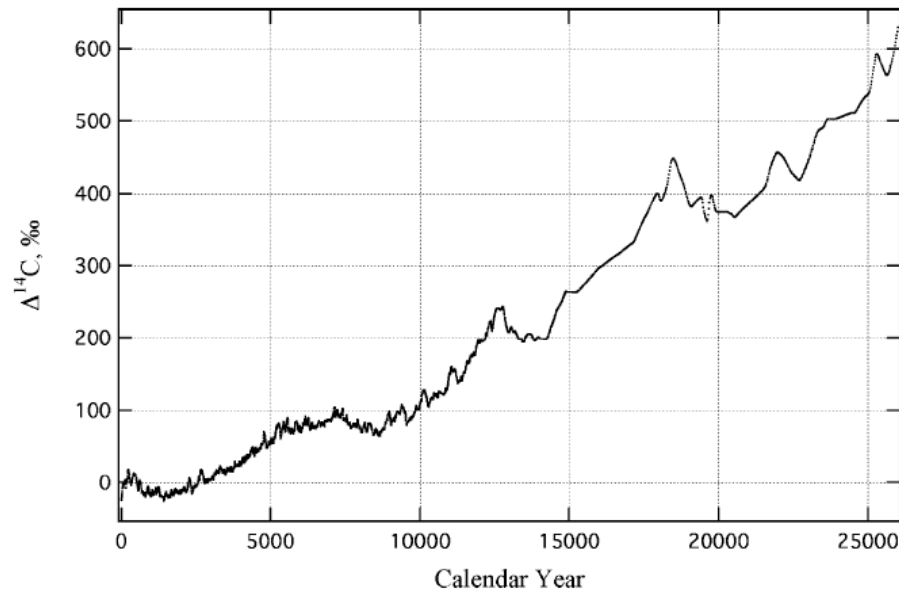
Data from Dennis Hansell (www.rsmas.miami.edu/groups/biogeochem/Data.htm)

DOC in the Deep Global Ocean (Hansell and Carlson, 1998)



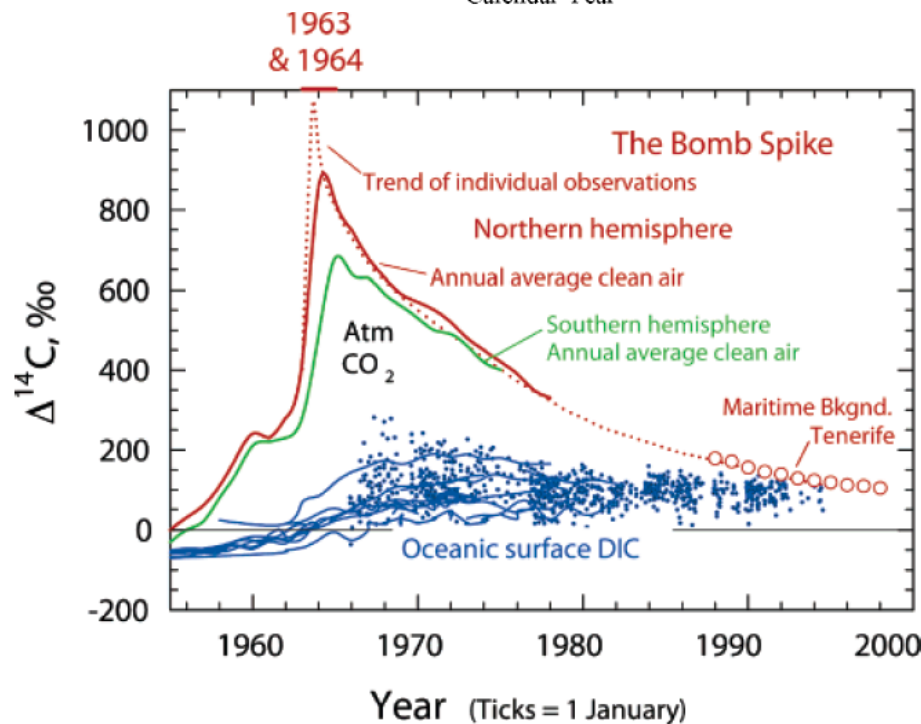
Natural abundance radiocarbon and DOC





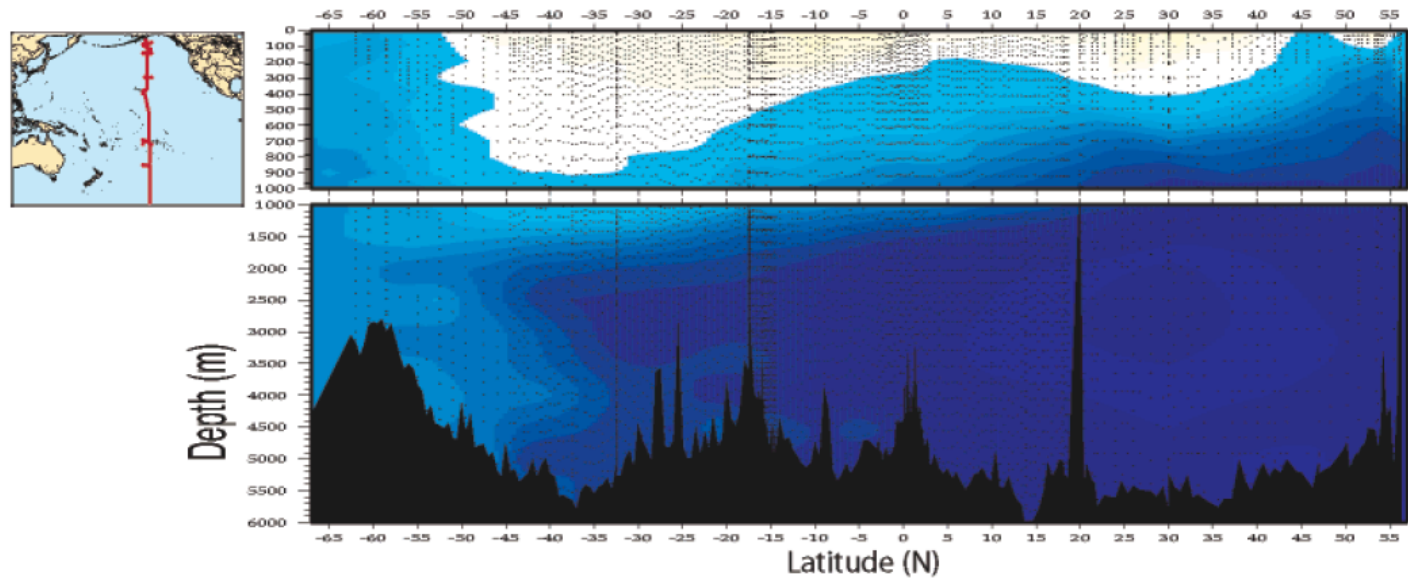
Natural radiocarbon production has changed over time, and is influenced by changes in the flux of cosmic rays, solar activity, and the earth's magnetosphere.

Atmospheric radiocarbon is adsorbed by the ocean through CO_2 gas exchange, but the rate of adsorption varies in space and time. Penetration of radiocarbon into the ocean interior is affected by mixing and circulation.

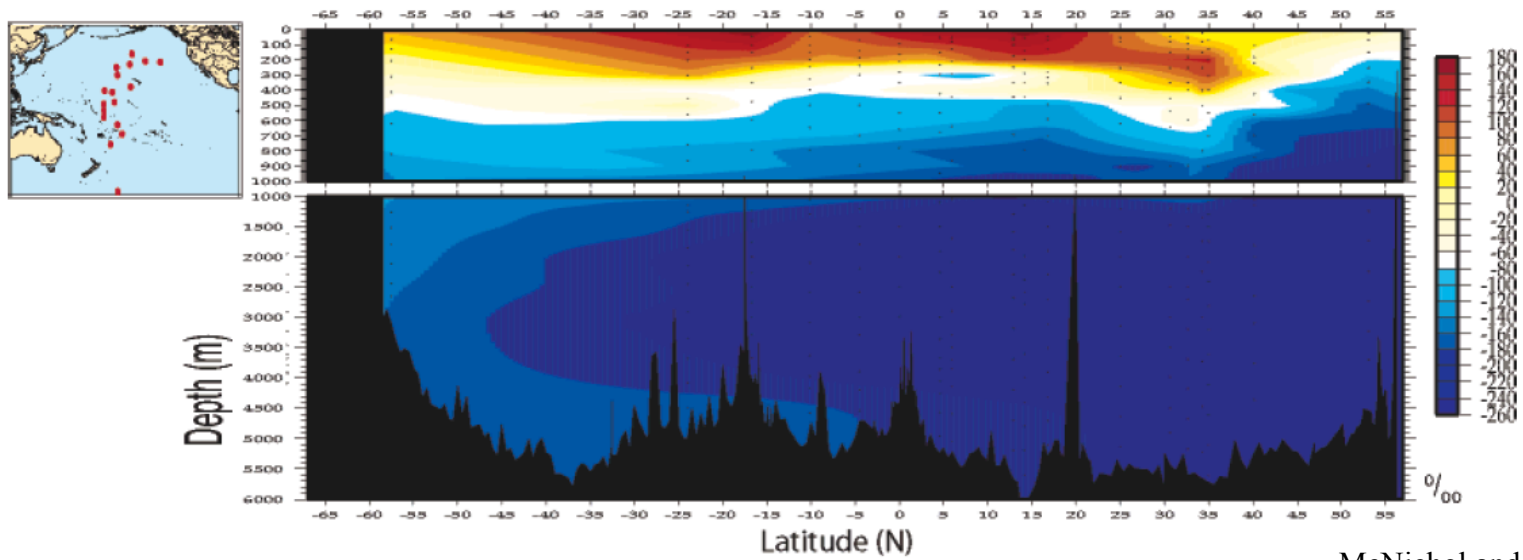


Atmospheric testing of nuclear weapons in the period of 1945-1962 introduced a large amount of anthropogenic radiocarbon into the atmosphere. This “bomb signal” is still being adsorbed by the ocean and incorporated into Organic matter.

Natural $\Delta^{14}\text{C}$ Pacific



Geosecs $\Delta^{14}\text{C}$ Pacific



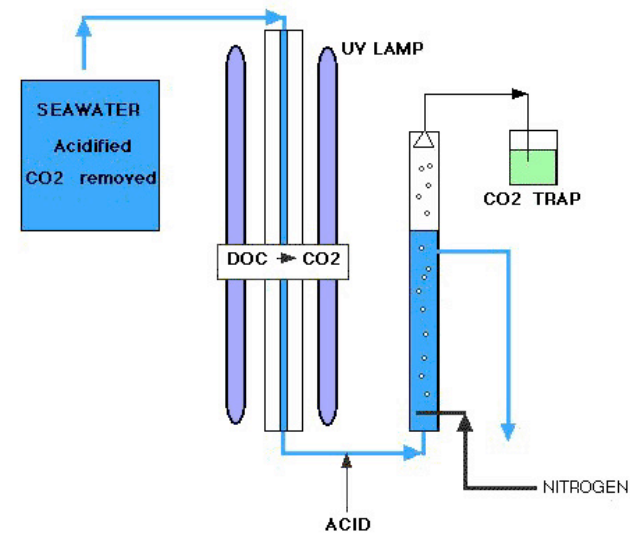
DOC cycling via DO^{14}C

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 time¹⁻³. 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 radiation⁴ (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 $\mu\text{g/l}$. 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^{5,6}. 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

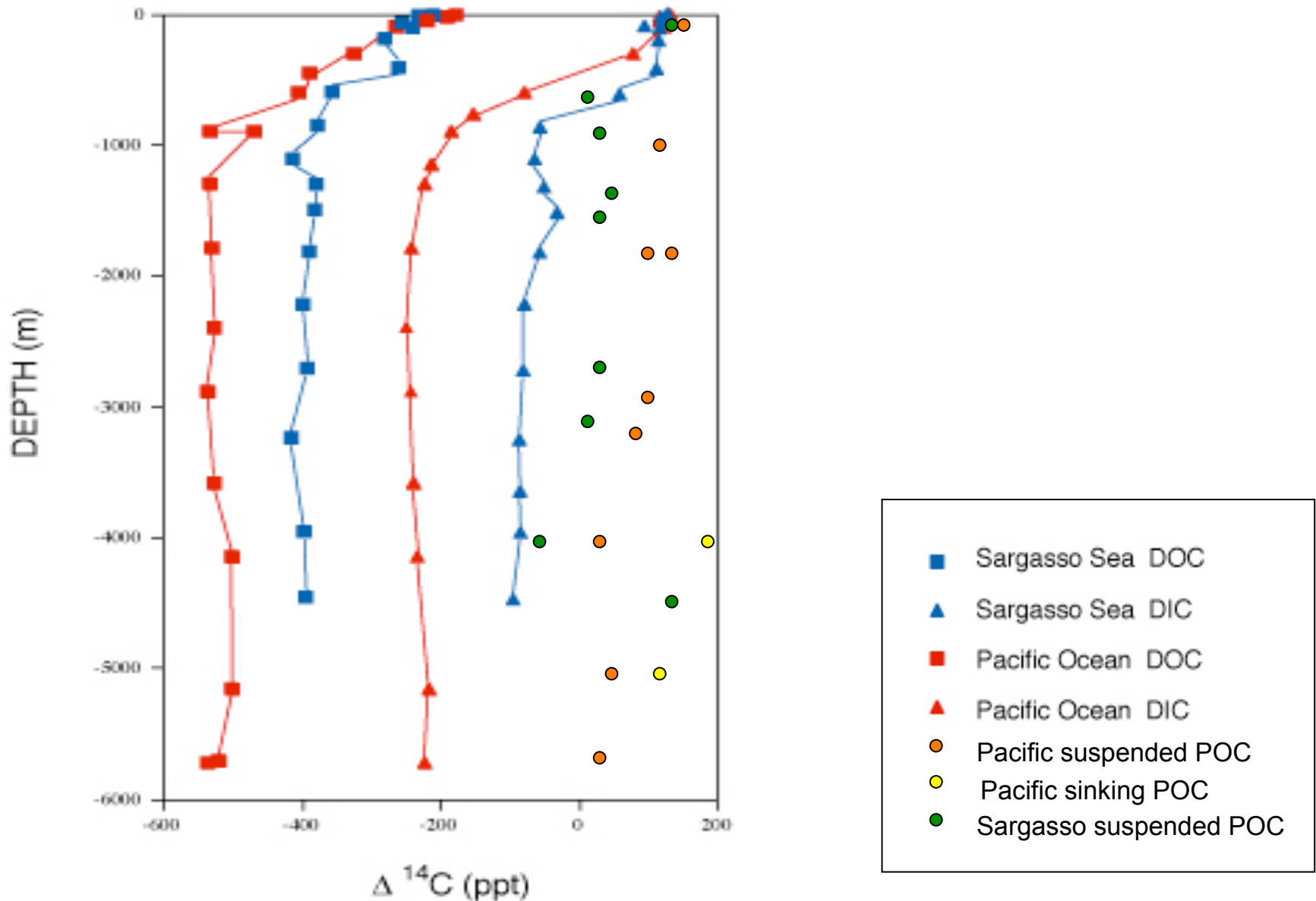
Accelerator Mass Spectrometry (AMS) NOSAMS at Woods Hole



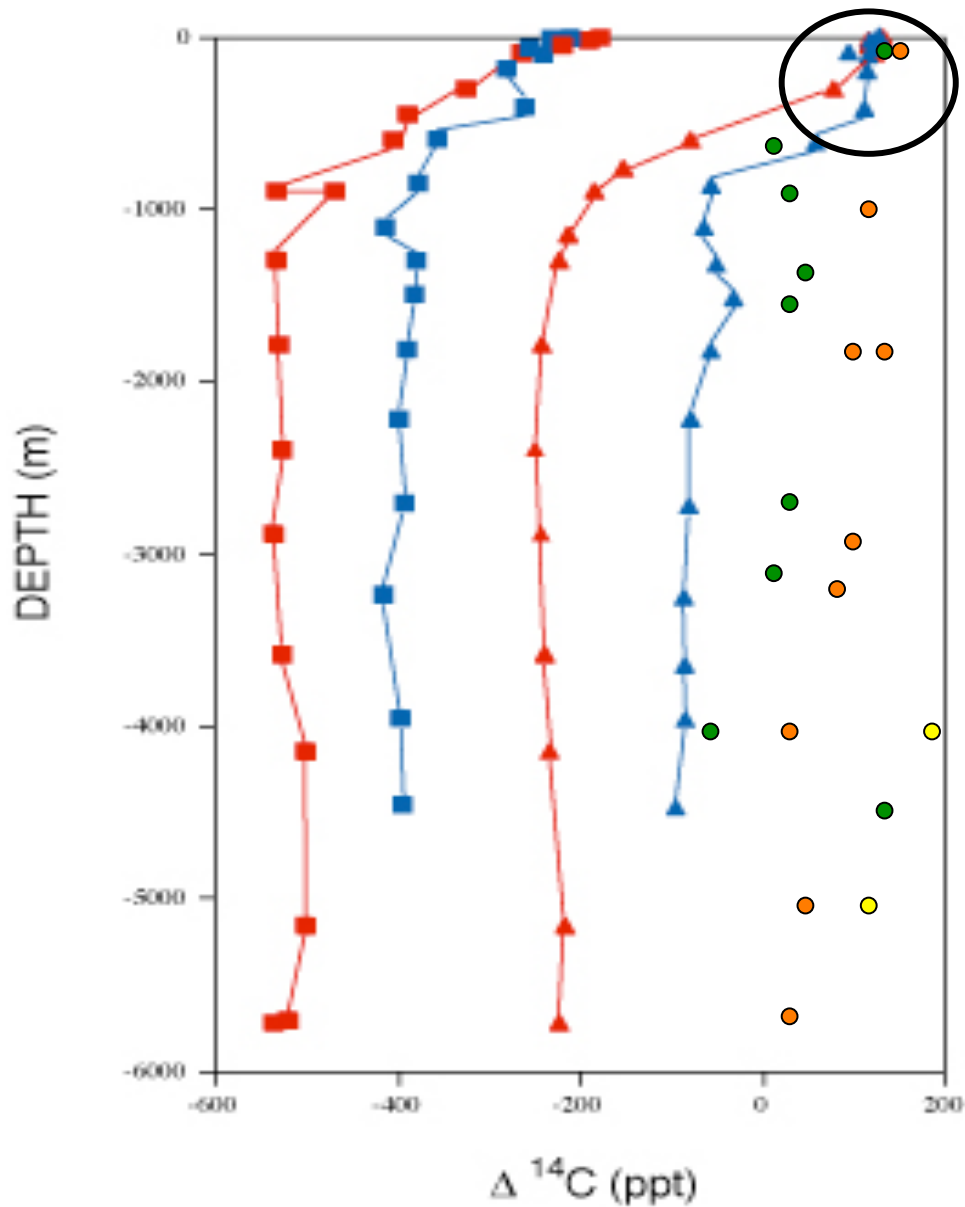
C-14 PP measurements use 10^6 x more C-14 than natural abundance!!!!

Radiocarbon in the Atlantic and Pacific Oceans

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



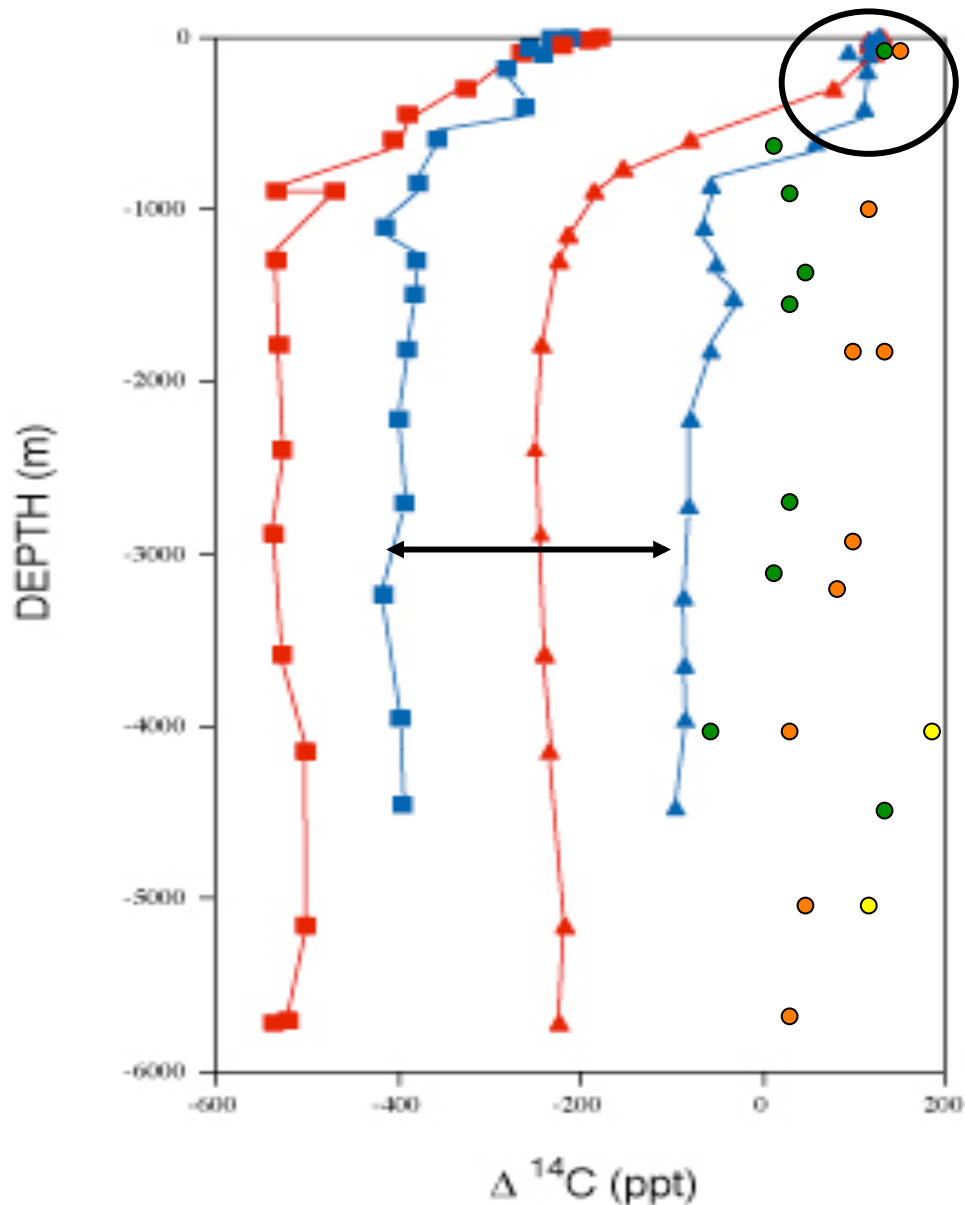
Radiocarbon in the Atlantic and Pacific Oceans



DIC ^{14}C in surface waters of the Atlantic and Pacific has the same isotopic value.

- 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



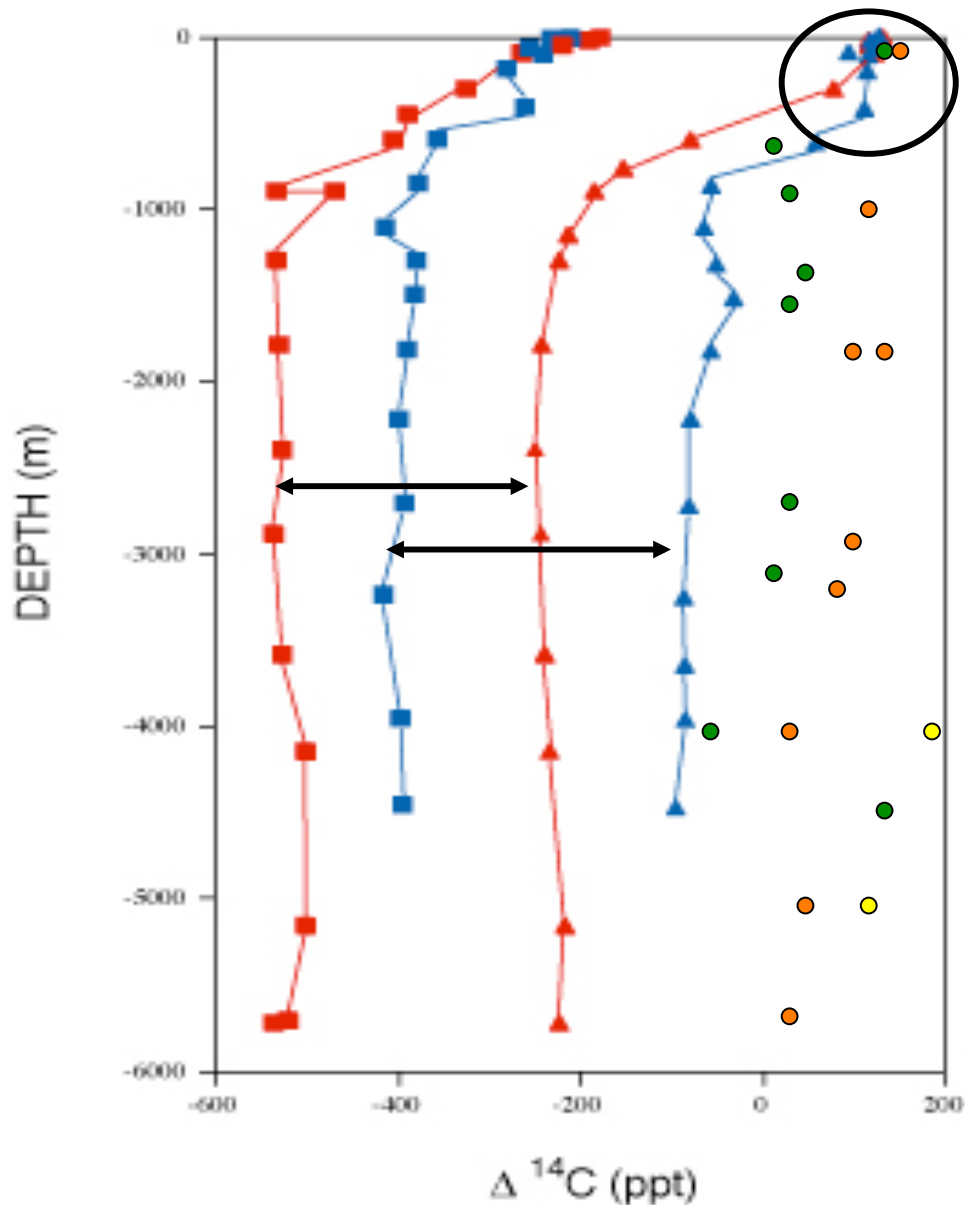
DIC ^{14}C in surface waters of the Atlantic and Pacific has the same isotopic value.

DOC is always older than DIC (by 4 kyrs in surface water)

DIC \rightarrow POC \rightarrow DOC

- 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



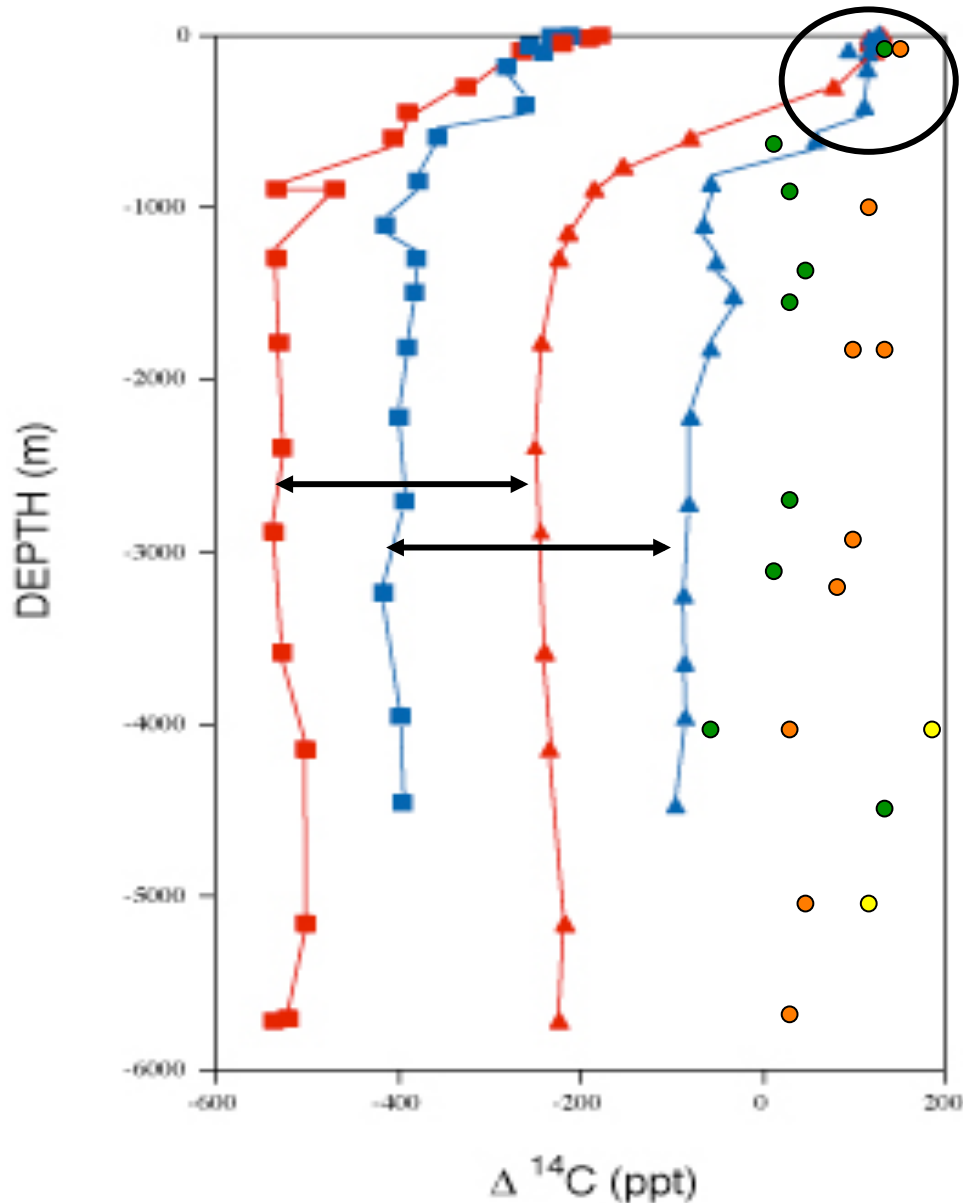
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$\Delta\Delta^{14}\text{C}$ of DIC and DOC is about the same in the deep Atlantic and Pacific

- Sargasso Sea DOC
- ▲ Sargasso Sea DIC
- Pacific Ocean DOC
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- Pacific suspended POC
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Radiocarbon in the Atlantic and Pacific Oceans



DIC ^{14}C in surface waters of the Atlantic and Pacific has the same isotopic value.

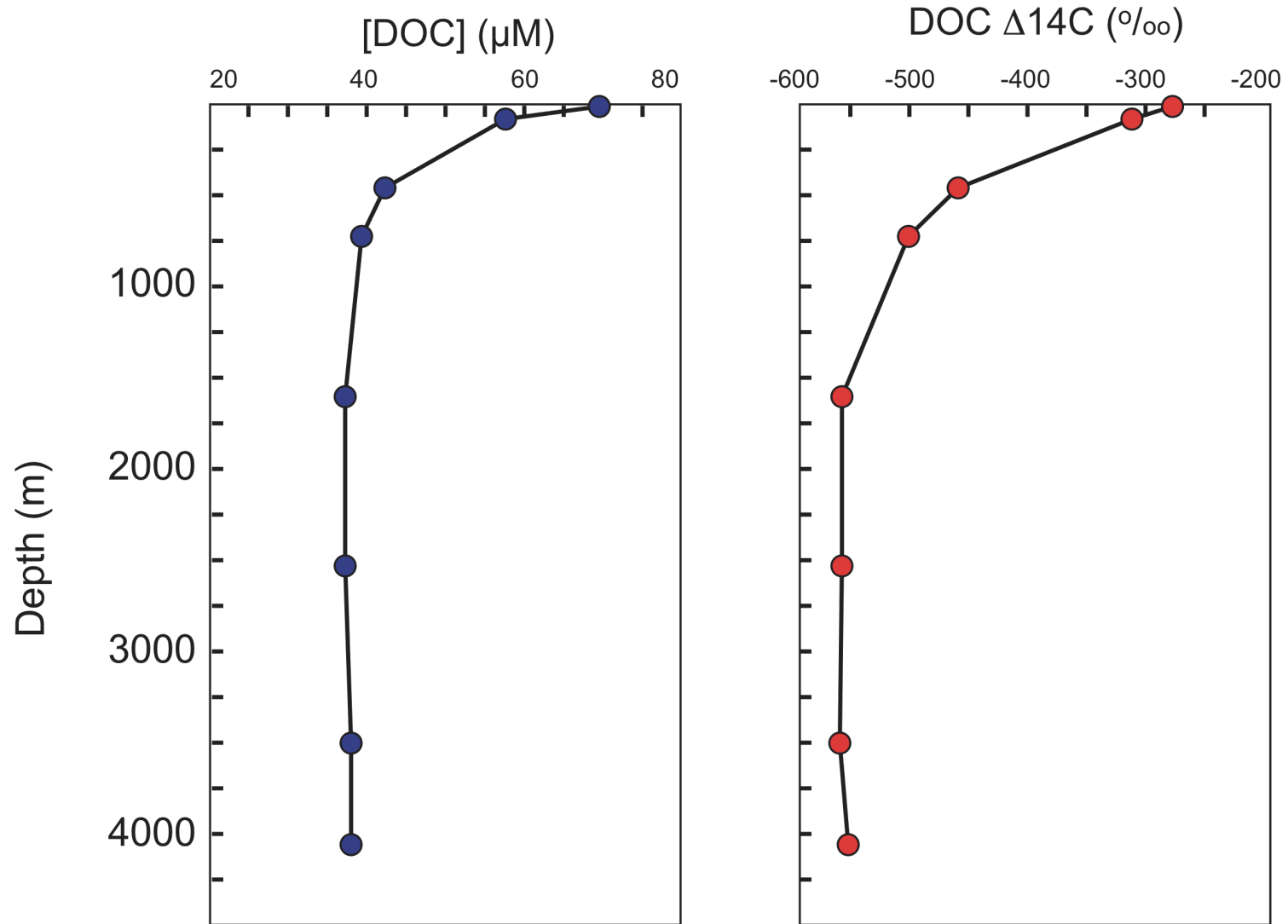
DOC is always older than DIC (by 4 kyrs in surface water)

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

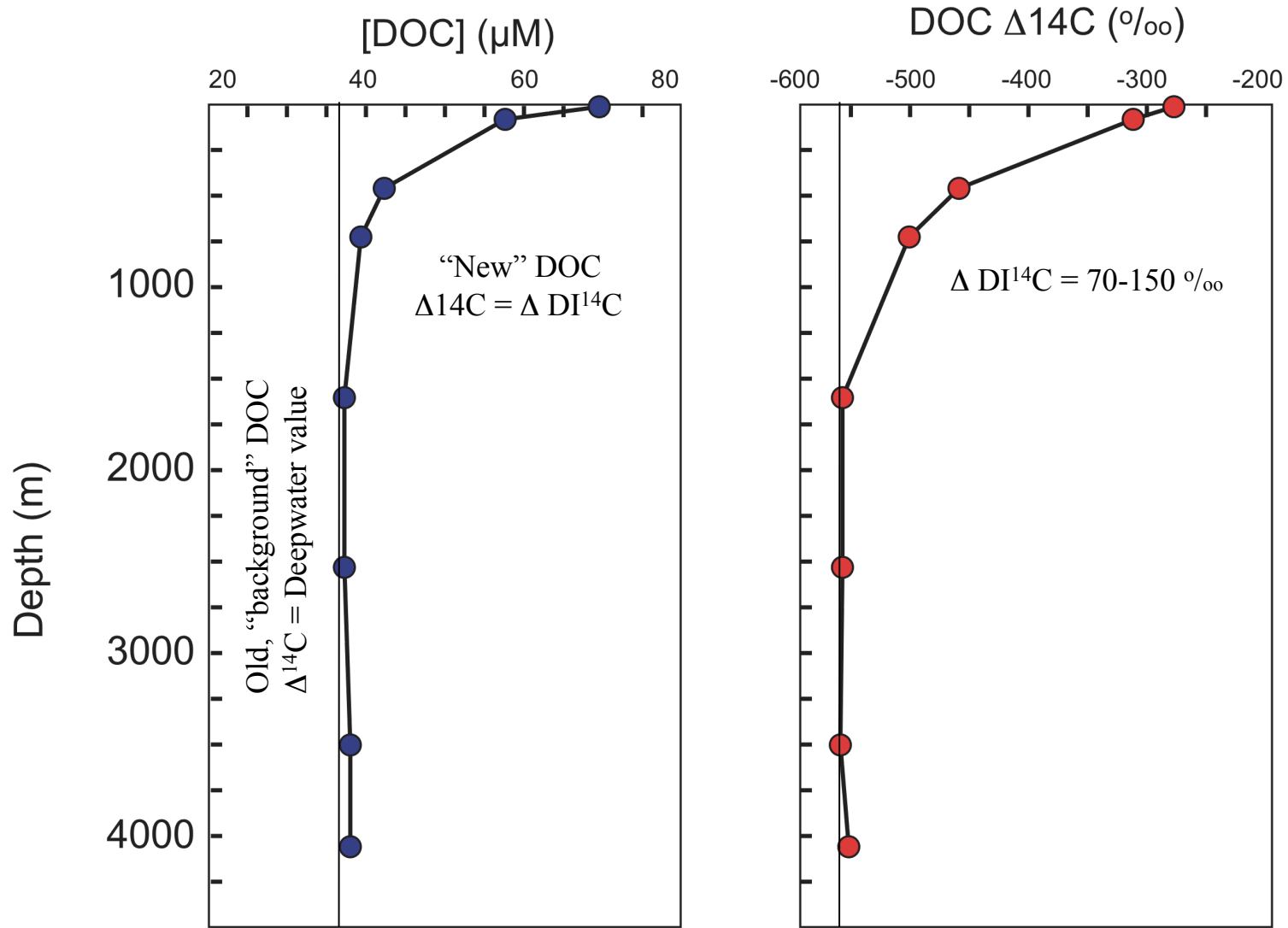
Deep ocean values of DOC are equal to a radiocarbon age of 4-6 kyrs

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:

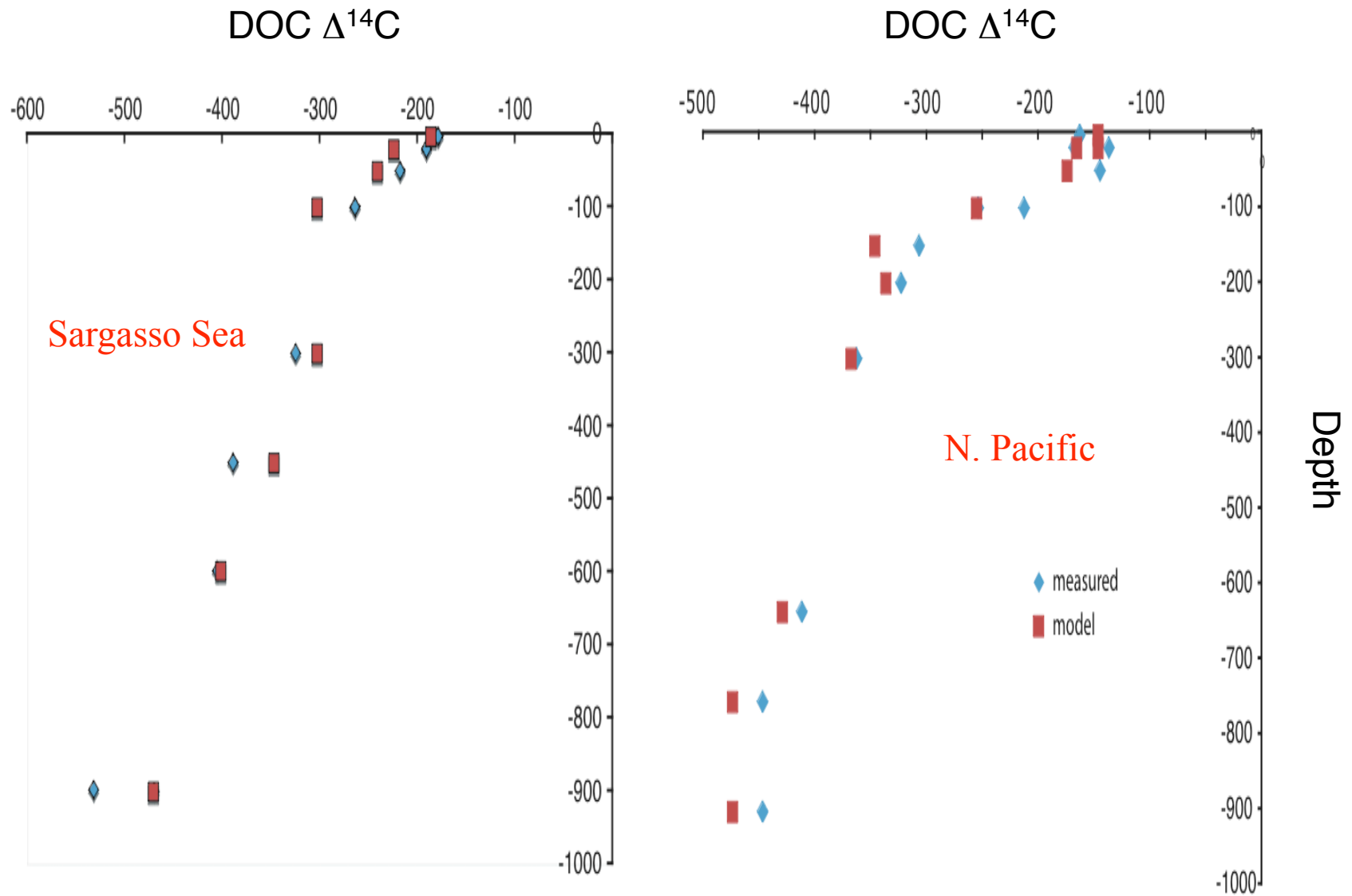
DIC -> POC-> DOC

Mass and isotopic balance can be expressed as:

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

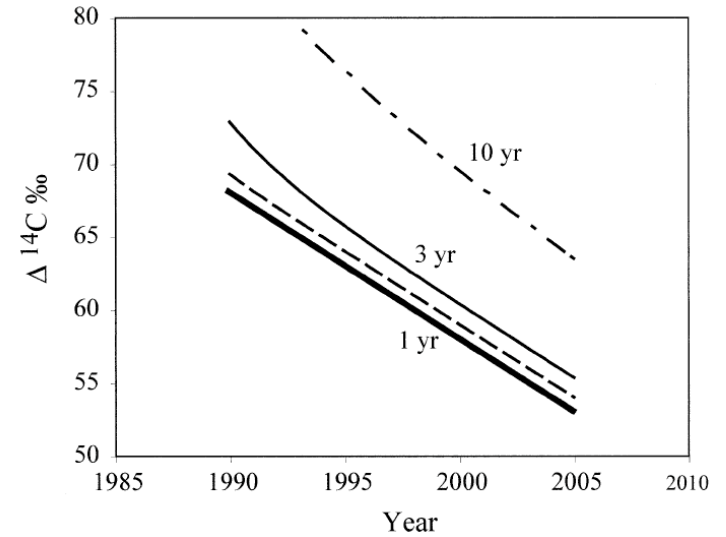
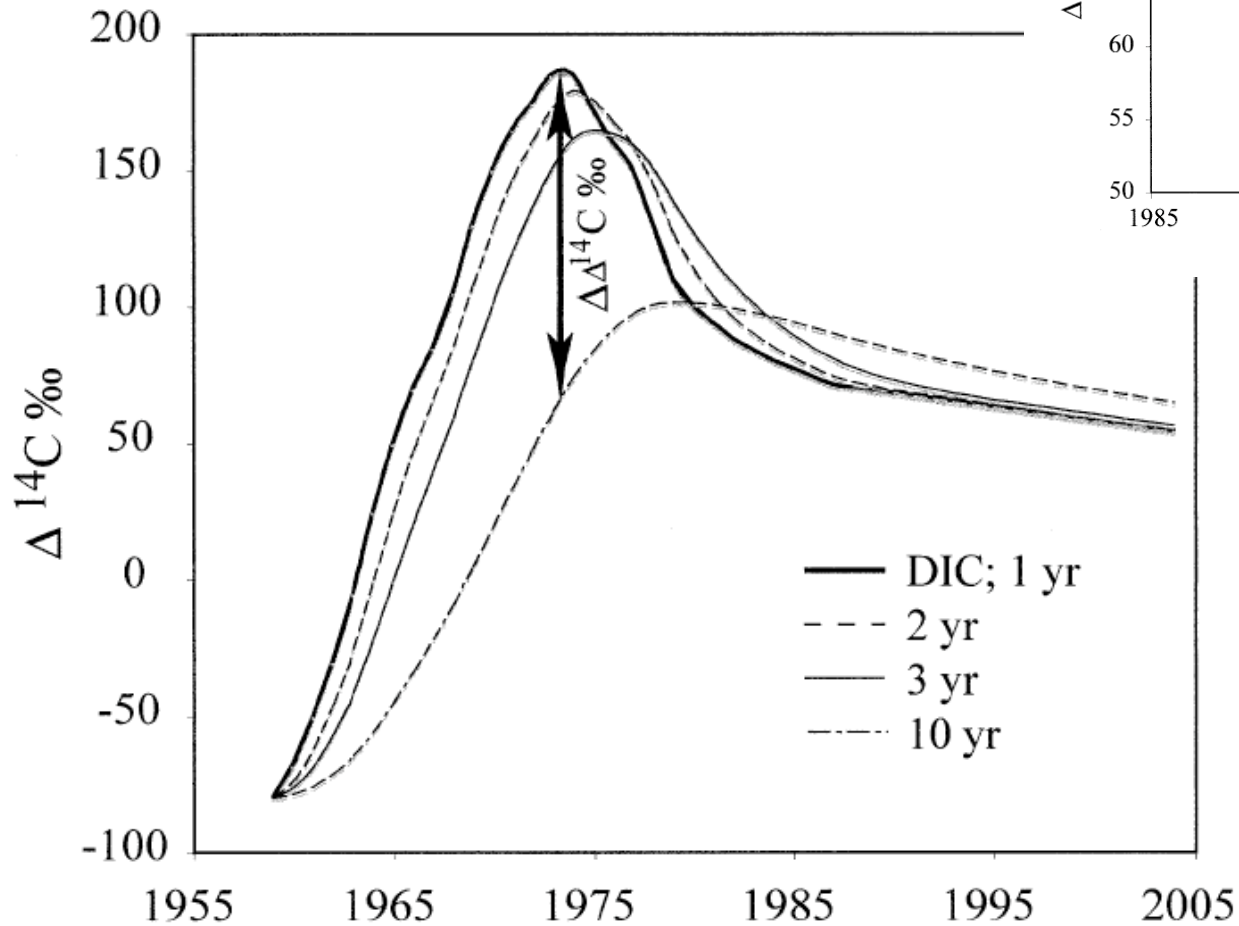
$$\Delta^{14}\text{C}_{\text{sur}} [\text{DOC}]_{\text{sur}} = \Delta^{14}\text{C}_{\text{deep}} [\text{DOC}]_{\text{deep}} + \Delta^{14}\text{C}_{\text{xs}} [\text{DOC}]_{\text{xs}}$$

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.



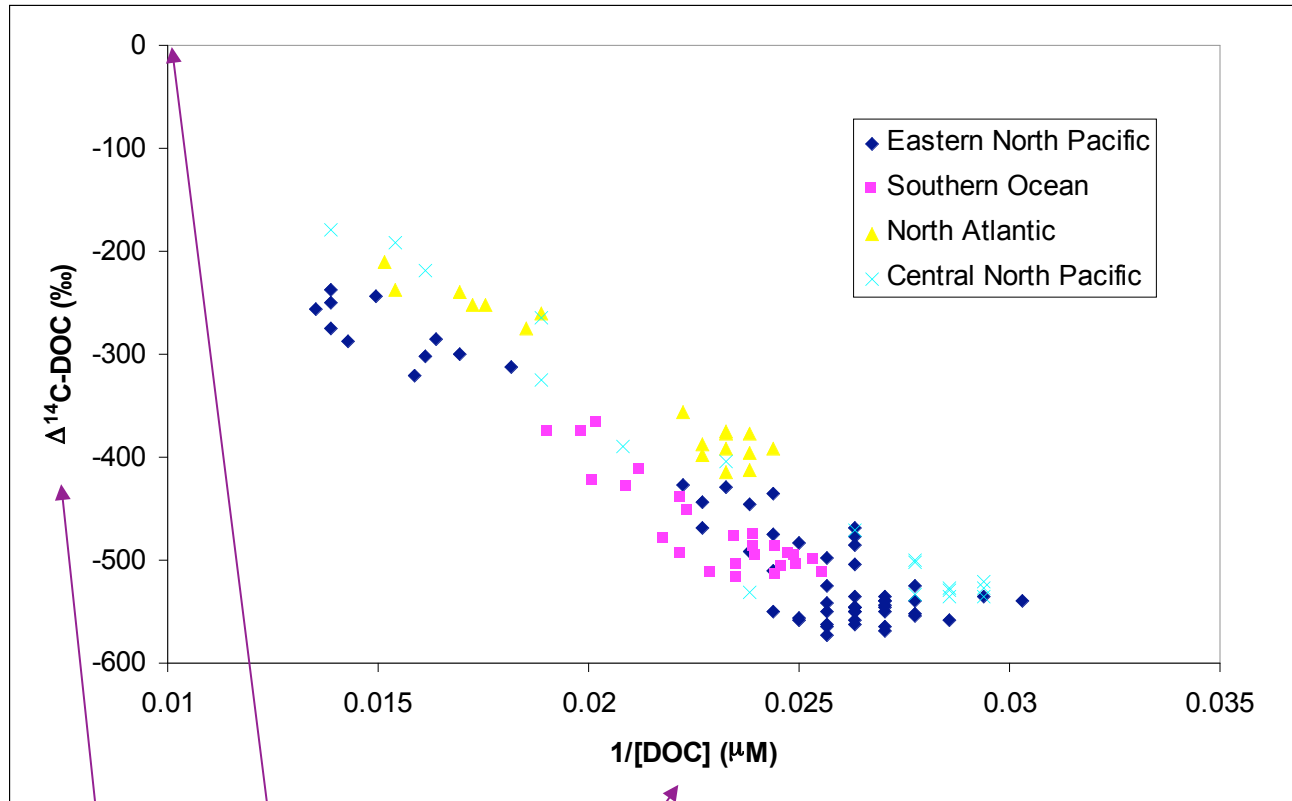
Williams and Druffel, 1987; Druffel et al. 1992

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?



Can we derive the radiocarbon value of DOC xs independently?

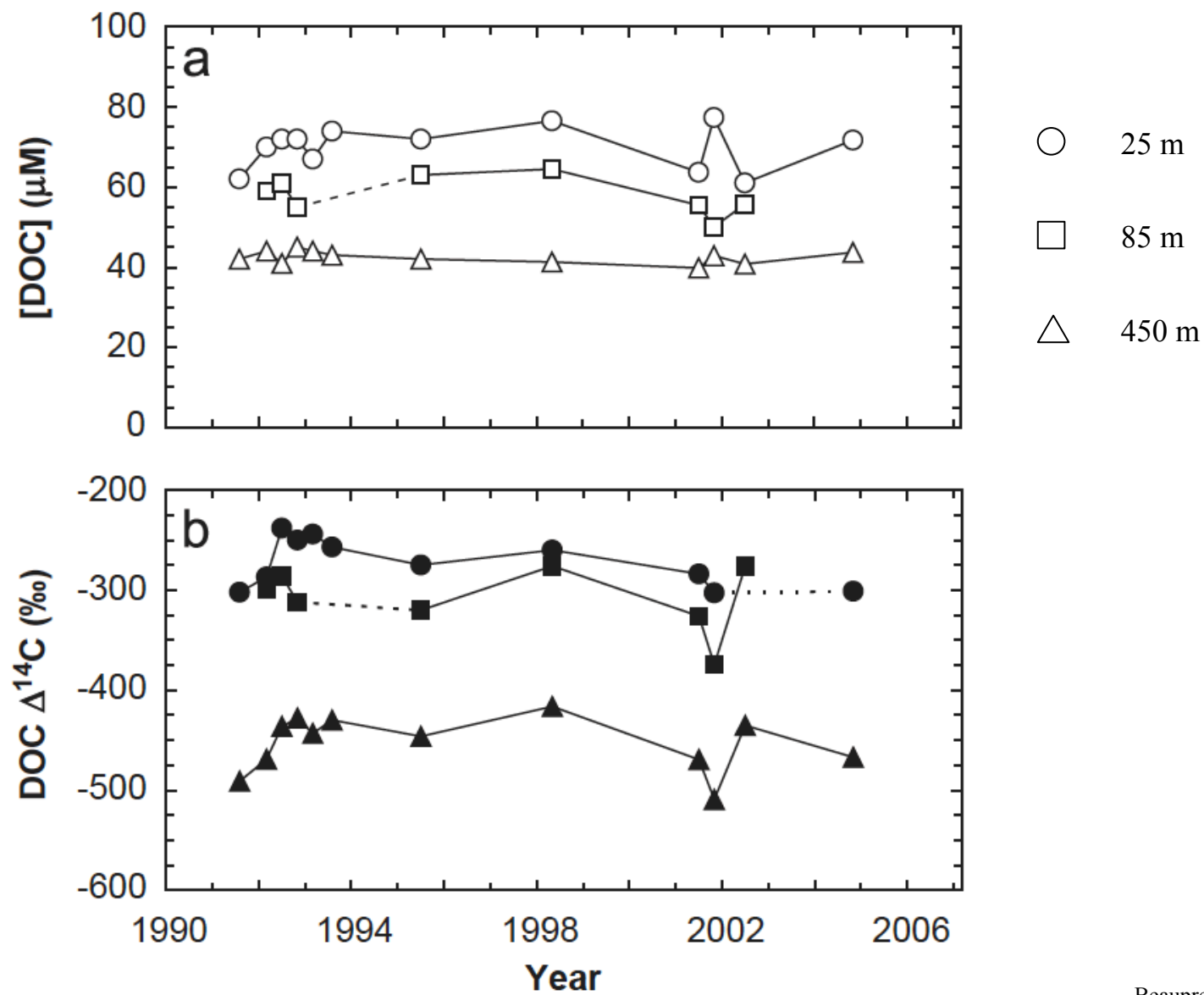
(Mortazani and Chanton, 2004)



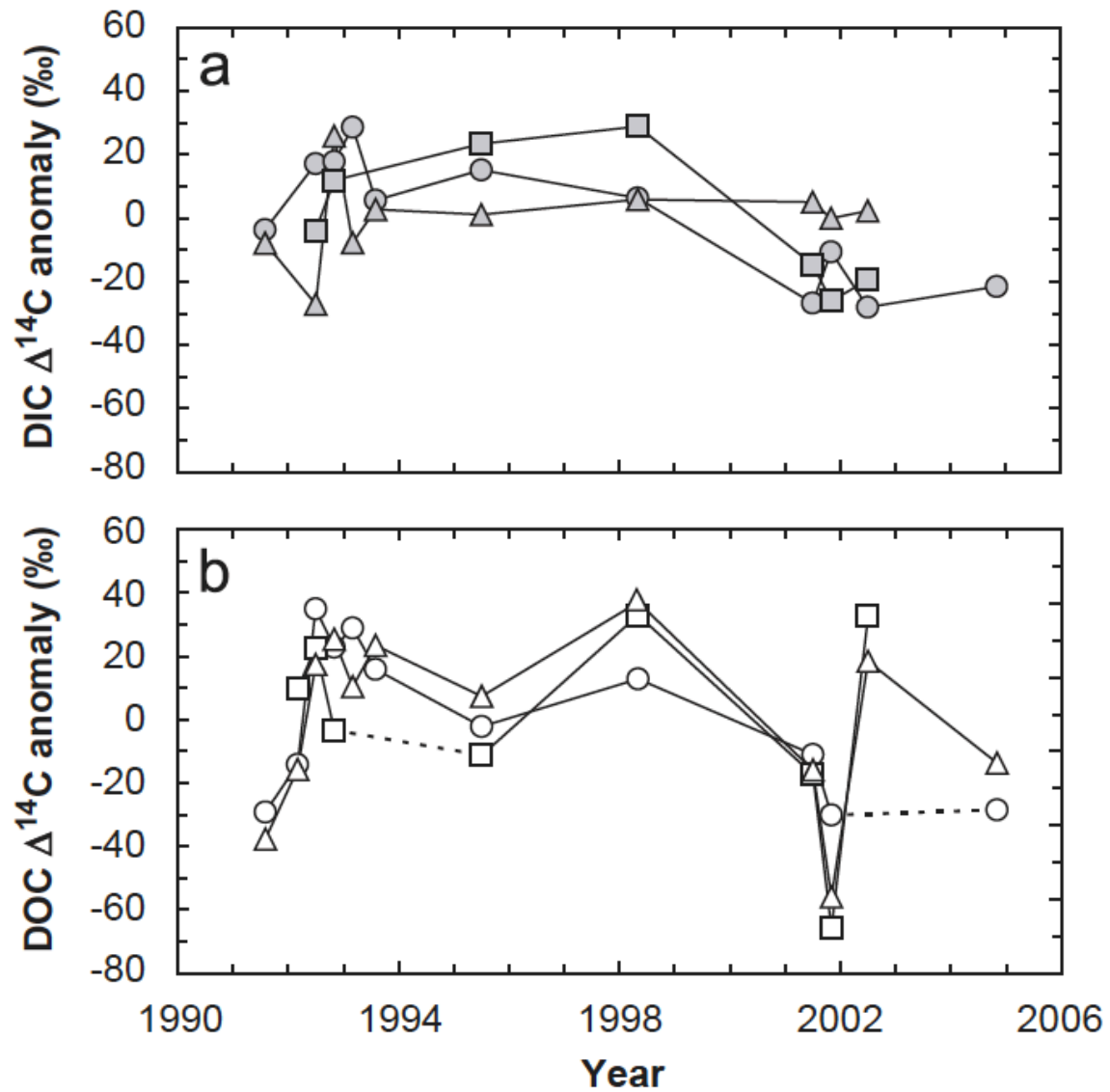
$\Delta^{14}\text{C}_{xs}$	
$73 \pm 23\text{‰}$	('91-'95)
$105 \pm 62\text{‰}$	('95/'96)
$135 \pm 26\text{‰}$	('89)
$162 \pm 39\text{‰}$	('87)

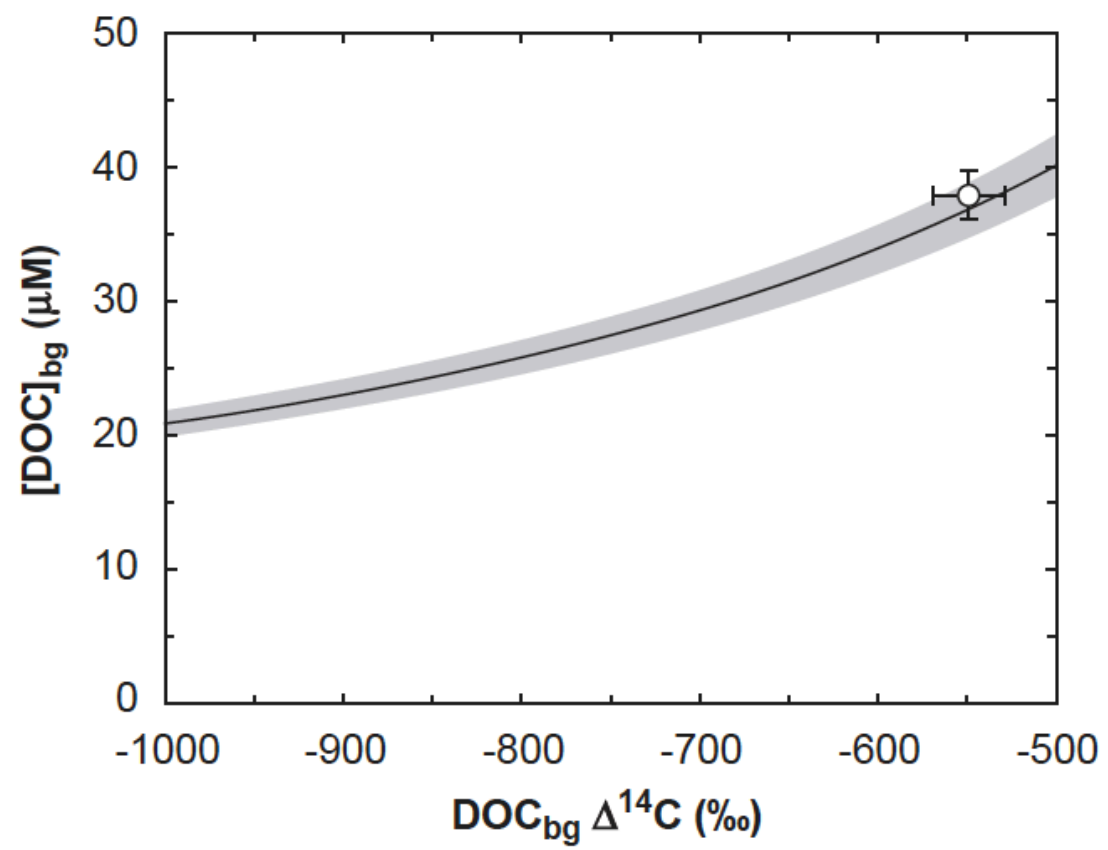
$$\Delta^{14}\text{C}_z = \Delta^{14}\text{C}_{xs} + \left(\frac{1}{\text{DOC}_z} \right) (\text{DOC}_b \Delta^{14}\text{C}_b - \text{DOC}_b \Delta^{14}\text{C}_{xs})$$

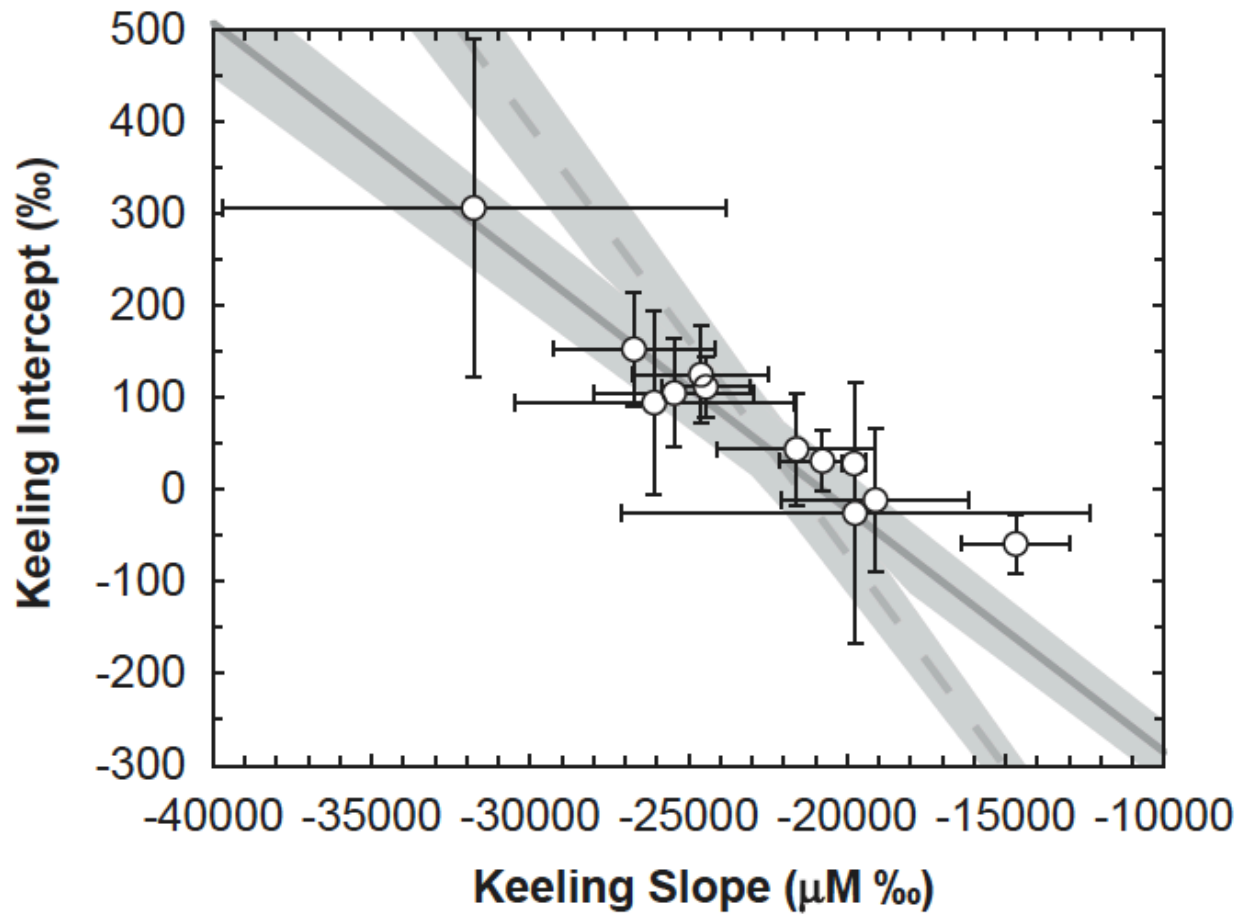
Time-series measurements of [DOC] and $\text{DOC } \Delta^{14}\text{C}$ at Station M



What drives the changes in [DOC] and DOD14C values
At Station M?







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.

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. There appears to be 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, but radiocarbon values can be modeled as two end member mixing. Deep sea values are consistent with an average residence time of 5000-6000 years. Several ocean mixing cycles!!!

