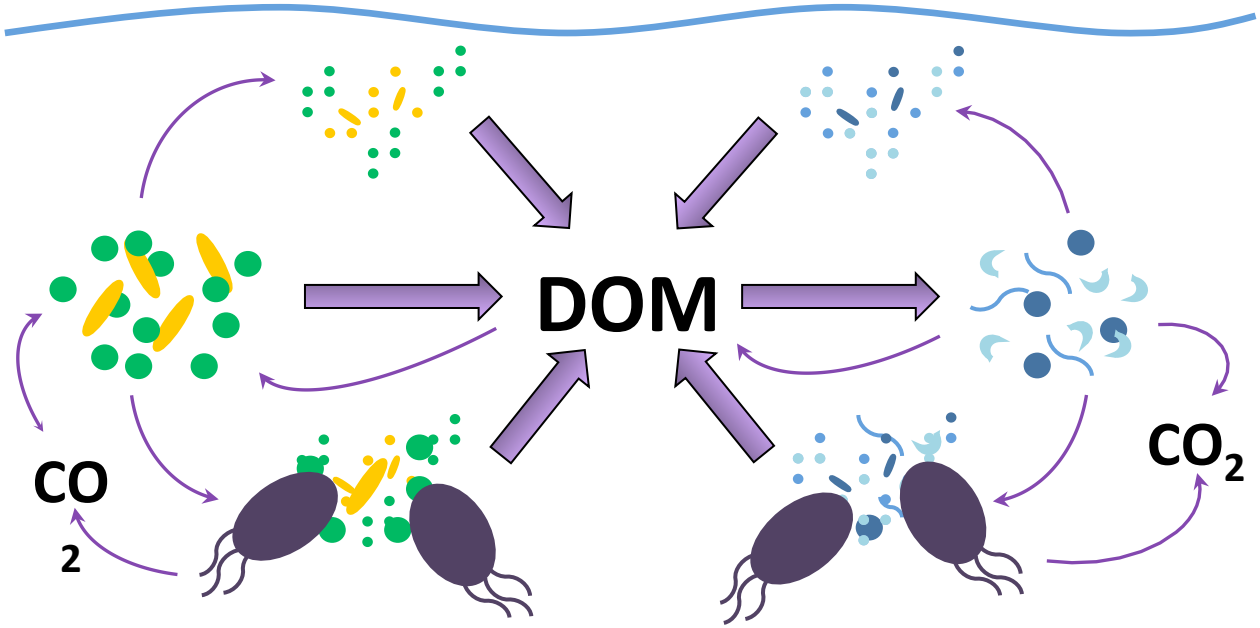
Dissolved Organic Matter (DOM) and the Microbial "loop"

"I presume that the numerous lower pelagic animals persist on the infusoria, which are known to abound in the open ocean: but on what, in the clear blue water, do these infusoria subsist?" - Charles Darwin (1845)



"Basic to the understanding of any ecosystem is knowledge of its food web, through which energy and materials flow. If microorganisms are major consumers in the sea, we need to know what kinds are the metabolically important ones and how they fit into the food web." - Lawrence Pomeroy (Bioscience, 1974)

Cycling and composition of marine Dissolved organic matter: A primer

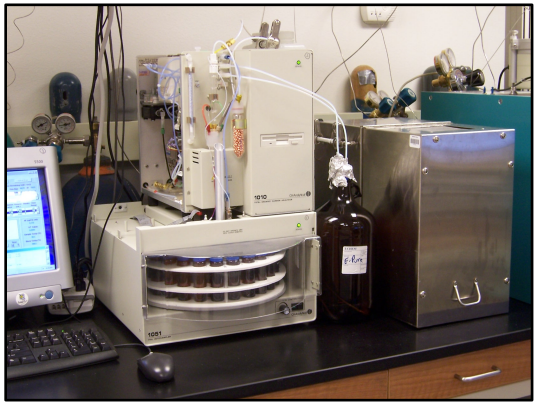
1) What is the global distribution of dissolved organic matter?

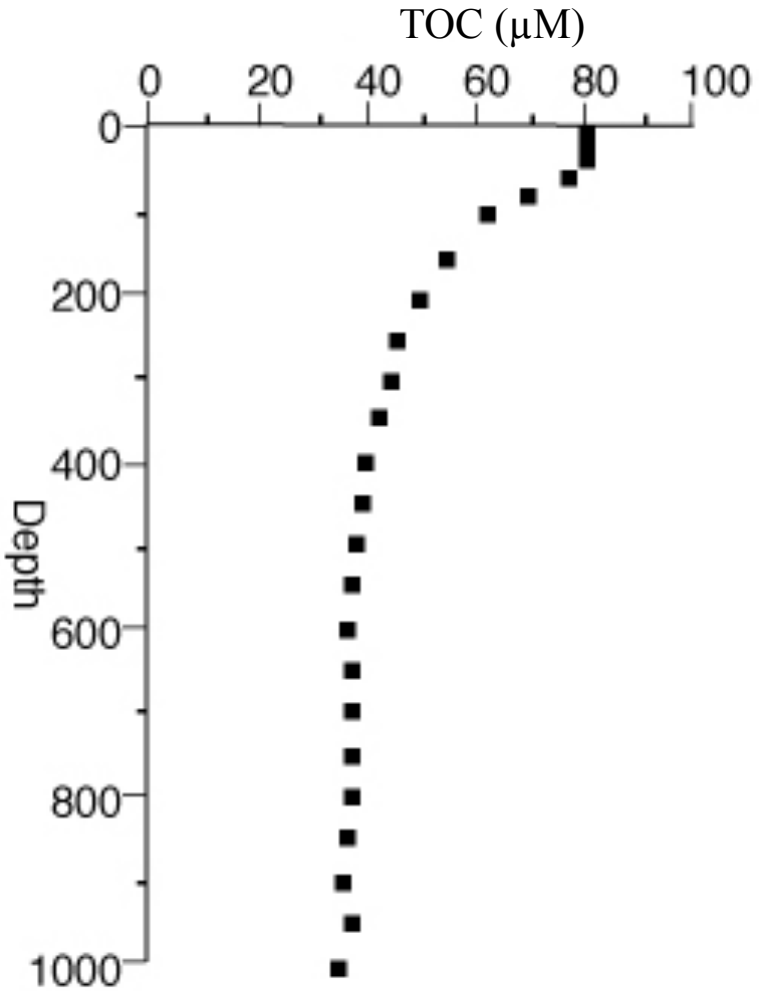
2) How do we approach an understanding of its cycling and reactivity?

3) What techniques are used to characterize DOM composition?

4) Can we link composition to source and putative sinks?

Typical 1D profile of dissolved organic carbon in the ocean





Often measured as TOC

Surface values typically 60-80 μM

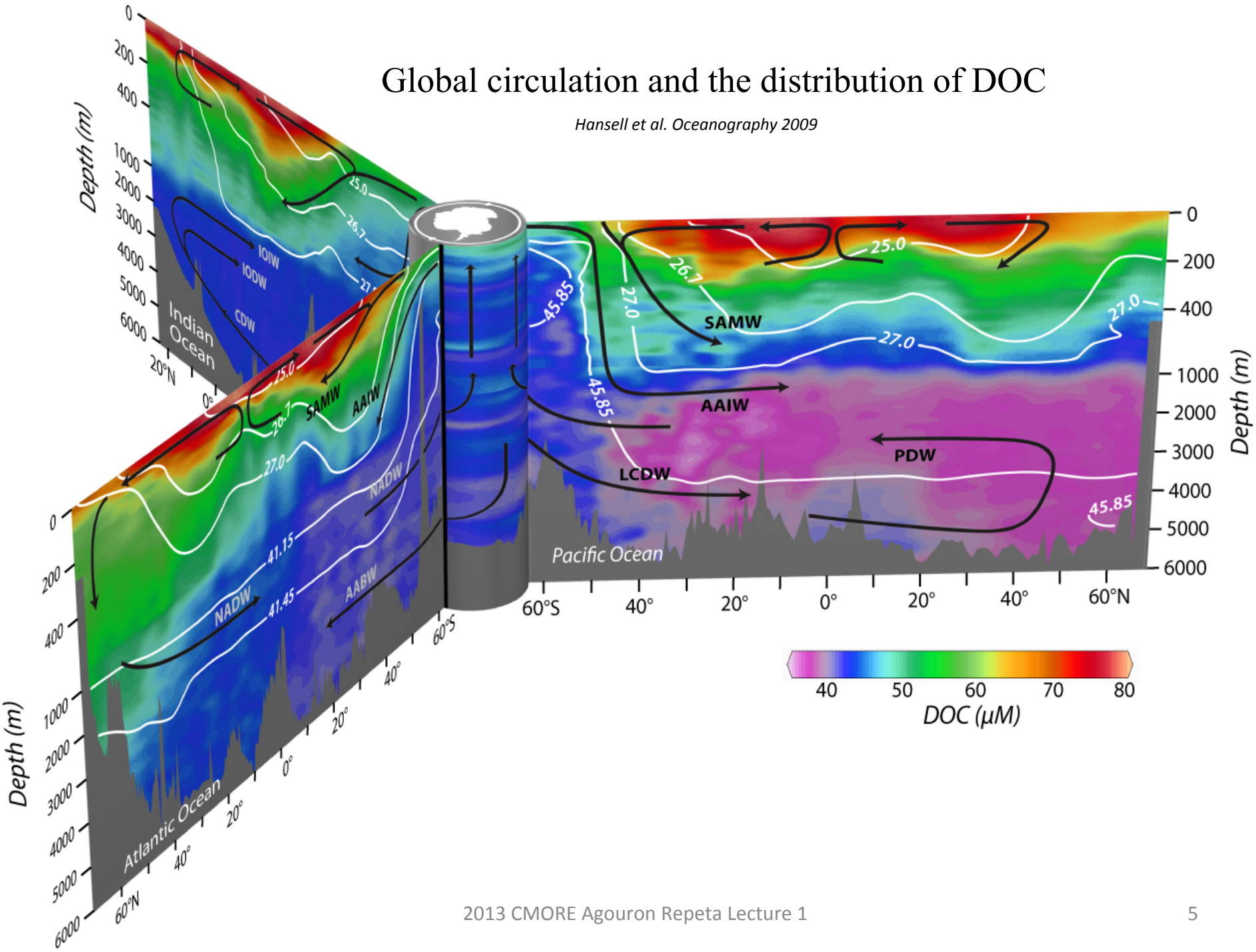
Deep water values @ 40 ±1 μM (implies some unknown feedback/ control of DOC values)

Global inventory about 660 GT C

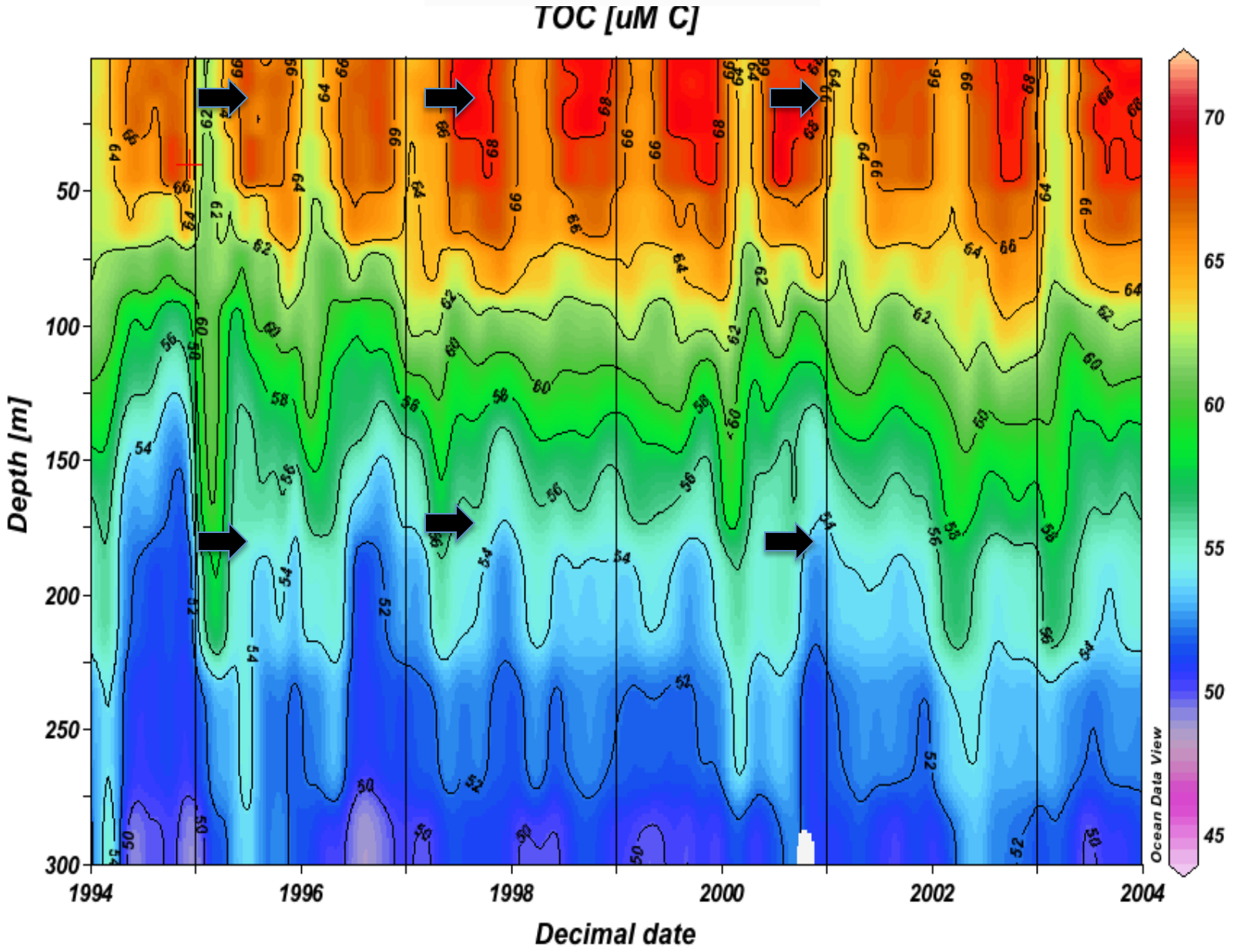
Data from Peltzer and Hayward (1996) DSR

Global circulation and the distribution of DOC

Hansell et al. Oceanography 2009



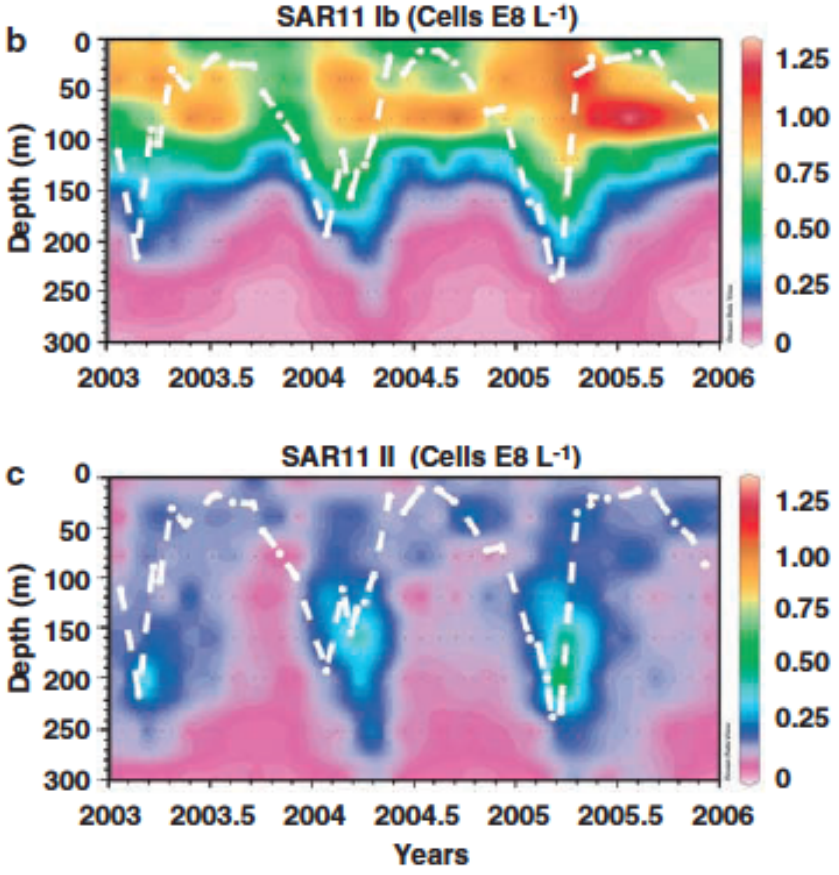
Time series analysis of DOC (µM C) at Bermuda

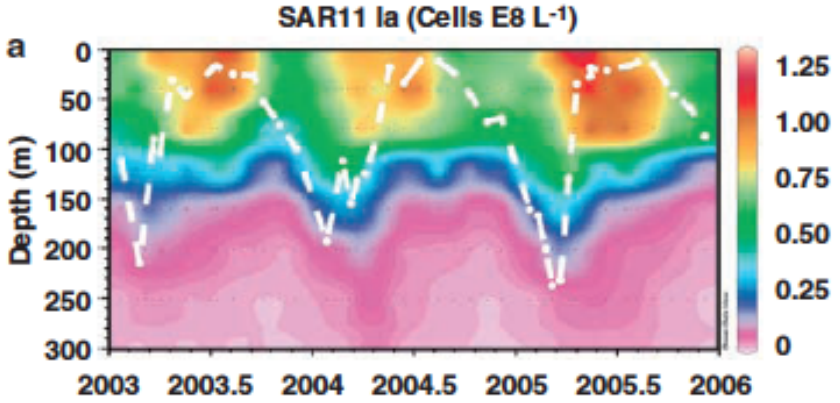


Data from Dennis Hansell and Craig Carlson

Seasonal dynamics of SAR11 populations in the euphotic and mesopelagic zones of the northwestern Sargasso Sea

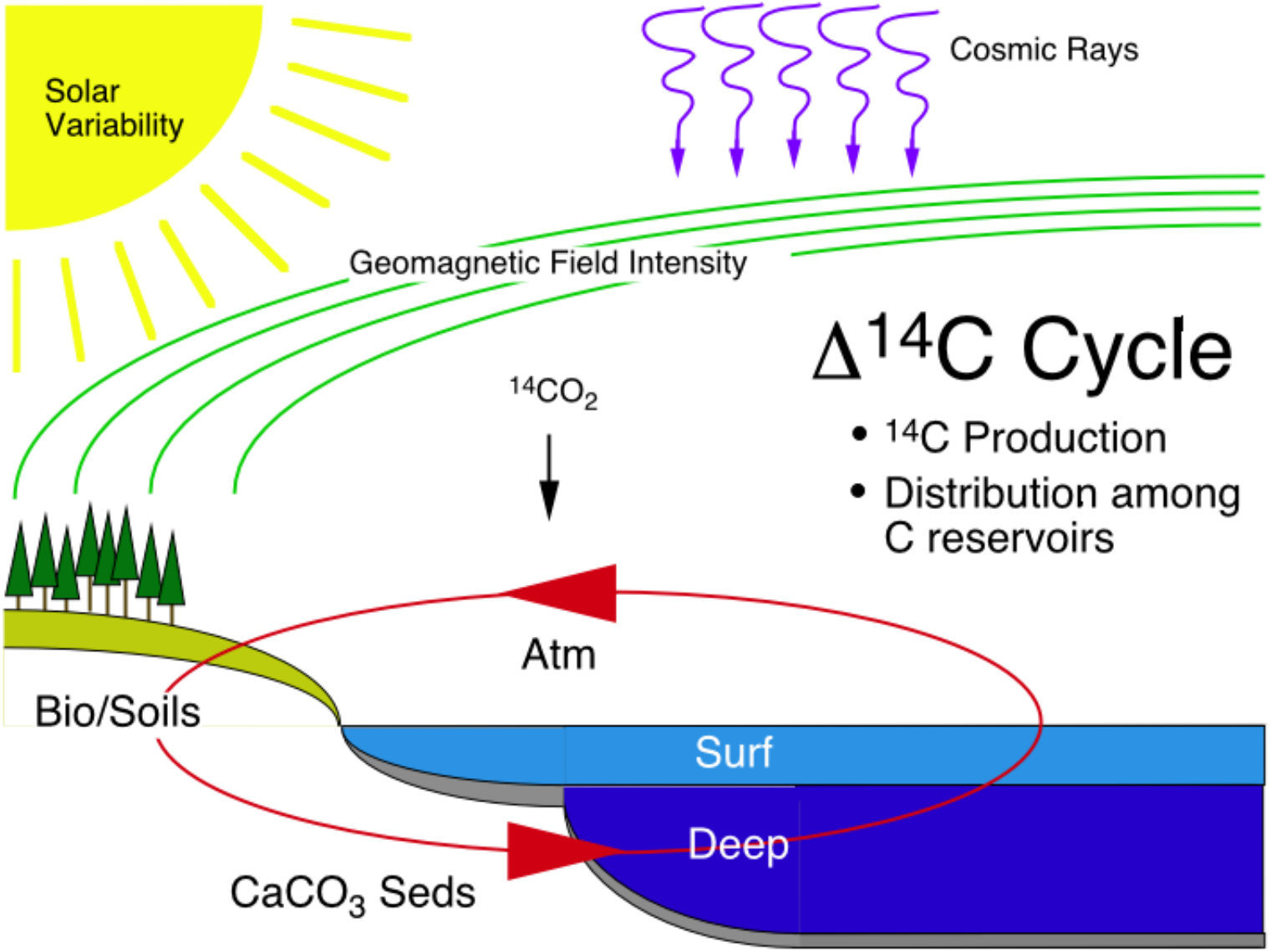
Craig A Carlson[1,5], Robert Morris[1,2,5], Rachel Parsons[3,5], Alexander H Treusch[4,5], Stephen J Giovannoni[4] and Kevin Vergin[4]



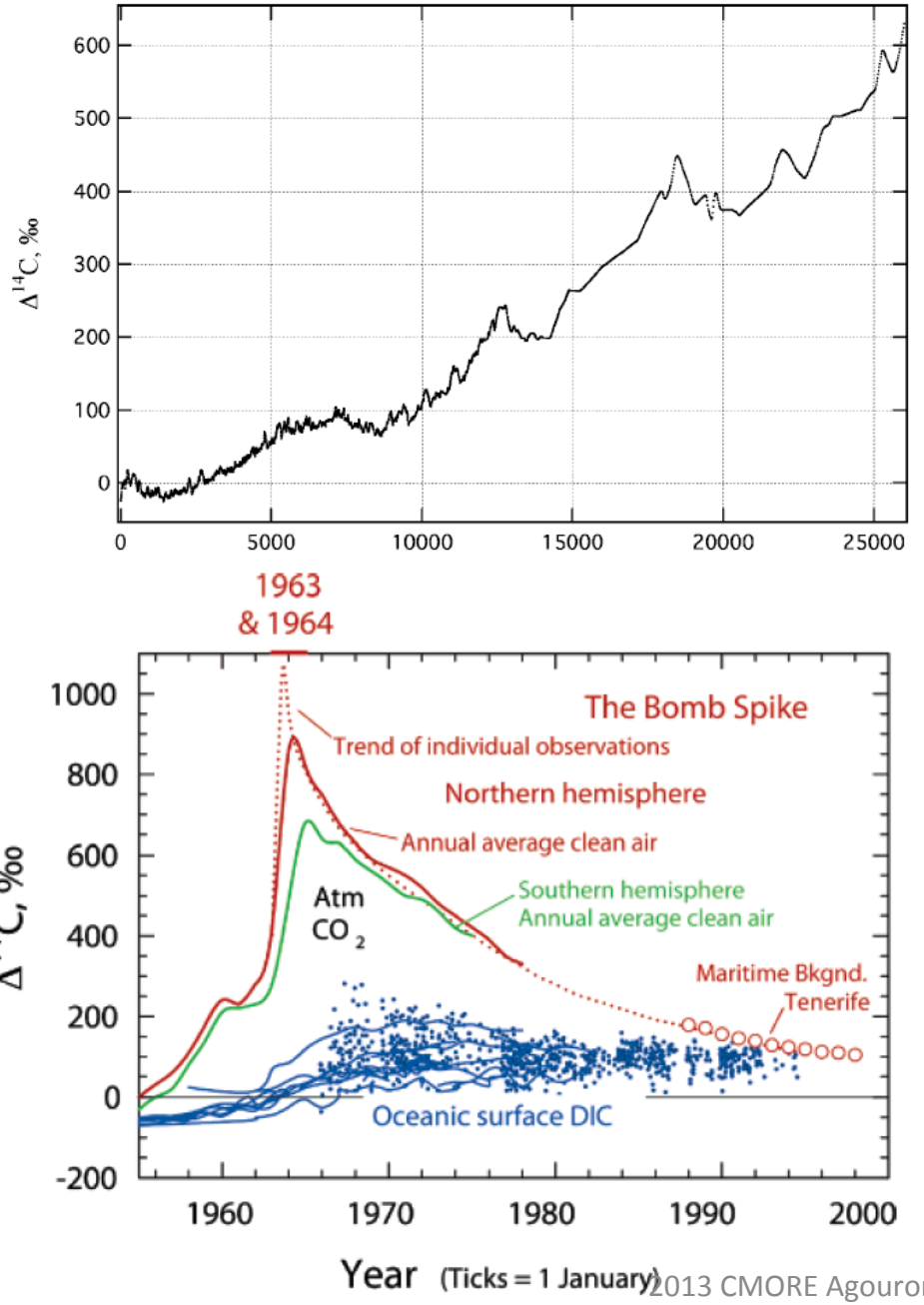


The ISME Journal (2009) 3, 283–295

How do we measure carbon fluxes in DOC ?



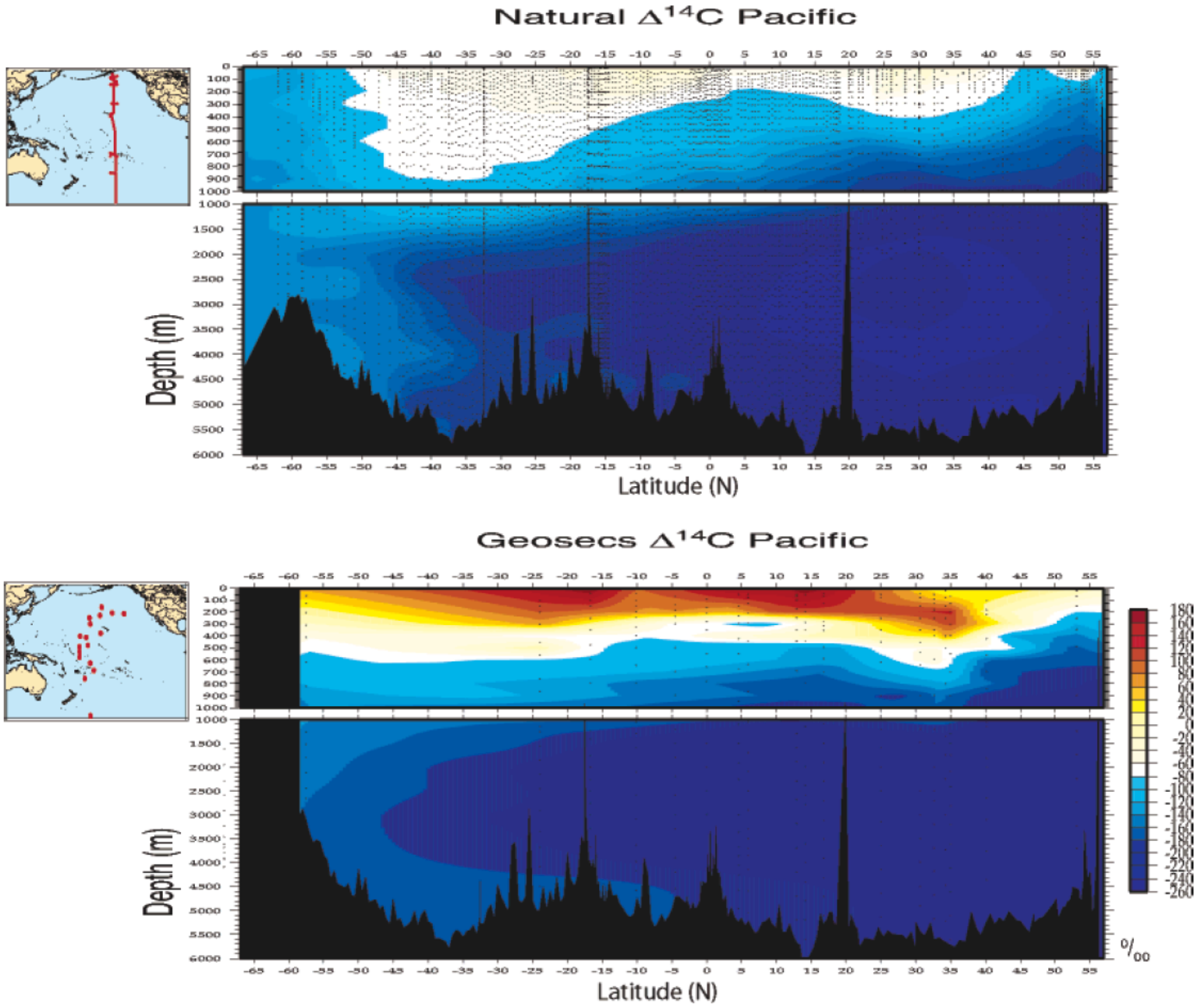
McNichol and Aluwihare, Chem Rev. 2007



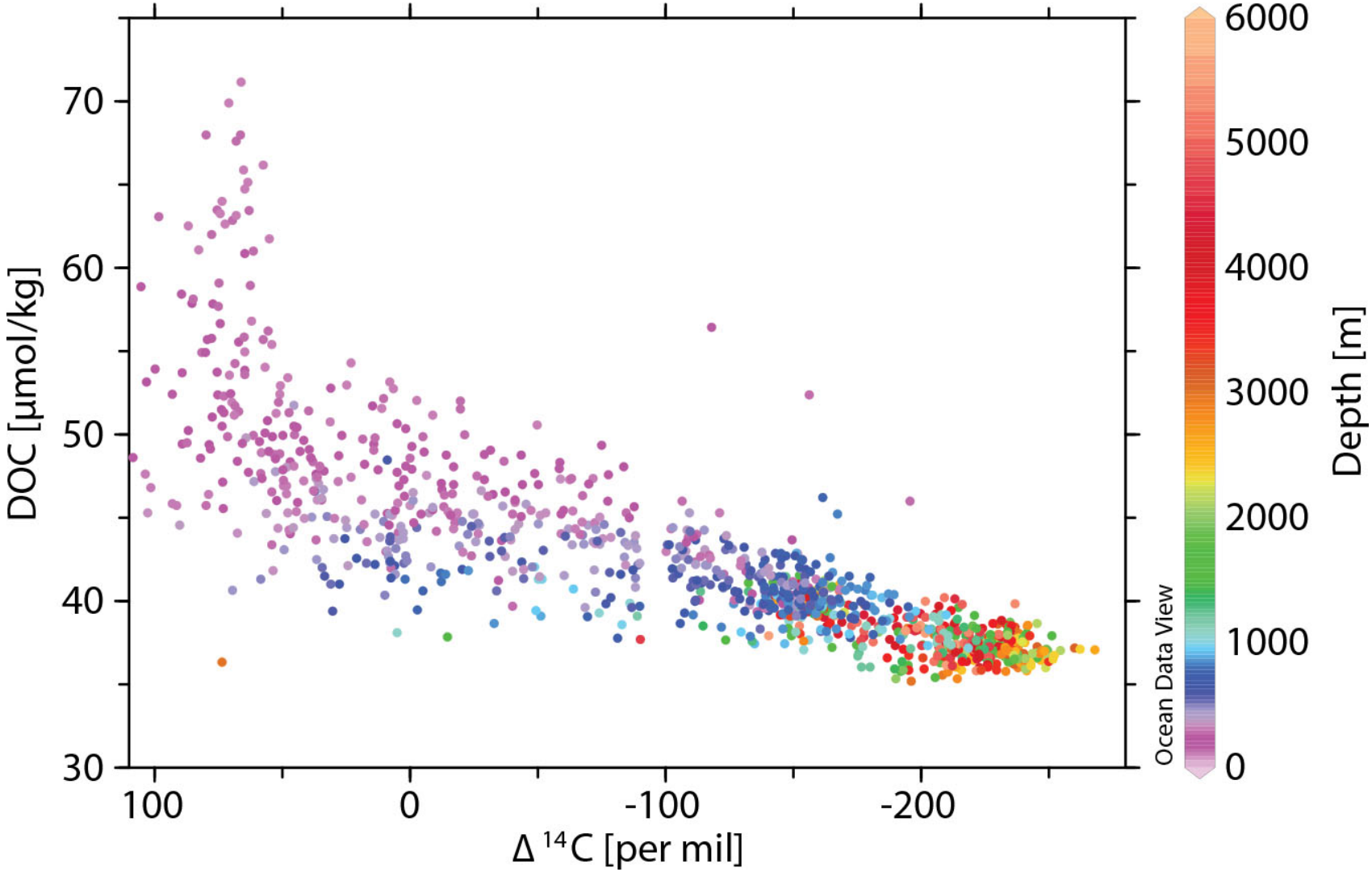
Natural radiocarbon production has changed over time, and is influenced by changes in the flux of cosmic rays, solar activity, and the earths magnetosphere.

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.



McNichol and Aluwihare 2007



(Inorganic carbon radicoarbon value))

Hansell et al. Oceanography 2009

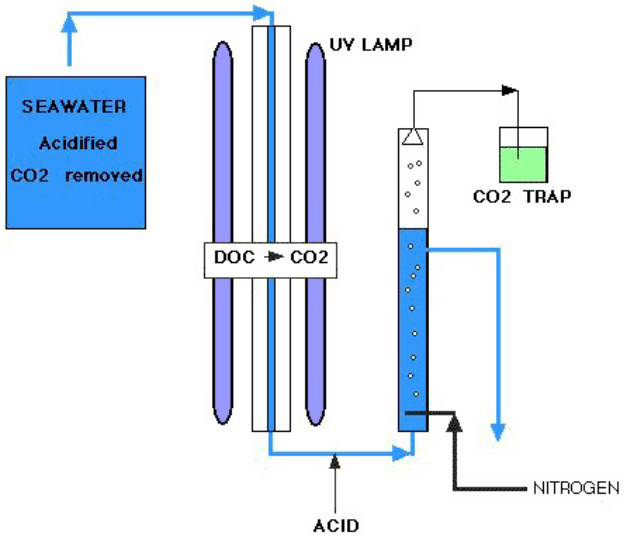
DOC cycling via $DO^{14}C$

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 time[1-3]. 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 radiation[4] (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 *p*H 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 15 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

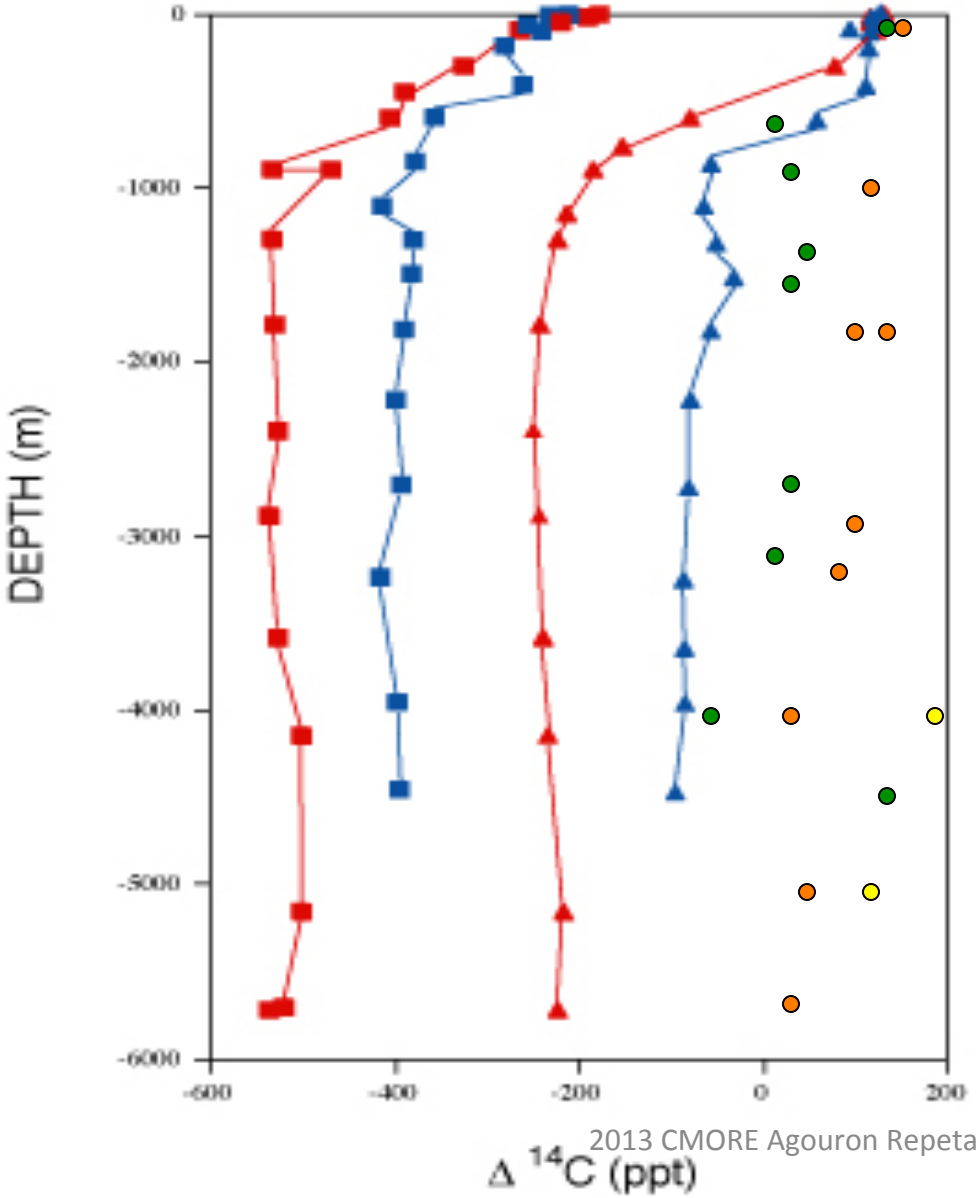


Depth	Δ14C(‰)	Age
1880m	-351 ‰	-3470±330 ybp
1920m	-341 ‰	-3350±300 ybp

Williams, Oeschger, and Kinney; Nature v224 (1969)

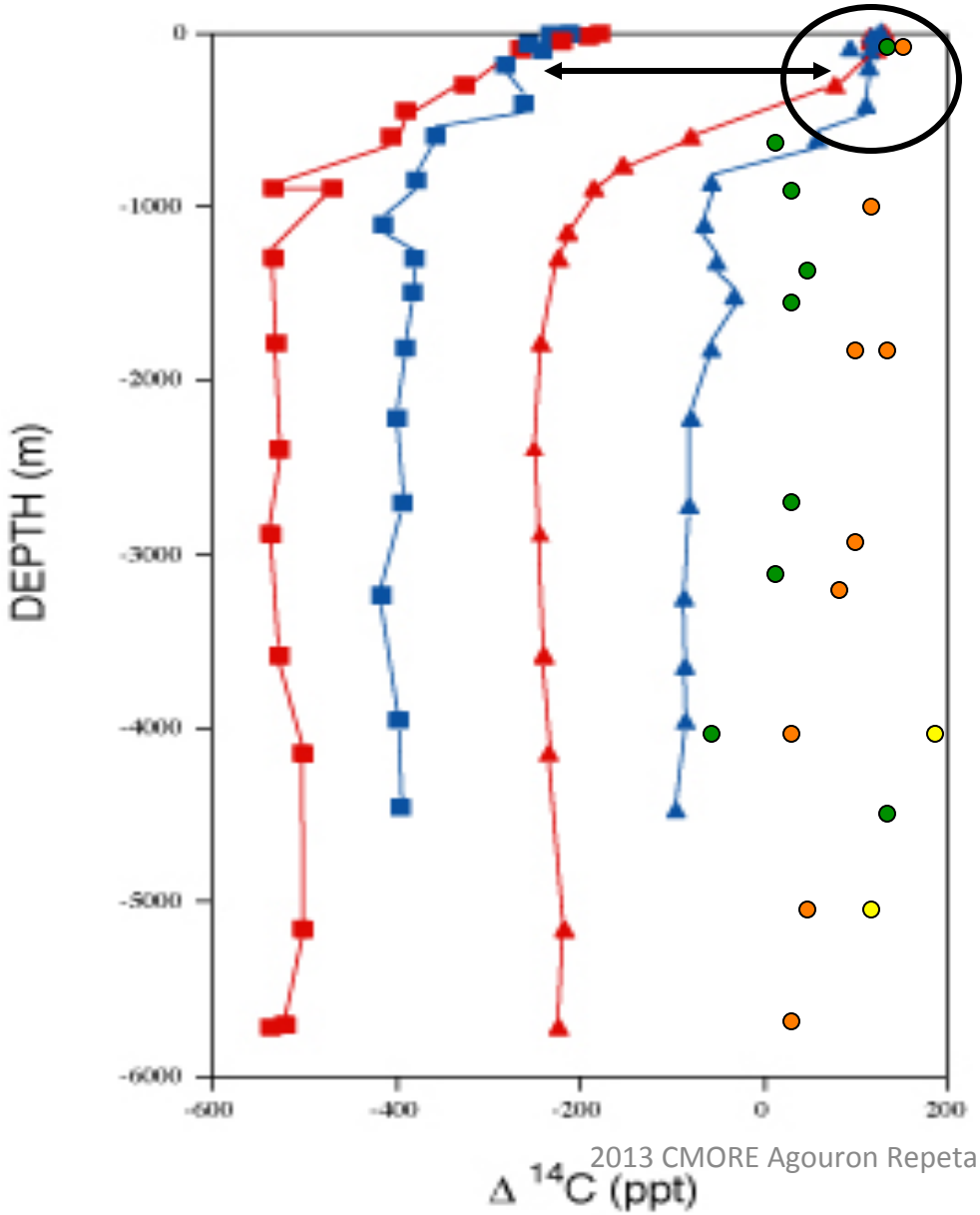
Radiocarbon in the Atlantic and Pacific Oceans

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



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



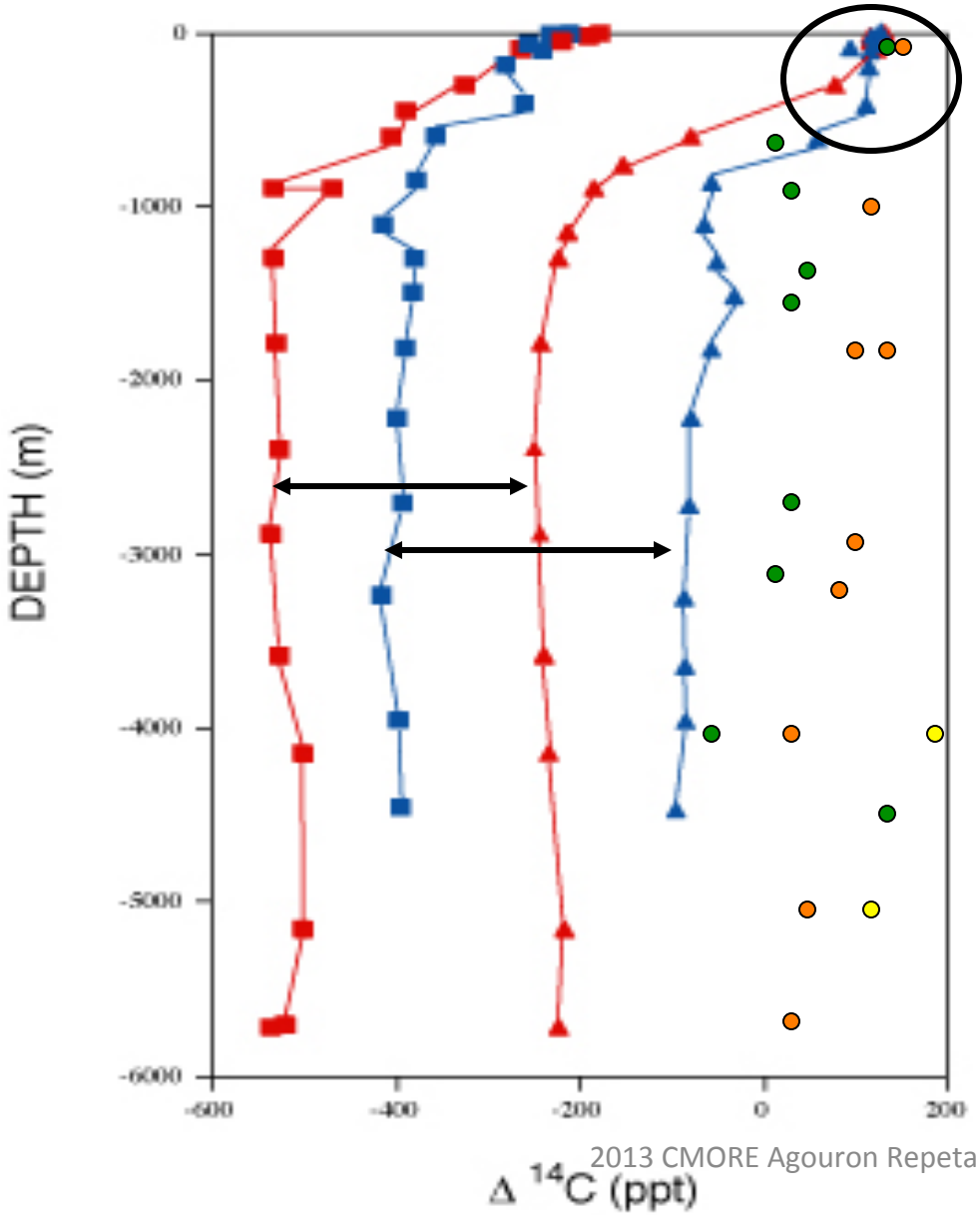
DIC ^{14}C in surface waters of the Atlantic and Pacific have similar isotopic values.

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

DIC ➡ POC ➡ 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



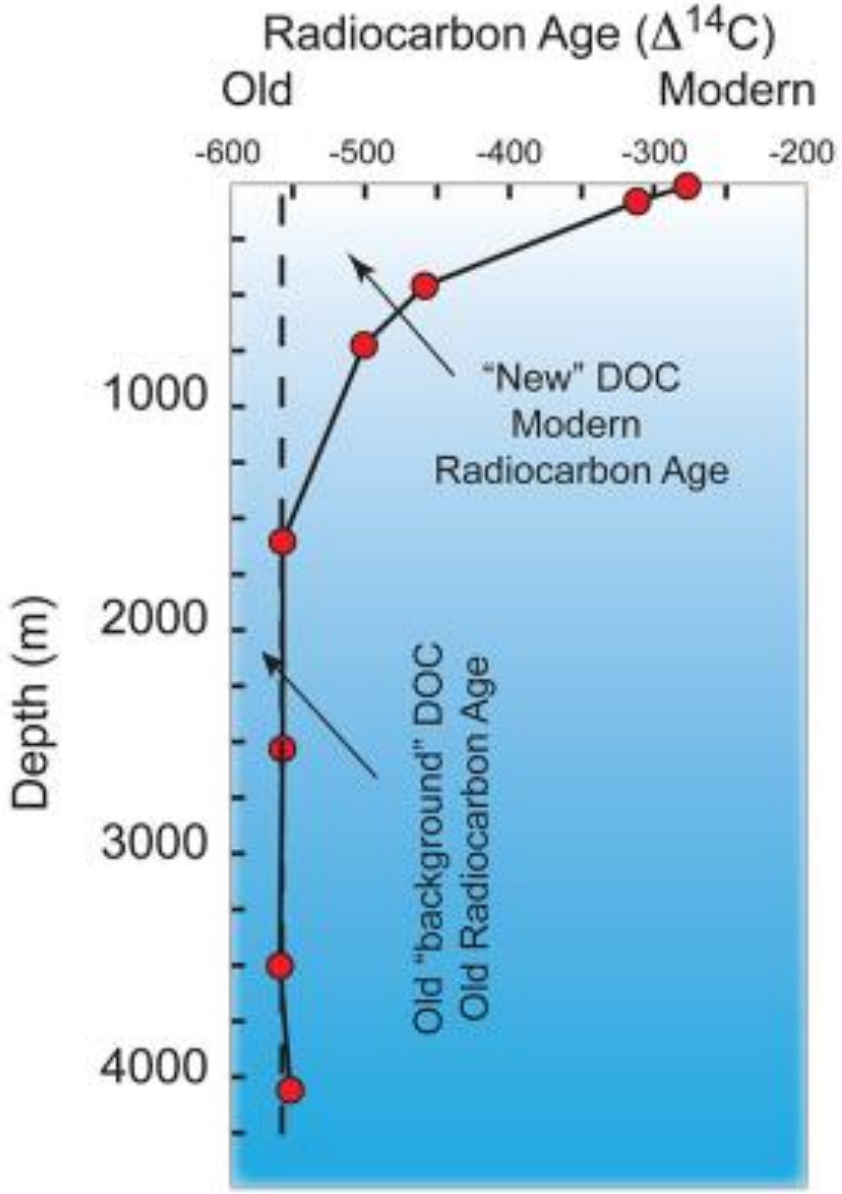
DIC ^{14}C in surface waters of the Atlantic and Pacific have similar isotopic values.

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

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

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

Radiocarbon based models of DOC cycling in the water column



DIC ➡ POC ➡ DOC

$$[DOC]_z(C14)_z = [Deep](C14)_D + [Z\text{-}Deep](C14)_{DIC}$$

Atlantic surface water

$^{14}C_{calc}$ = -120 ‰

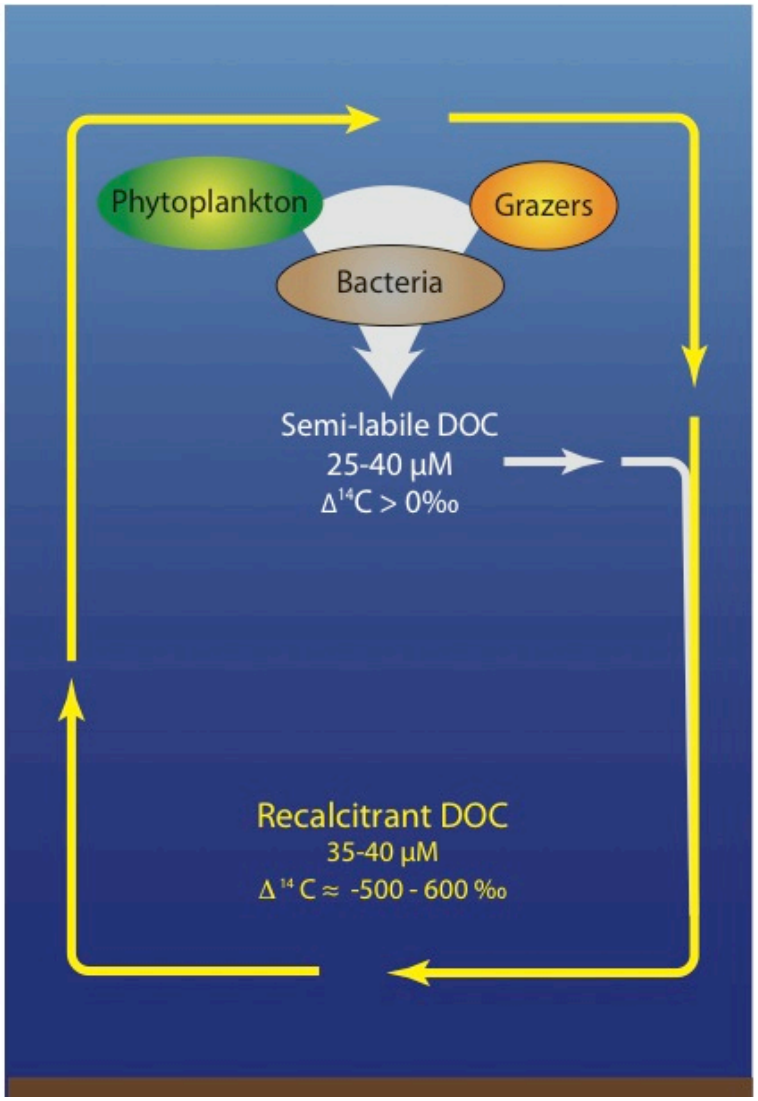
$^{14}C_{obs}$ = -127 ‰

Pacific surface water

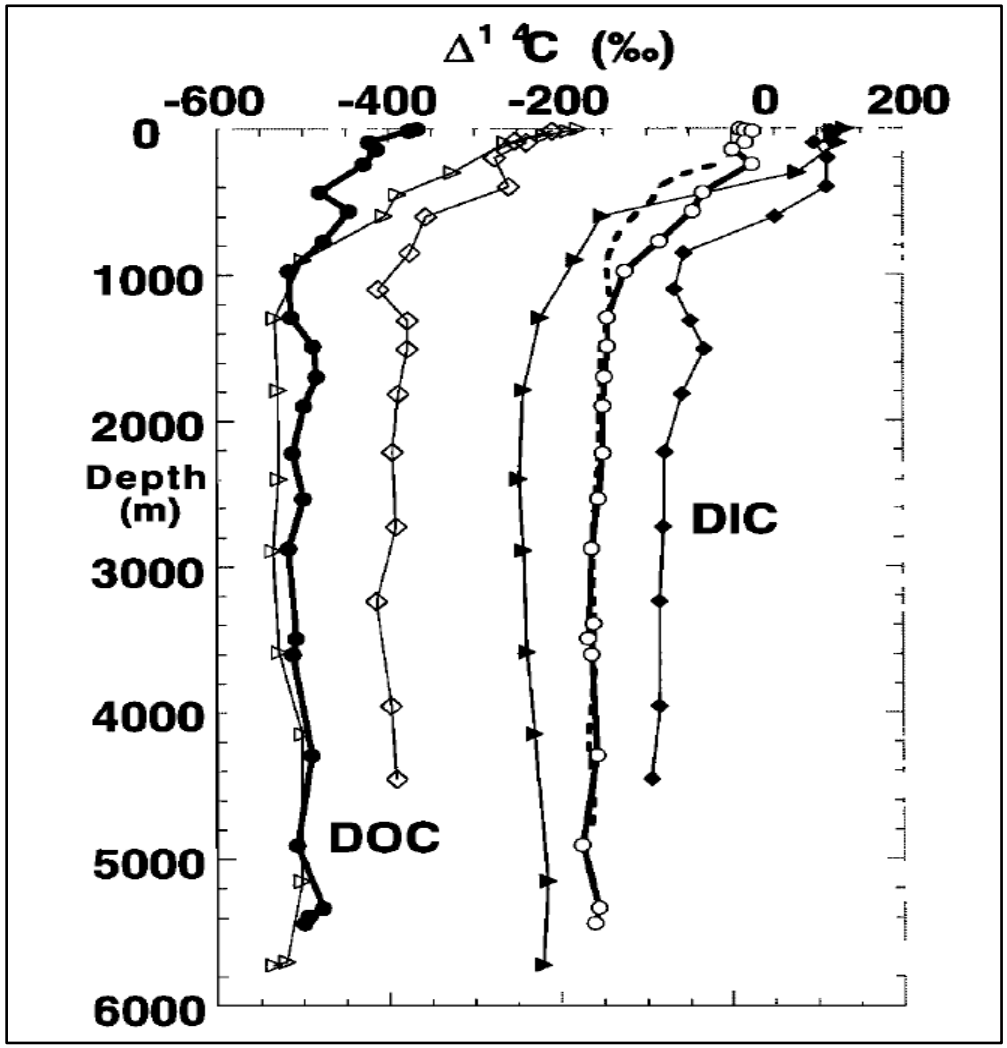
$^{14}C_{calc}$ = -147 ‰

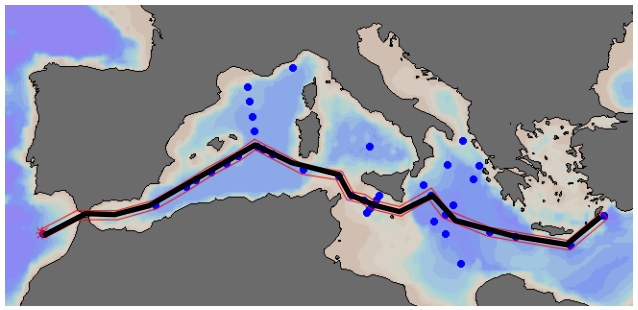
$^{14}C_{obs}$ = -148 ‰

Under this perspective, DOM is produced and rendered recalcitrant by marine microbes. Combined with the two component model of radiocarbon and deep sea DOC, it suggests no or at best very slow removal of DOM in the deep sea

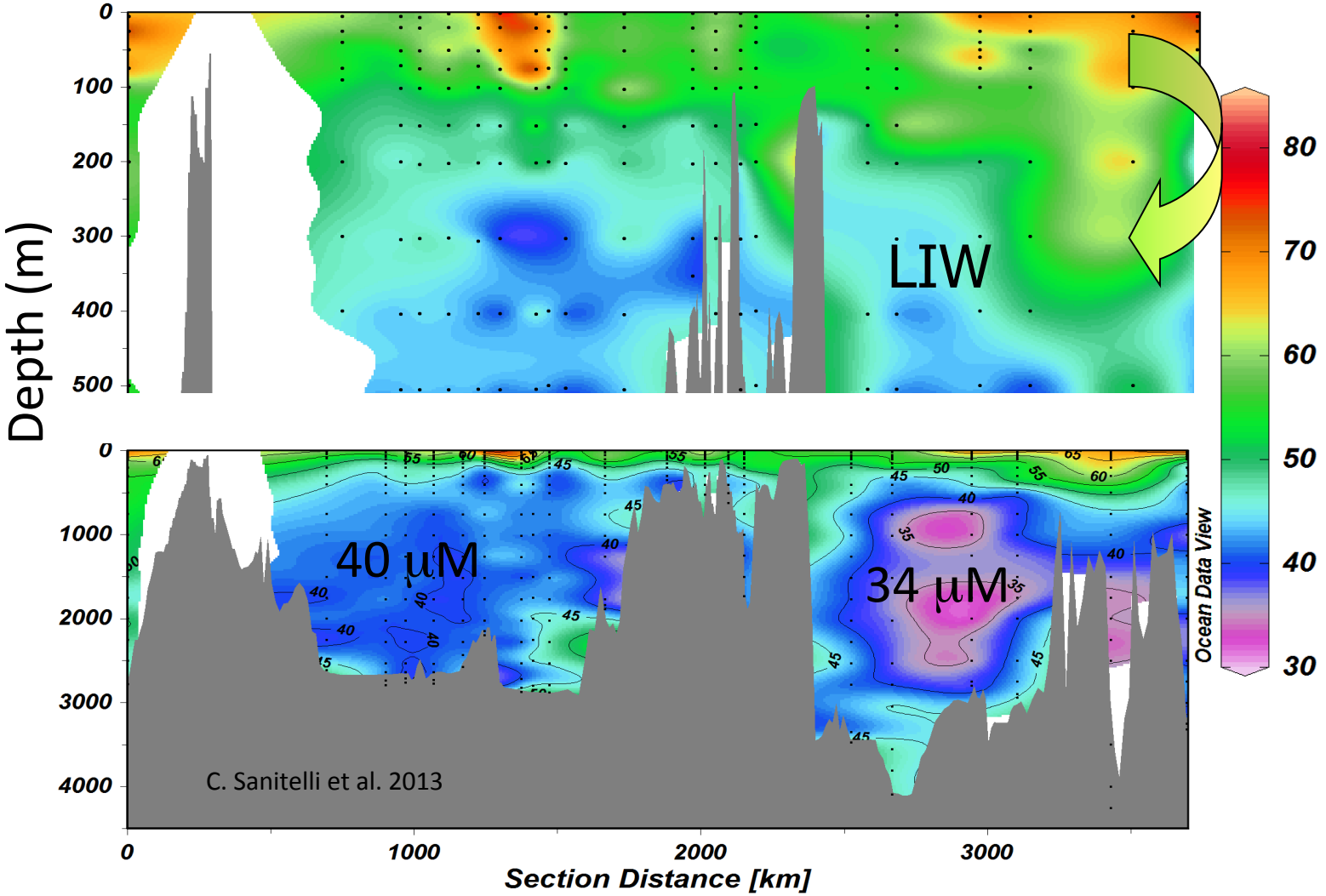


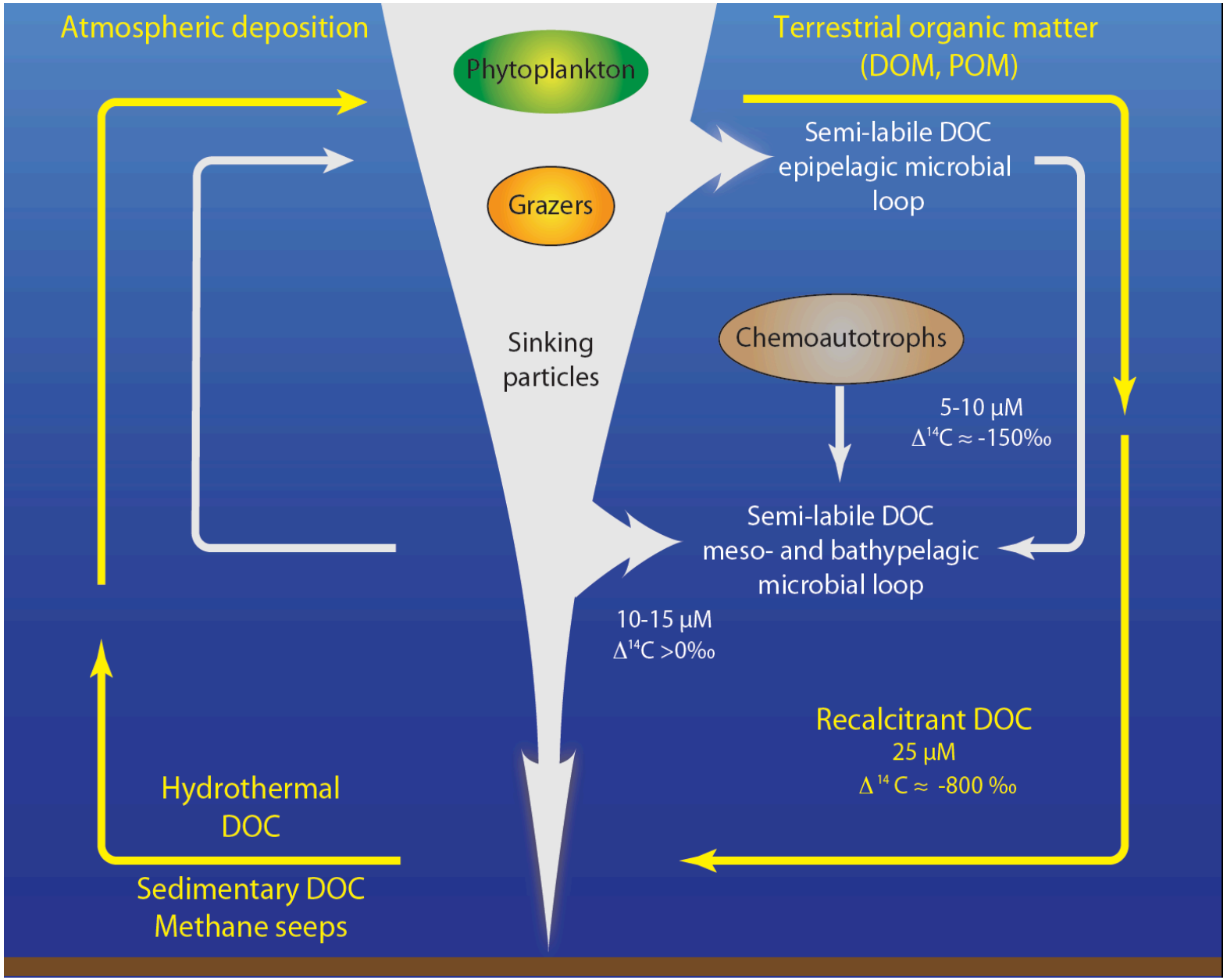
Southern Ocean DOC-14 data suggests the two component model cannot be correct.





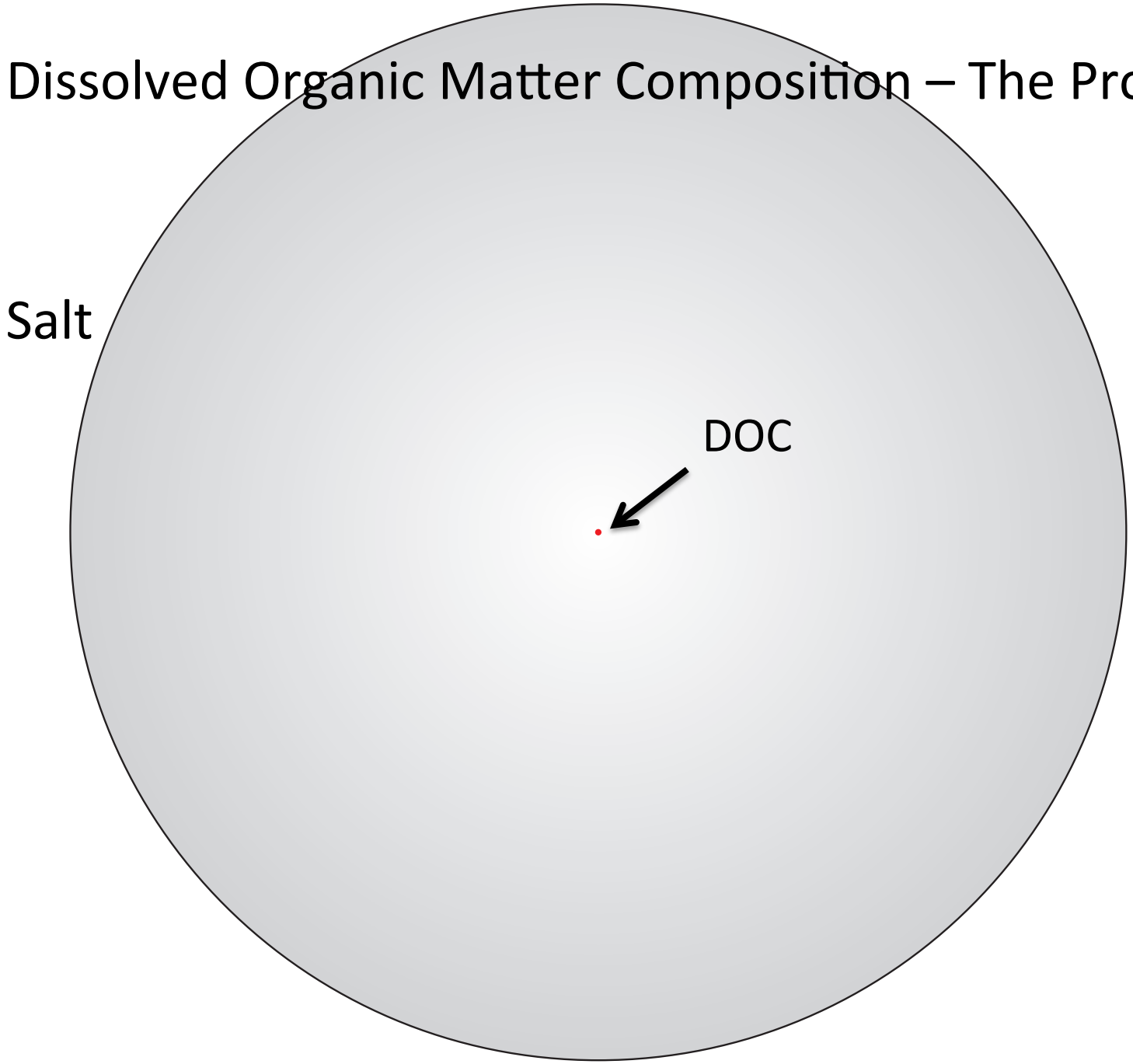
Very rapid degradation of DOC in the Mediterranean Sea. If DOC is refractory, why does this happen?



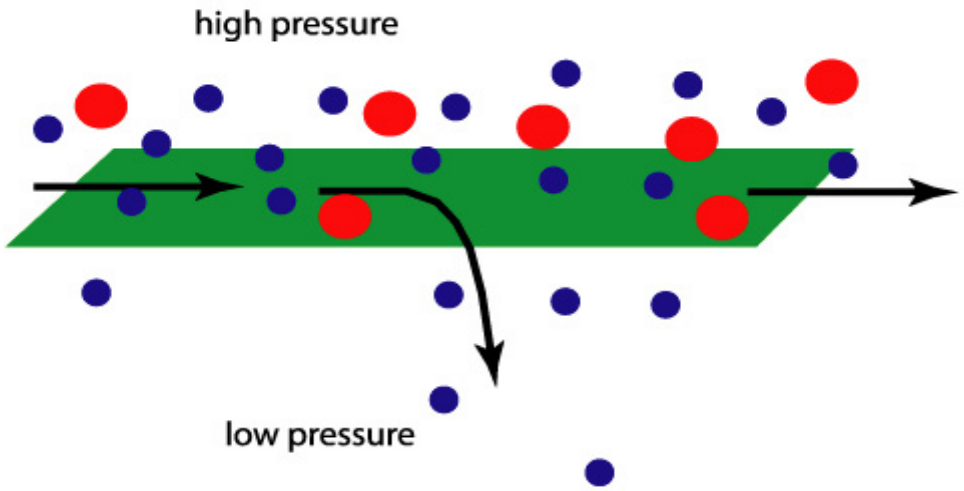

Atmospheric deposition
Phytoplankton
Terrestrial organic matter
(DOM, POM)
Semi-labile DOC
epipelagic microbial
loop
Grazers
Sinking
particles
Chemoautotrophs
5-10 µM
Δ14C ≈ -150‰
Semi-labile DOC
meso- and bathypelagic
microbial loop
10-15 µM
Δ14C >0‰
Recalcitrant DOC
25 µM
Δ 14 C ≈ -800 ‰
Hydrothermal
DOC
Sedimentary DOC
Methane seeps

The cycling and composition of marine Dissolved organic matter: a primer

Dissolved Organic Matter Composition – The Problem



Cross or tangential flow filtration, Ultra- or nanofiltration



Separation based on size

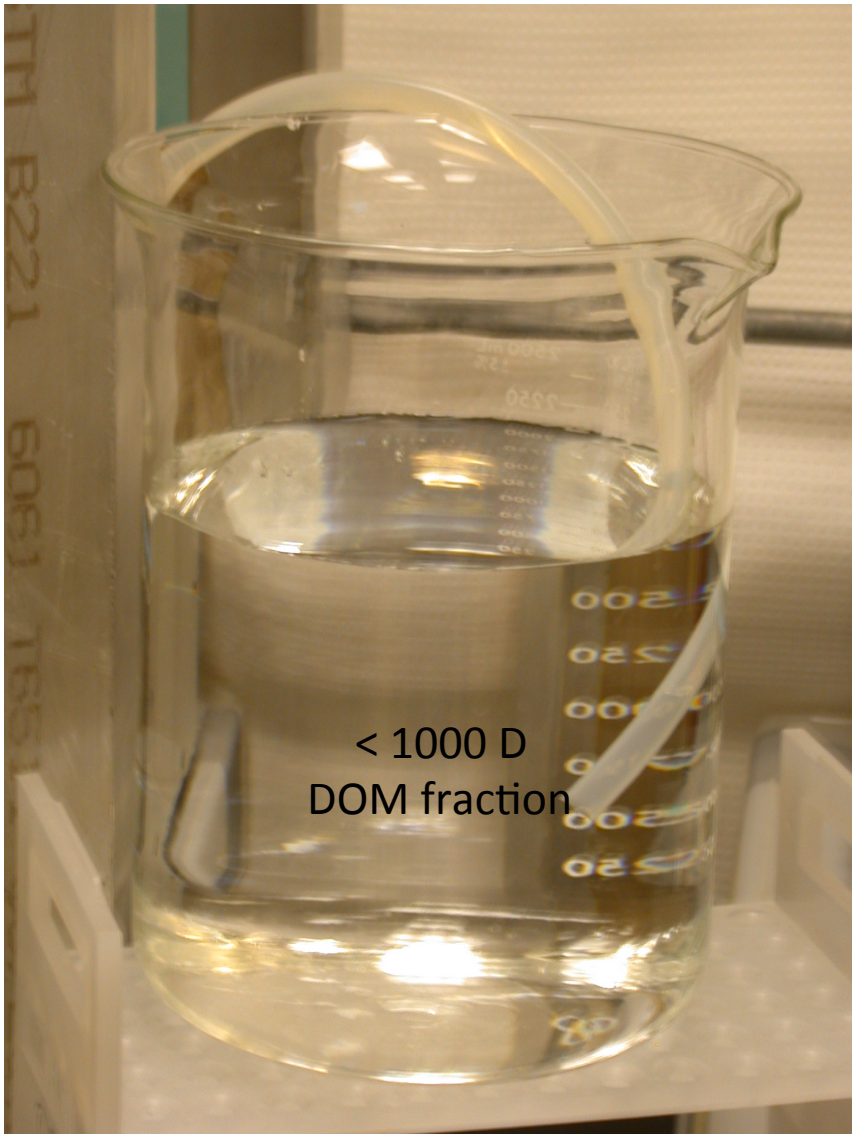
1 nm pore @ 1 kD

Selects for larger size (**H**igh **M**olecular **W**eight) fraction

About 30-35% TOC (now up to 60% using electrically assisted UF)

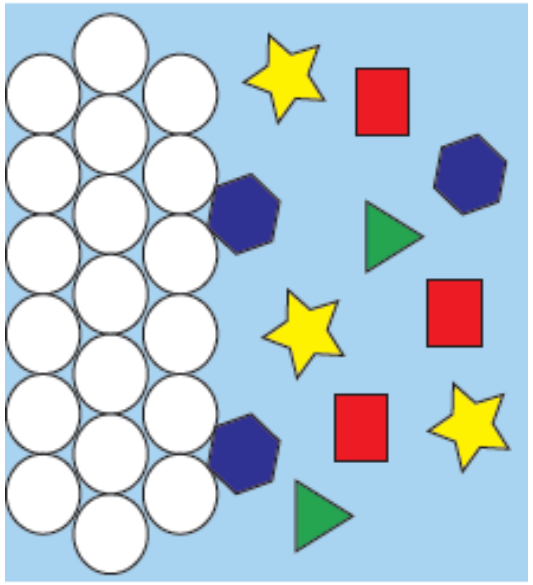
Membrane effects what is collected

Ultrafiltration of high molecular weight DOM (HMWDOM)

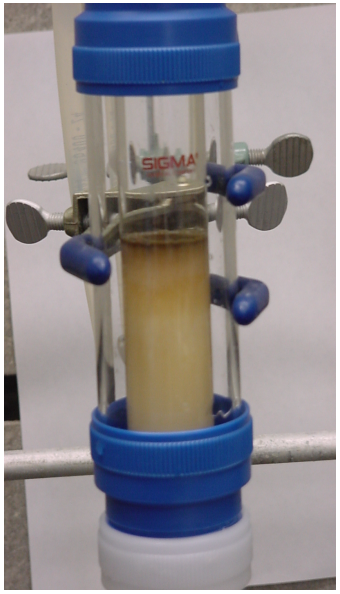


Isolation of DOM by adsorption onto hydrophobic resins

Selective chemical Adsorption

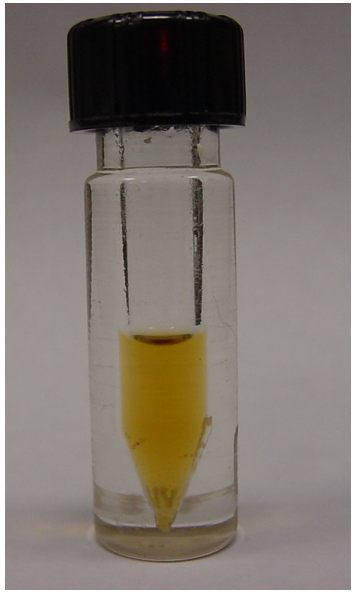


Seawater
(filtered; pH = 2)



Methanol
or
Ammonium hydroxide
wash

10-20% of DOC



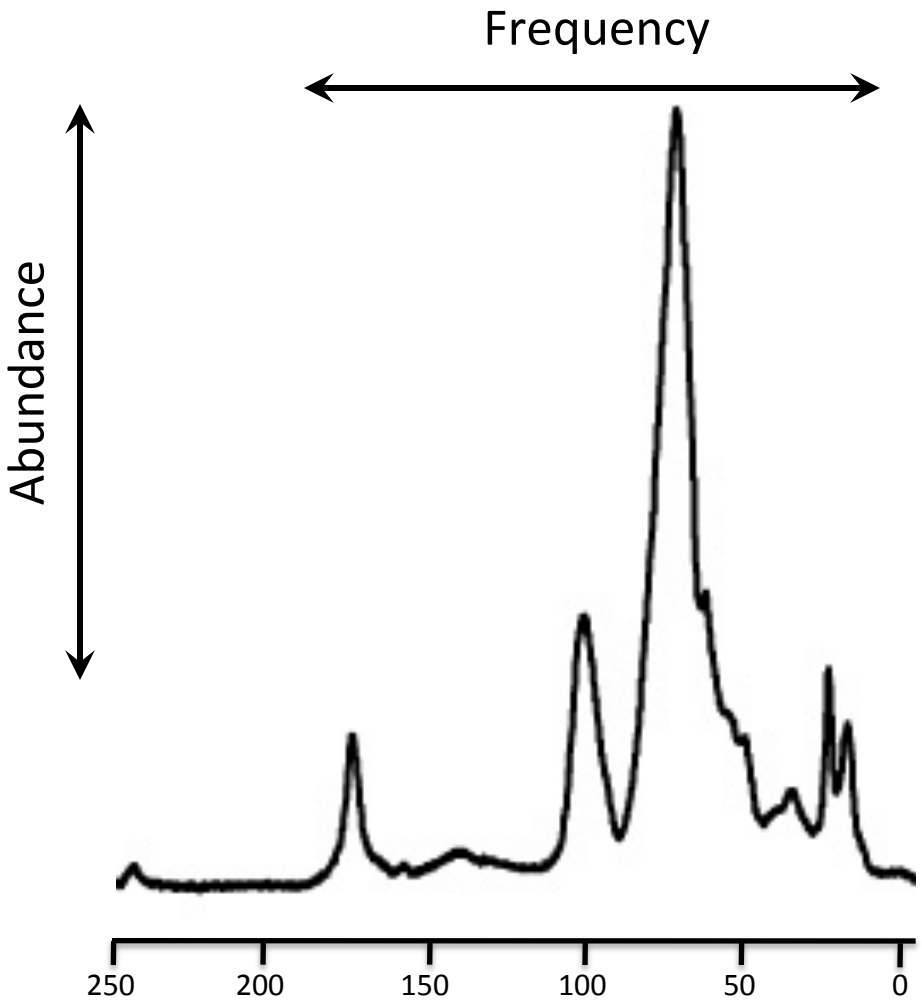
Nuclear Magnetic Resonance Spectroscopy (NMR)

Can be tuned to different Nuclei of interest (C,N,P…).

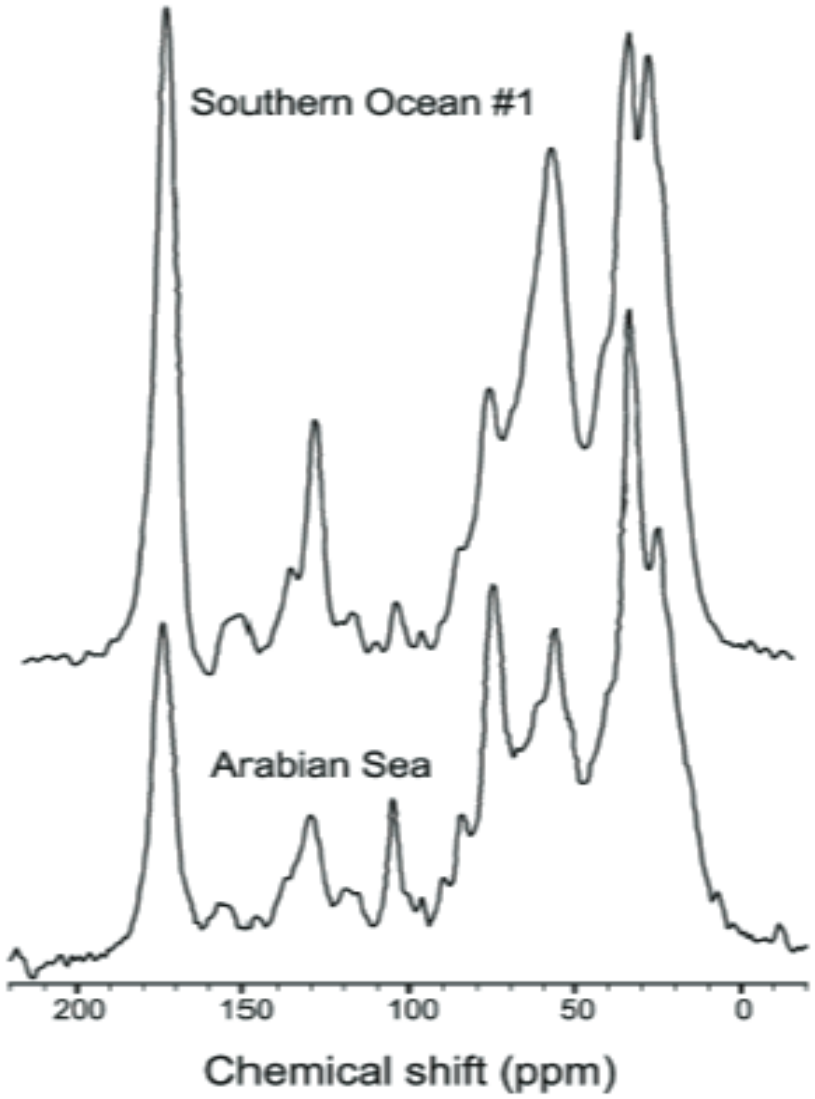
Gives information on functional groups which, combined with a knowledge of biochemicals can be used to deduce composition and origin.

Internally quantitative.

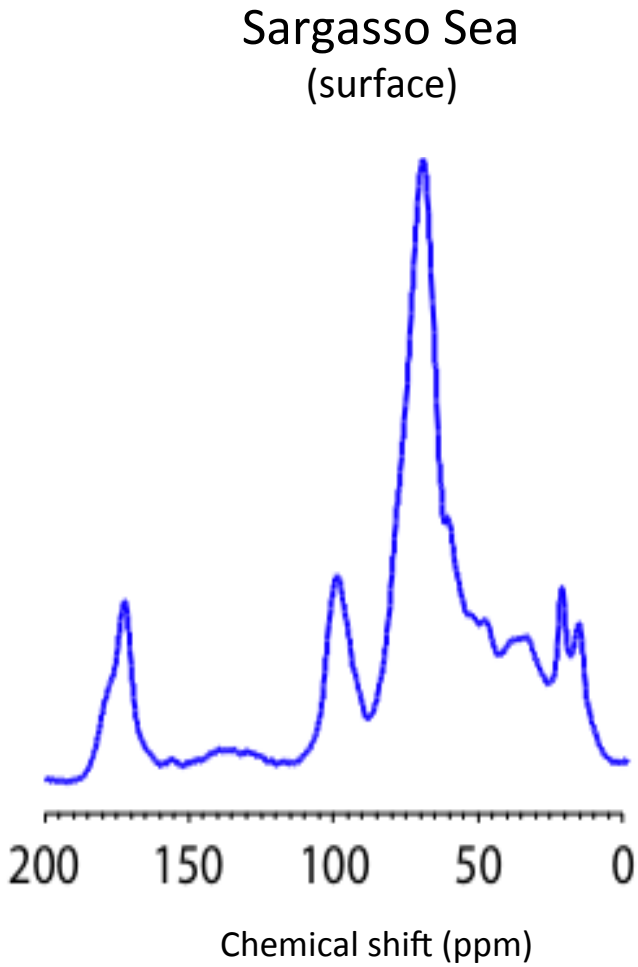
^{13}C Nuclear Magnetic Resonance Spectrum of high molecular weight dissolved organic matter (C/N = 15)



^{13}CNMR of plankton tows



^{13}CNMR of HMWDOM

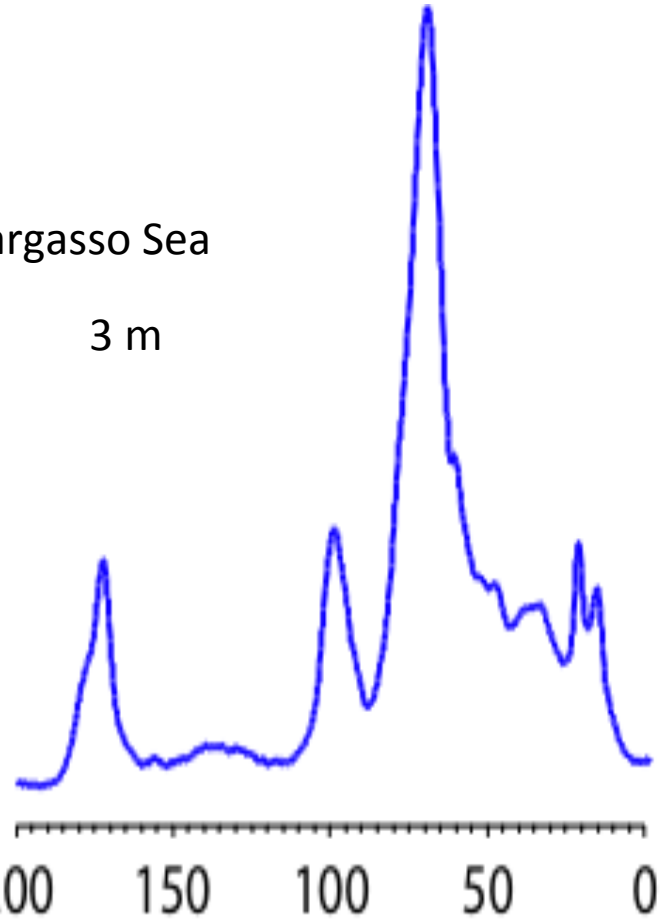


Hedges et al GCA 2001

^{13}CNMR spectra of HMWDOM

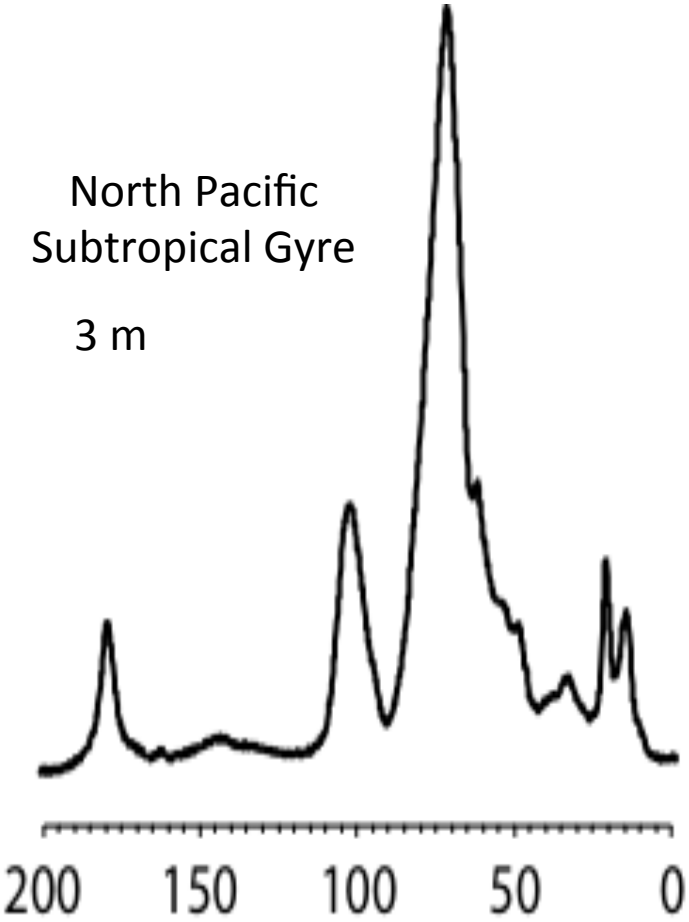
Sargasso Sea

3 m

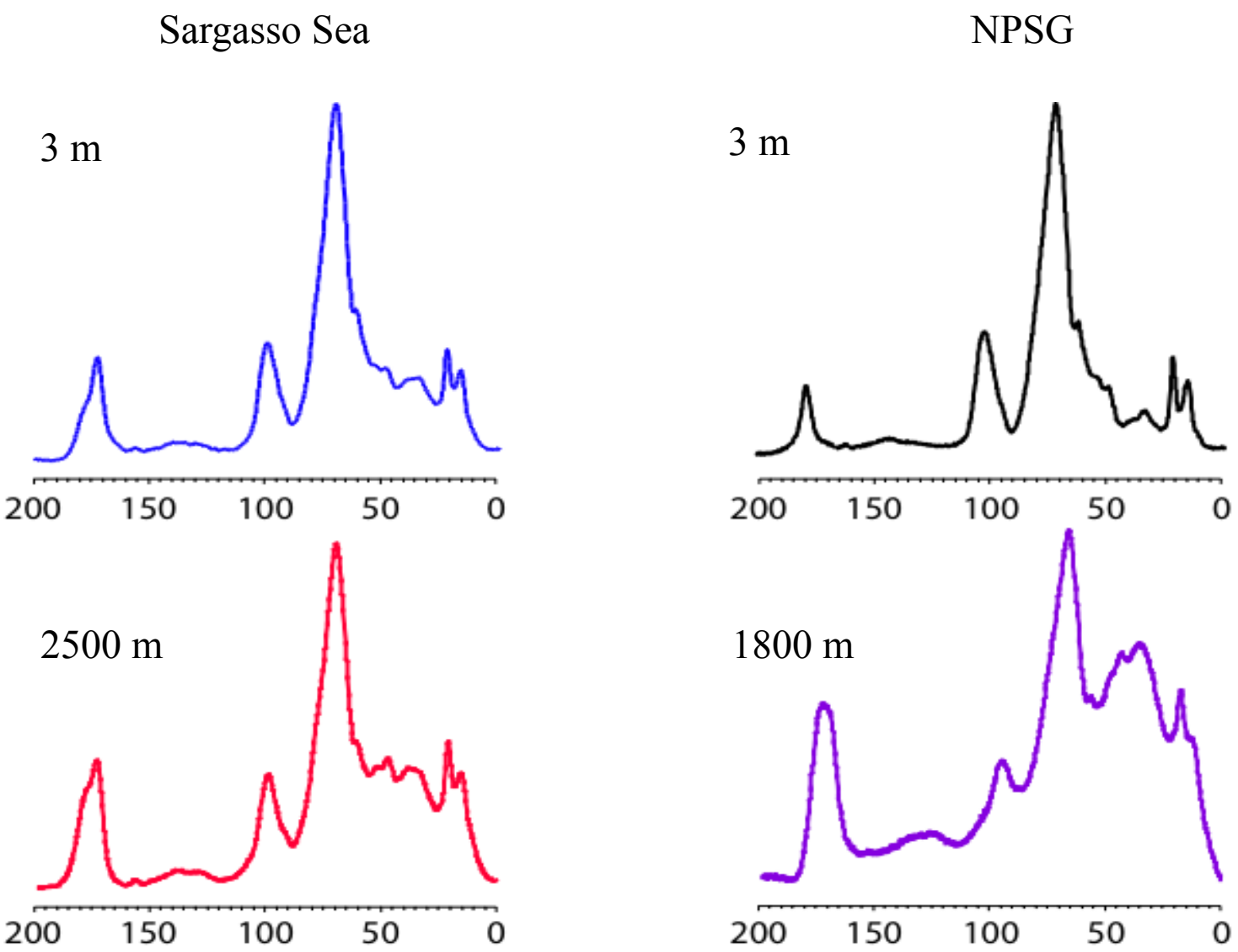


North Pacific
Subtropical Gyre

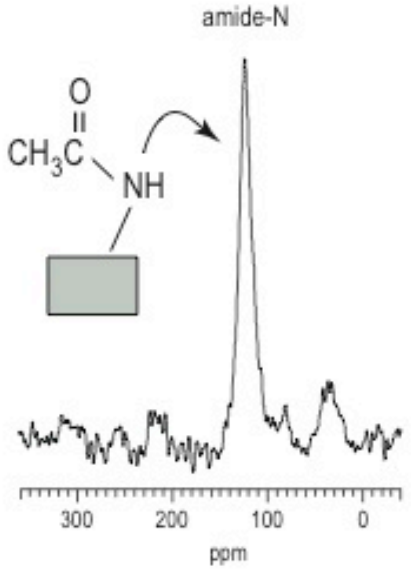
3 m

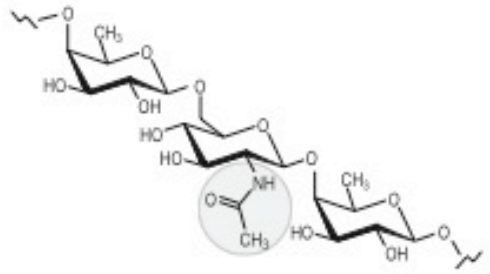


HMWDOM in the deep sea

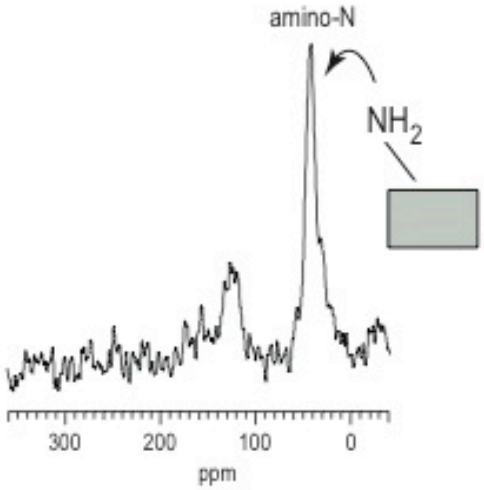


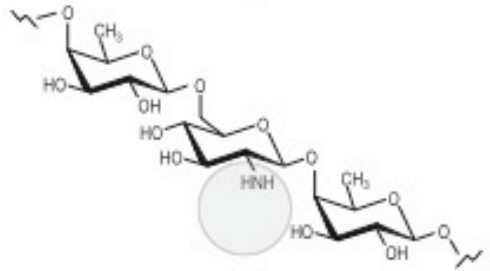
^{15}N-NMR of DOM
shows most N is in aminopolysaccharides





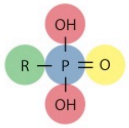
mild acid hydrolysis



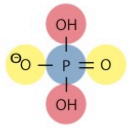


Composition of HMWDOP

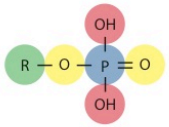
Organic phosphorus nomenclature



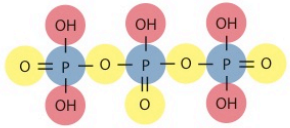
phosphonate



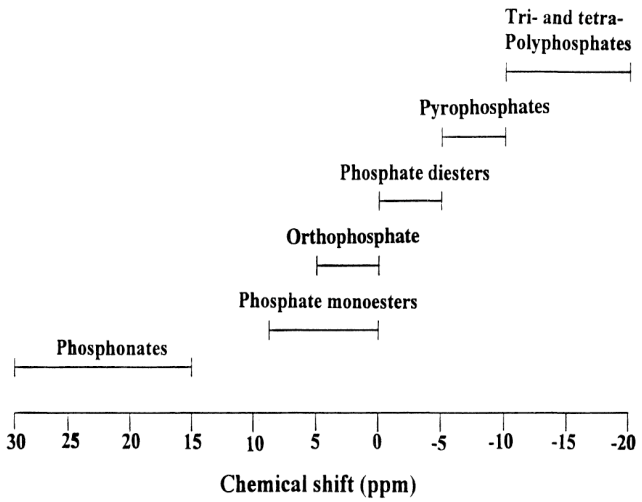
(ortho) phosphate



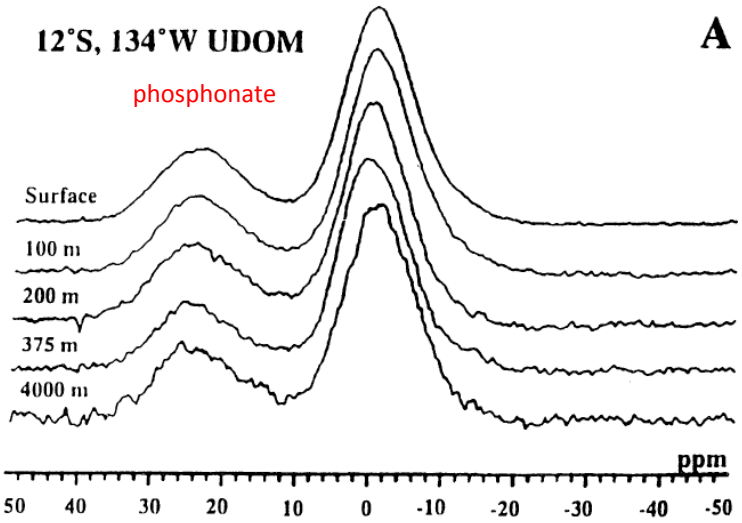
phosphate monoester

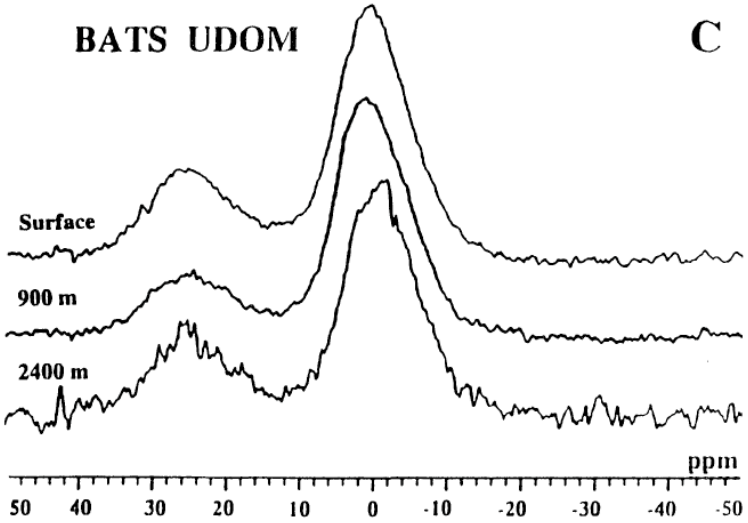


polyphosphate



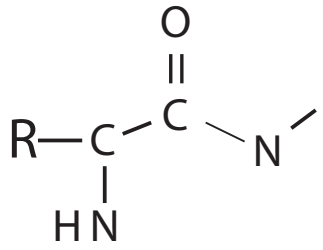
phosphate mono- & di-esters



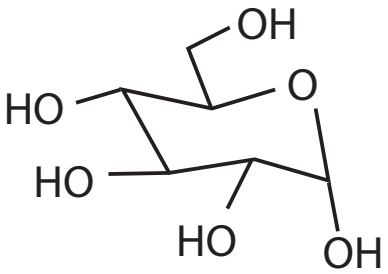


Kolowith et al., L&O 2001

Spectral modeling of major biochemicals in DOM



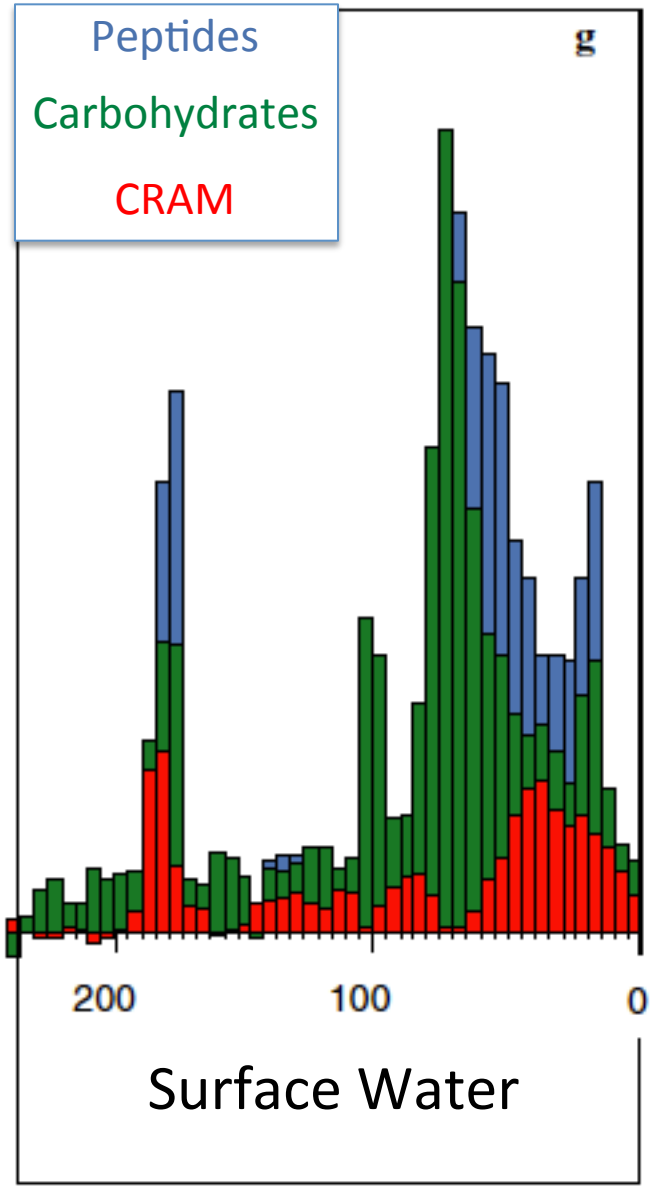
Proteins

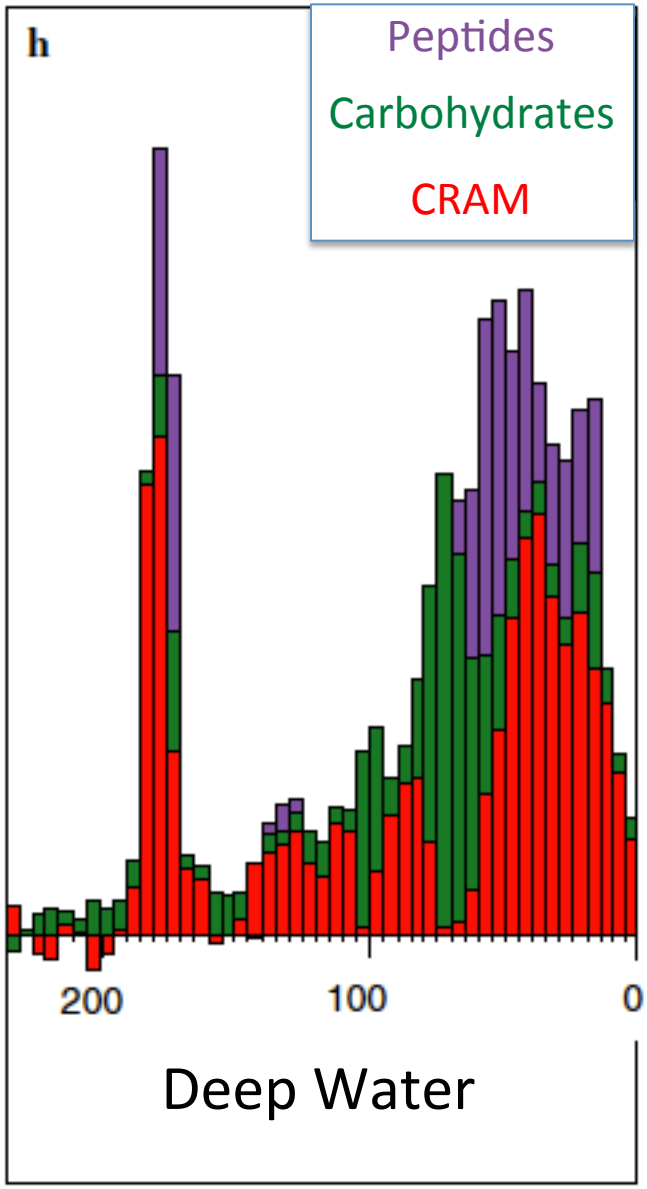


Carbohydrates

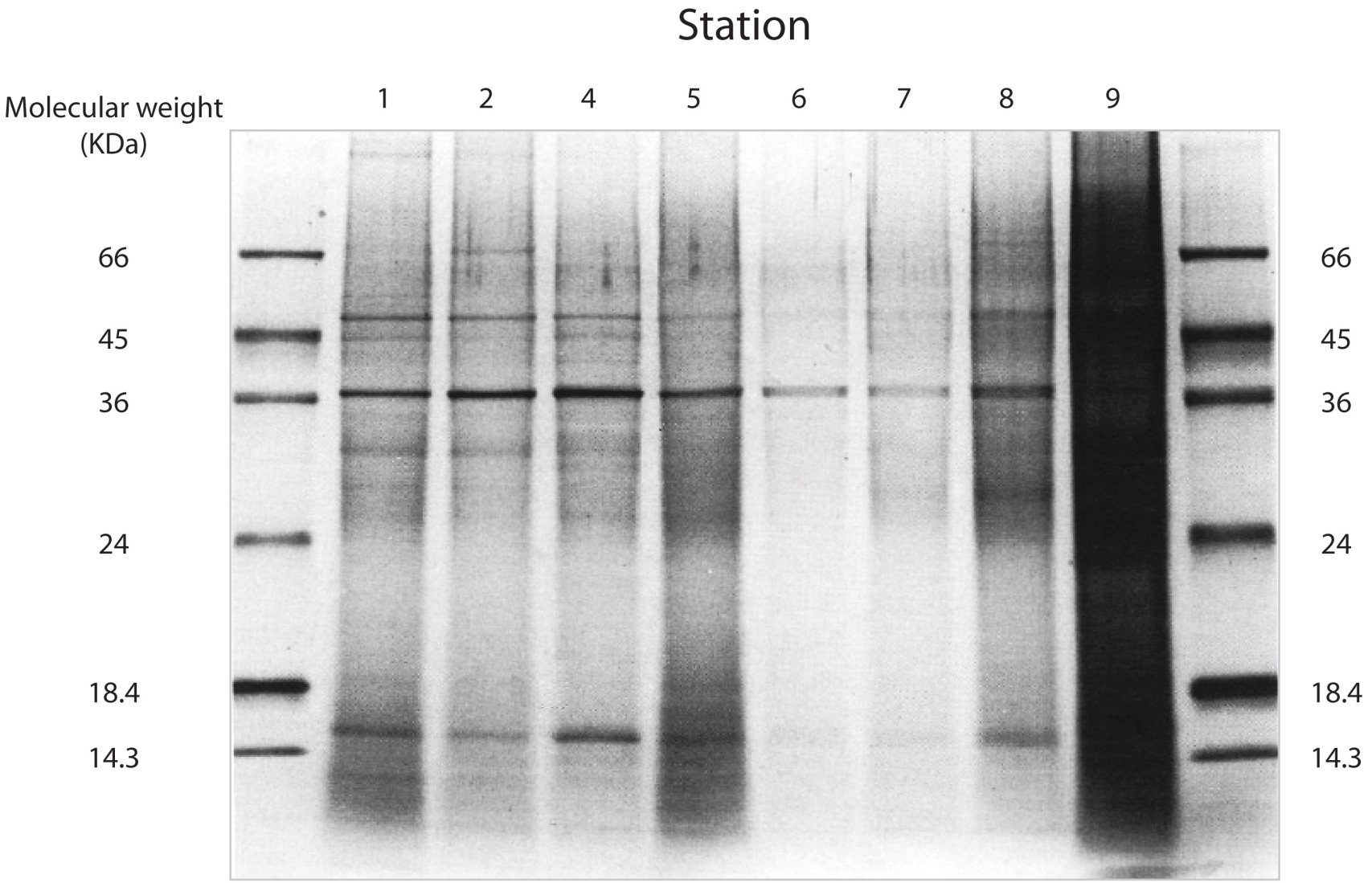
CH_3-[CH_2]n-COOH

Lipids (CRAM)

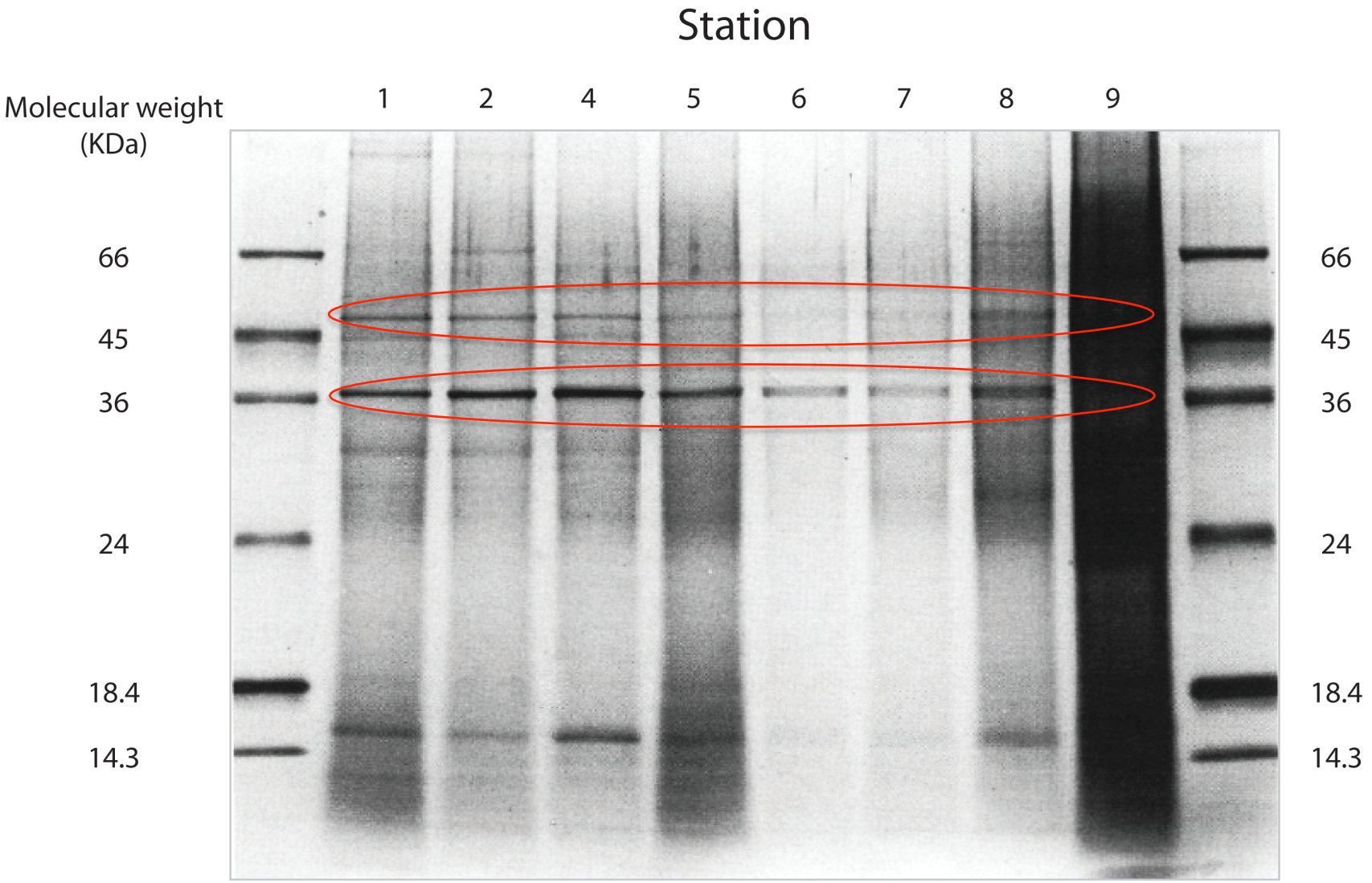




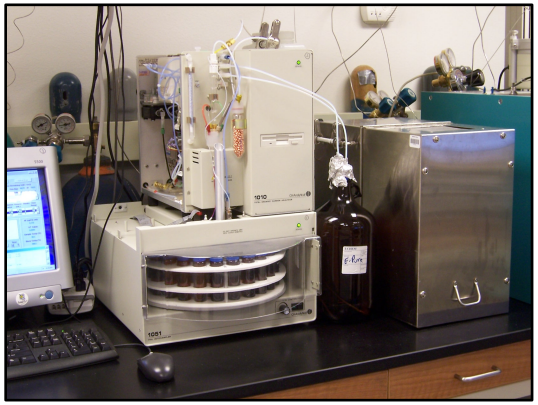
Proteomics of dissolved proteins



Proteomics of dissolved proteins



Typical 1D profile of dissolved organic carbon in the ocean

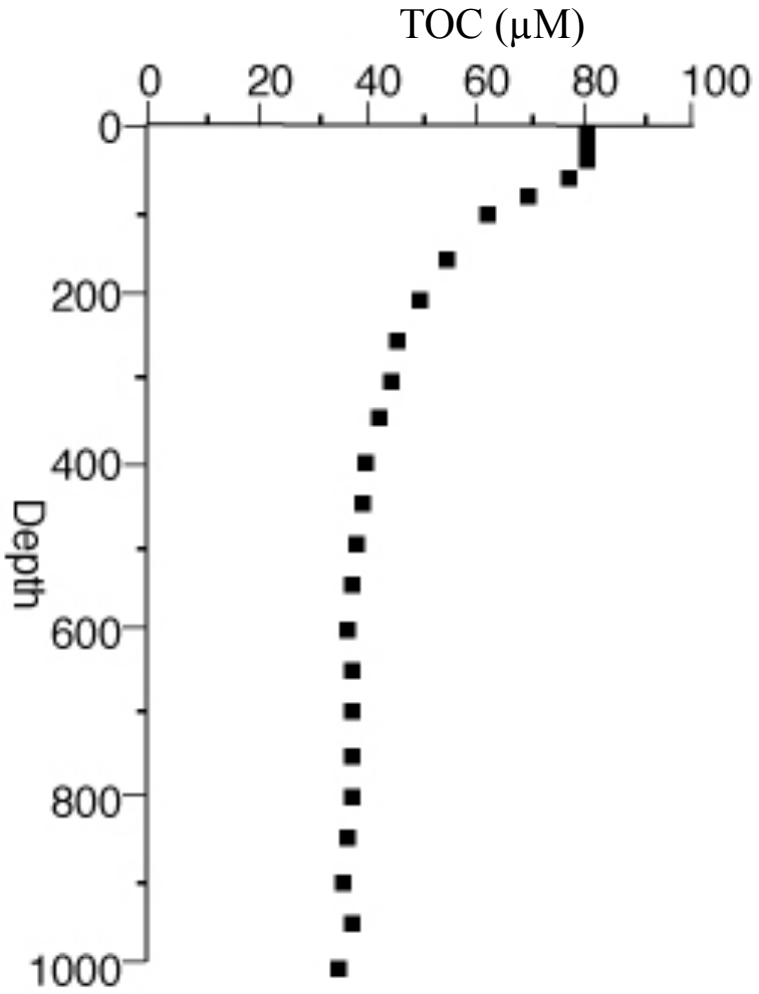


Often measured as TOC

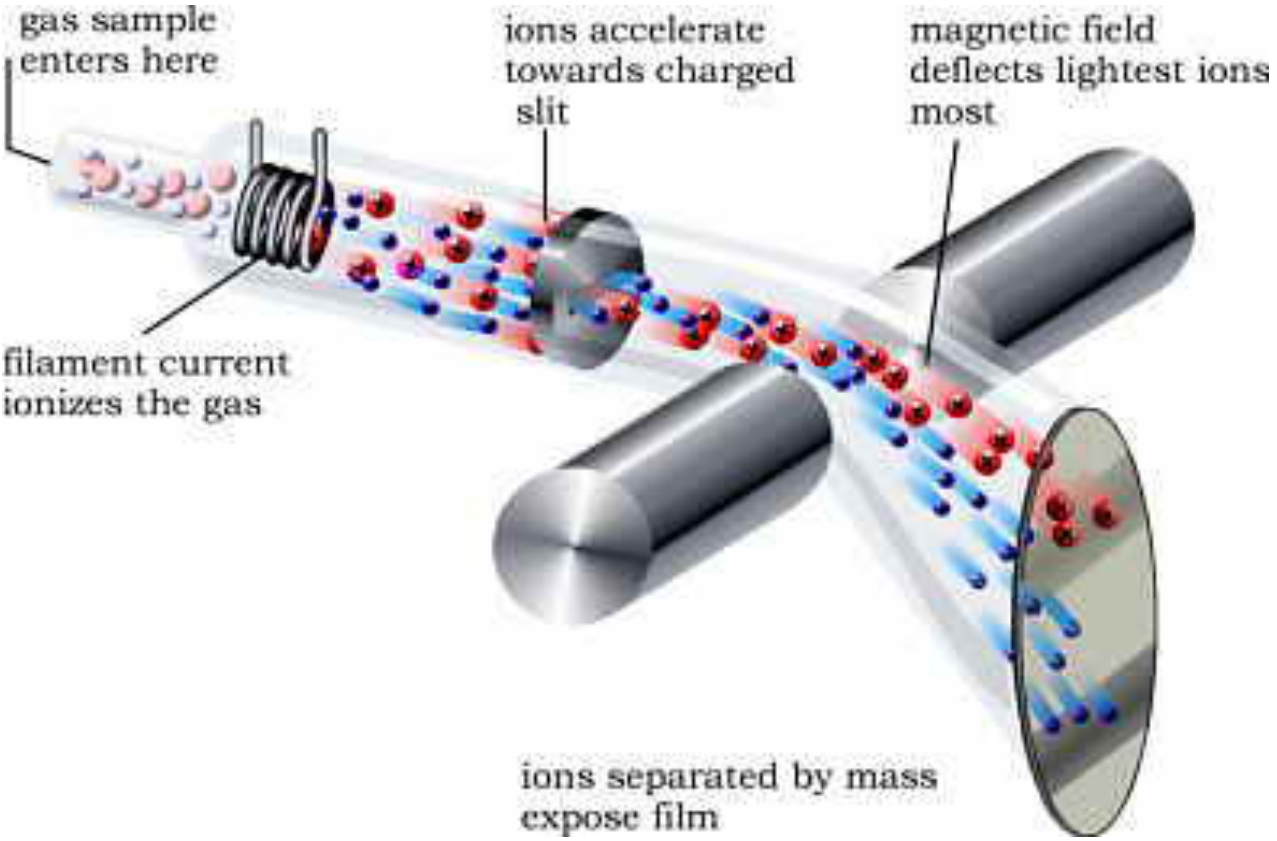
Surface values typically 60-80 µM

Deep water values @ 40 ±1 µM (implies some unknown feedback/ control of DOC values)

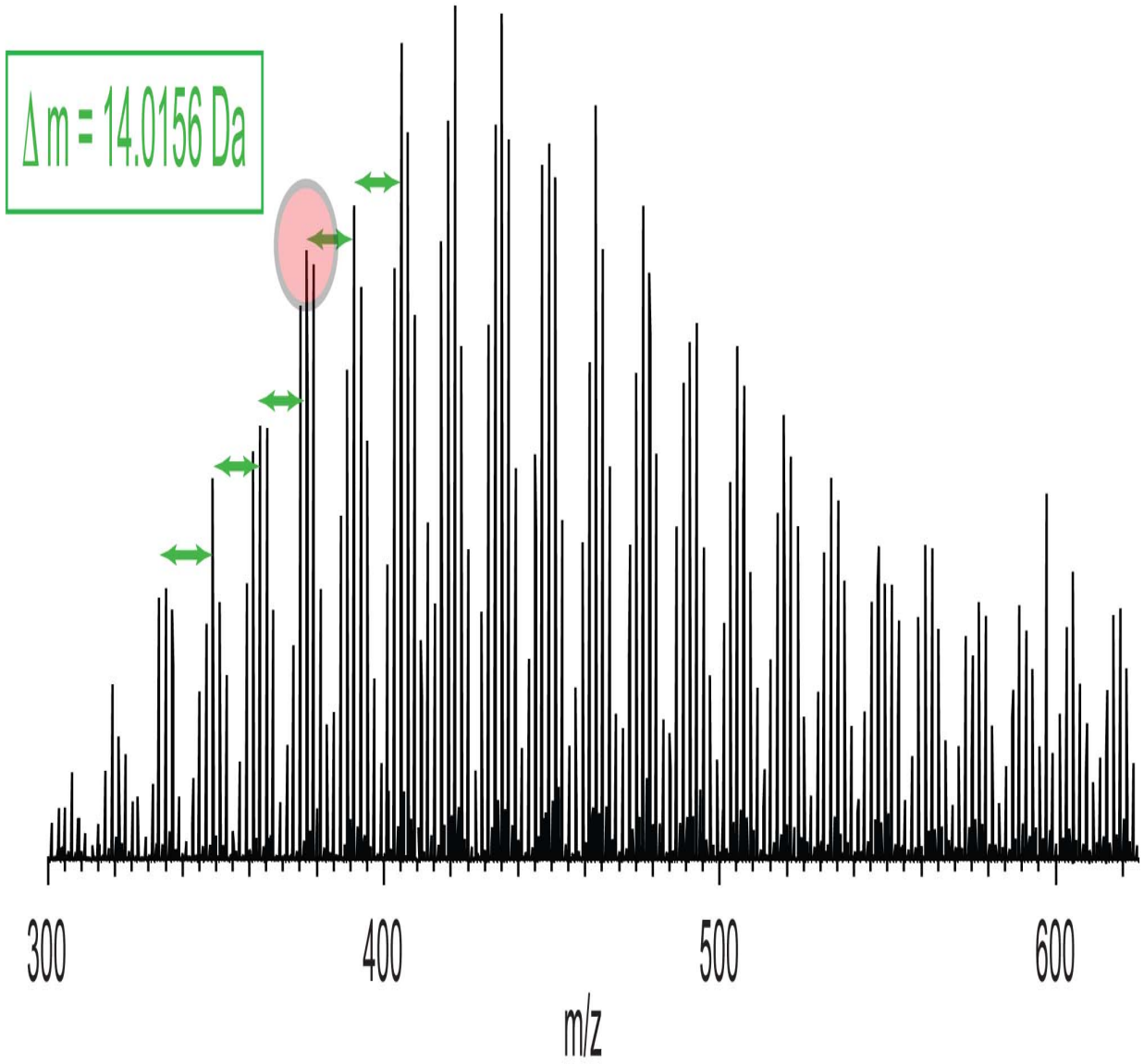
Global inventory about 660 GT C

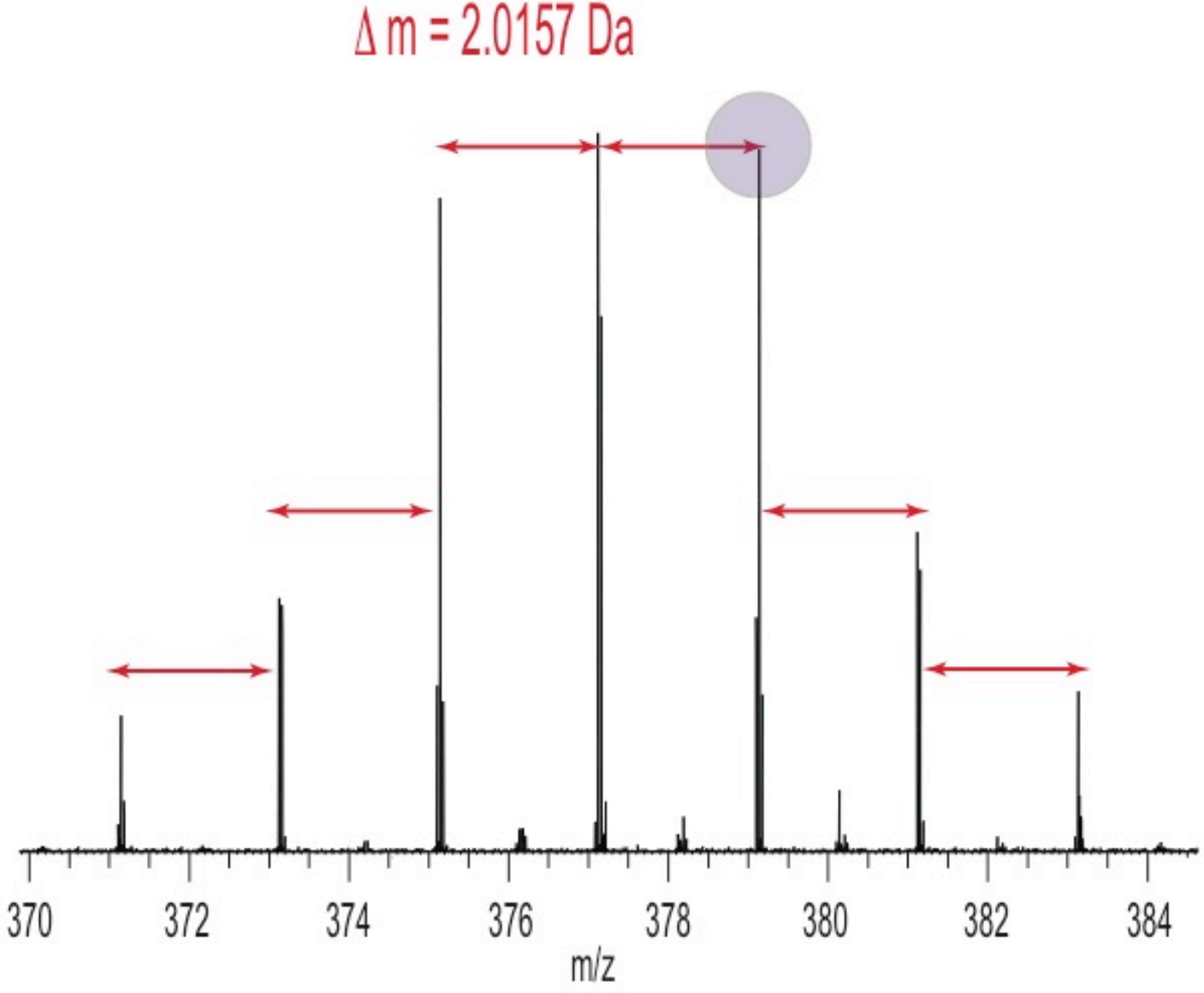


Data from Peltzer and Hayward (1996) DSR



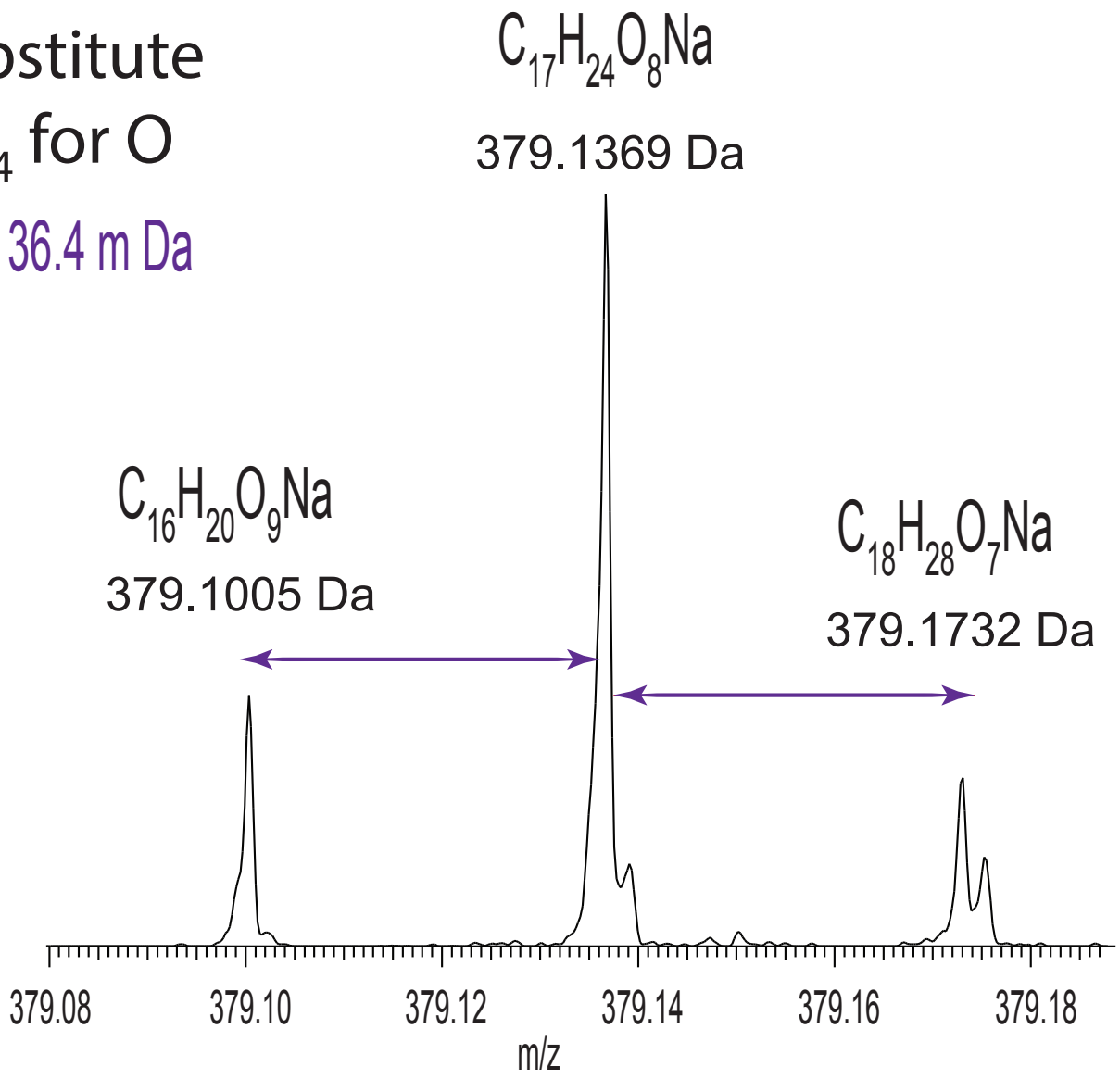
http://antoine.frostburg.edu/chem/senese/101/glossary/m.shtml


Δ m = 14.0156 Da
300
400
500
600
m/z


Δ m = 2.0157 Da
370
372
374
376
378
380
382
384
m/z

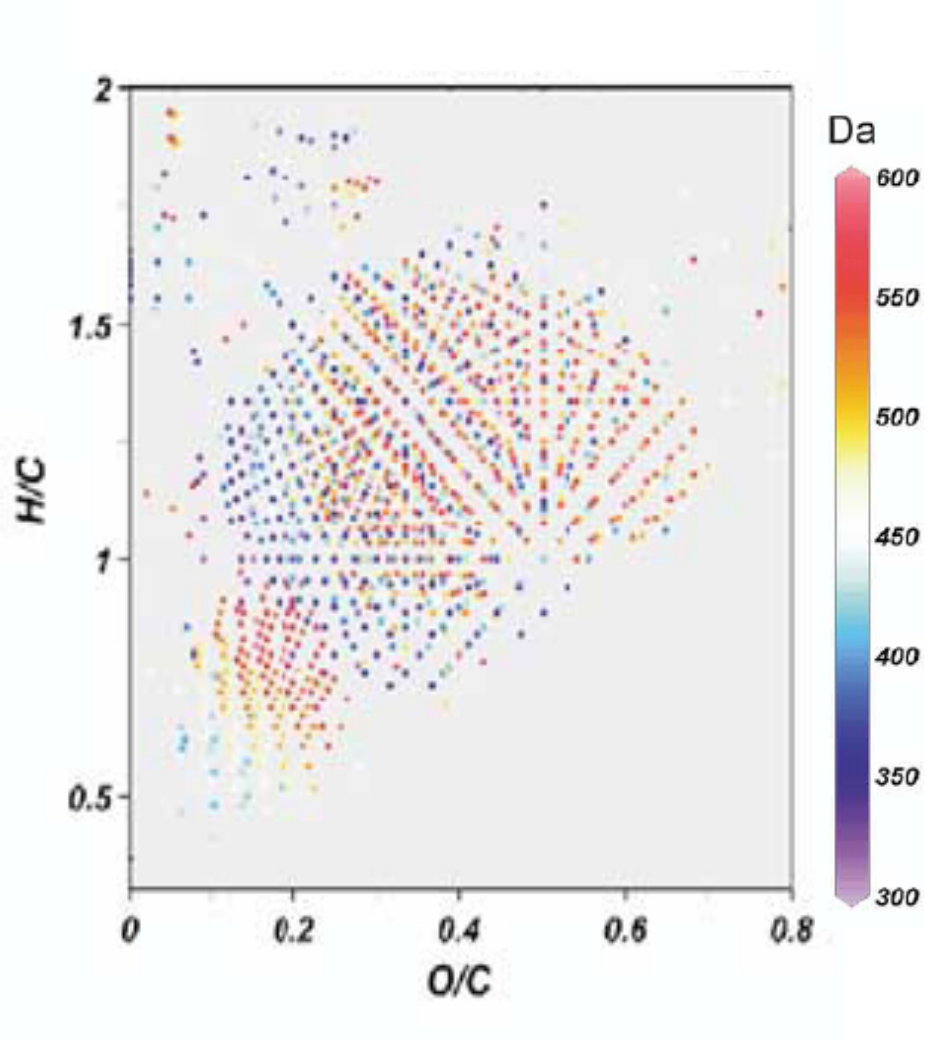
Substitute
CH_4 for O

Δ m = 36.4 m Da



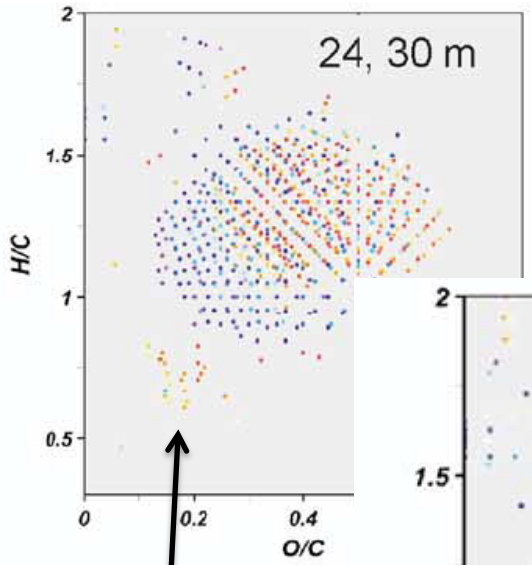
Elemental Analysis of DOM in Weddell Sea Seawater

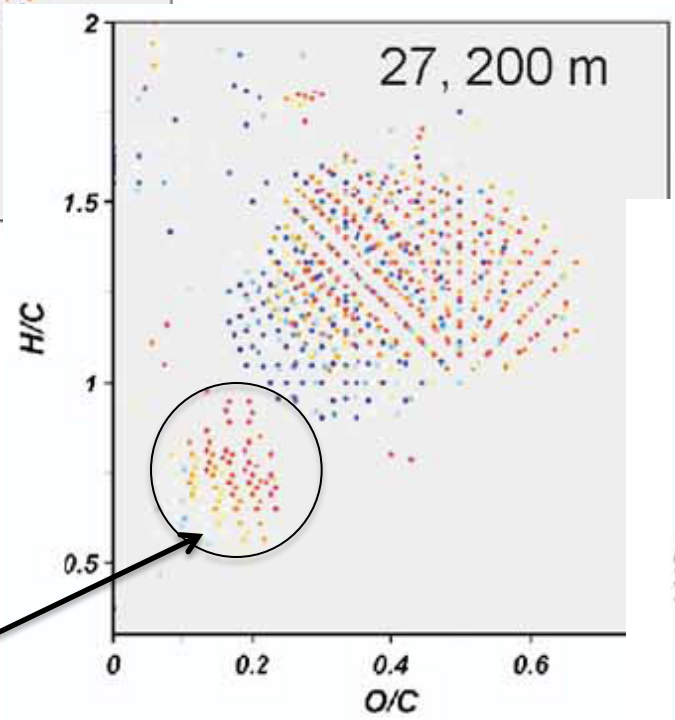
Count	A Exp	B Theory	C Error (ppm)	D C	E H (M)	F O
1	415,10141	415,10236	2,29	21	18	9
2	415,13797	415,13874	1,85	22	22	8
3	415,17405	415,17513	2,6	23	26	7
4	417,08070	417,08162	2,21	20	16	10
5	417,11720	417,11801	1,94	21	20	9
6	417,15349	417,15439	2,16	22	24	8
7	417,19014	417,19078	1,53	23	28	7
8	419,09650	419,09727	1,84	20	18	10
9	419,13277	419,13366	2,12	21	22	9
10	419,16910	419,17004	2,24	22	26	8
11	419,20525	419,20643	2,81	23	30	7
12	421,07604	421,07654	1,19	19	16	11
13	421,11206	421,11292	2,04	20	20	10
14	421,14848	421,14931	1,97	21	24	9
15	421,18488	421,18569	1,92	22	28	8
16	423,09139	423,09219	1,89	19	18	11
17	423,12766	423,12857	2,15	20	22	10
18	423,16415	423,16496	1,91	21	26	9
19	423,20011	423,20194	4,32	22	30	8
20	425,10680	425,10784	2,45	19	20	11
21	425,14331	425,14422	2,14	20	24	10
22	425,17971	425,18061	2,12	21	28	9

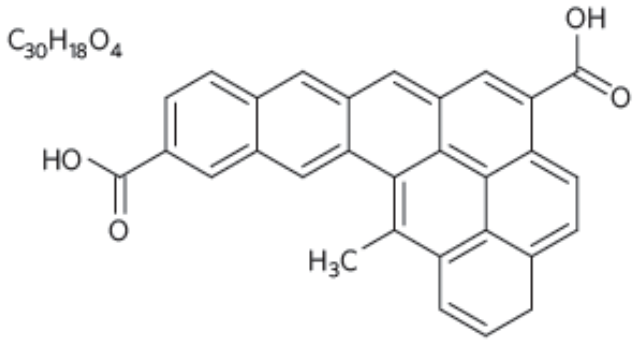


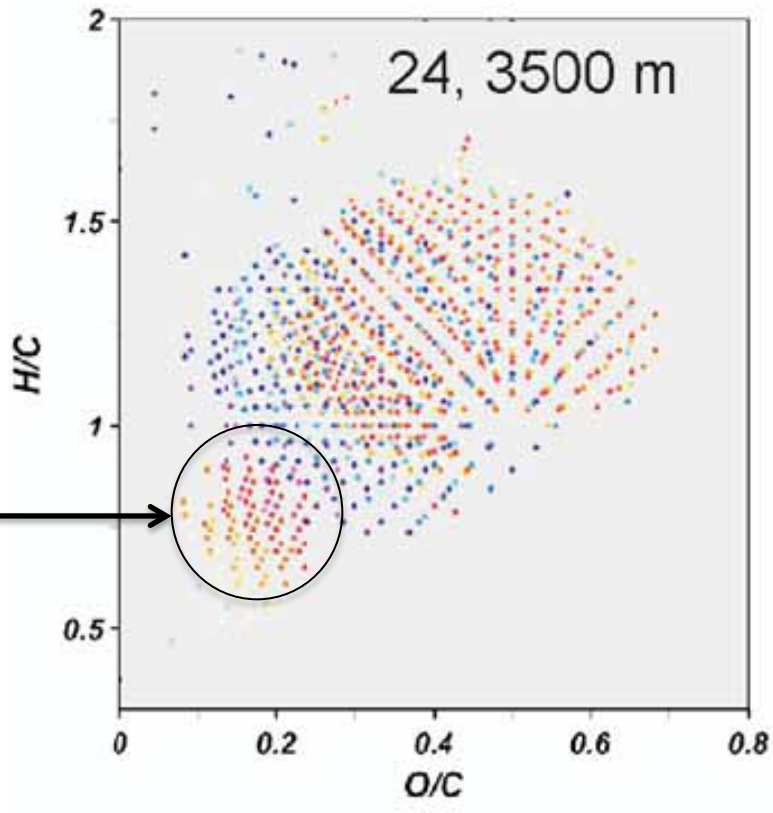
Hertkorn

Unusual molecular masses in DOM

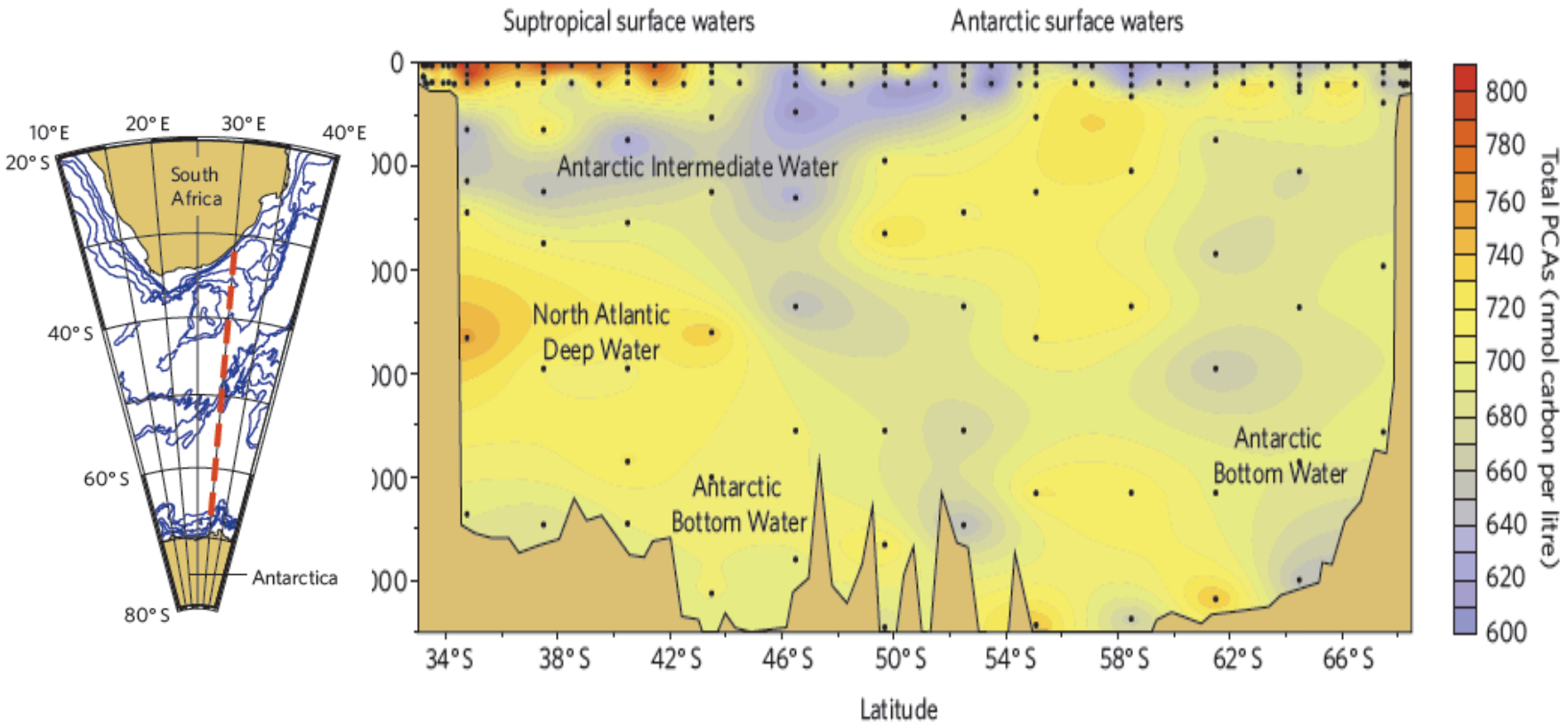








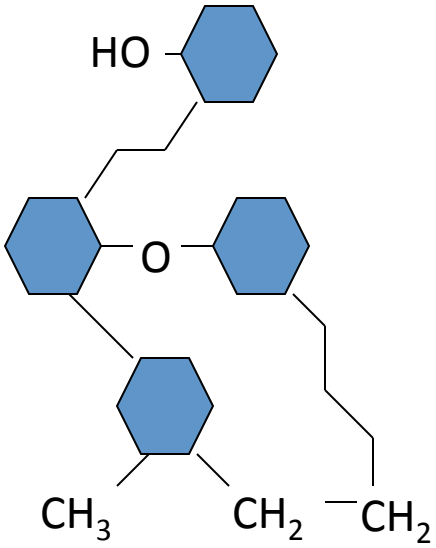
Surprisingly, there is a population of very low H/C and O/C organic matter



Dittmar & Paeng Nature 2009

Composition, reactivity, flux and distribution of DOM

Non-reactive DOM



Aliphatic or "Humic" substances

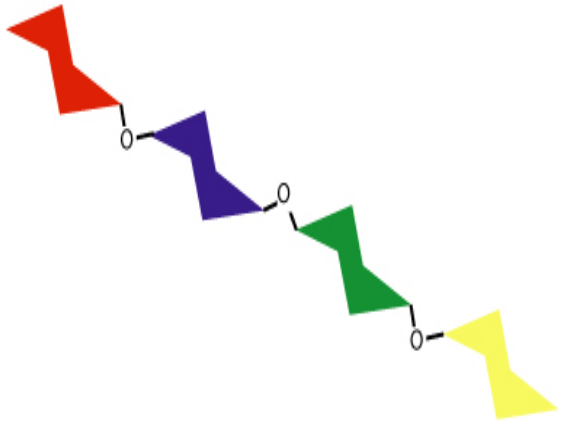
Concentration 40 µM

Inventory = 640 GT C

$\Delta^{14}C$= -400 to -600‰

Annual flux = 0.1 GTC

Semi-reactive DOM



Biopolymers

(polysaccharides, proteins)*

Concentration 0-40 µM

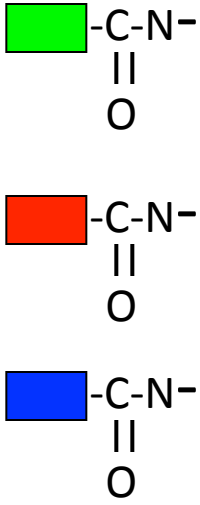
Inventory = 10-20 GT C

$\Delta^{14}C$= modern (DIC)

Annual flux = 10's GT C?

* = 80% of cell C, N

Very reactive DOM



Simple biomolecules

(amino acids, sugars)*

Concentration 1-2 µM

Inventory = 0.1-0.3 GT C

$\Delta^{14}C$= modern (DIC)

Annual flux = 10's GT C?

* = 10-20% of cell C, N

Lecture 2. Summary

There is a large vertical gradient in DOC between surface and deep waters. Net production in the euphotic zone, net respiration in the mesopelagic zone.

Radiocarbon measurements show that there is "new" DOC in the surface ocean, very "old" DOC at depth.

Loss of about 30% of deep DOC between the North Atlantic and the North Pacific, along the path of deep water drift.

Studies of chemical composition are handicapped with by our ability to sample DOM. DOM is sampled by two techniques, ultrafiltration which is based on the larger molecular size of some DOM relative to water and salt (high molecular weight DOM; HMWDOM) and solid phase extraction (SPE) that relies on chemical adsorption onto a hydrophobic surface.

Lecture 2. Summary

Of the ~ 50-60% of DOM that can be recovered, and therefore characterized. Major techniques used to characterized DOM are nuclear magnetic resonance spectroscopy (NMR) and high resolution mass spectrometry (HR-MS). HMWDOM is largely "new" DOC and has a modern radiocarbon age when purified. HMWDOM is largely carbohydrate with a small amount of protein. HMWDOM carbohydrate has an unusual composition that has not been fully characterized. The source of the carbohydrate is not known.

SPE extracted DOM has an old radiocarbon age. SO far this is very hard to analyze and characterize. It is clearly a complex mixture of organic matter with a significant amount of aliphatic character. The source of this DOM and the pathways that lead to its formation are not known.