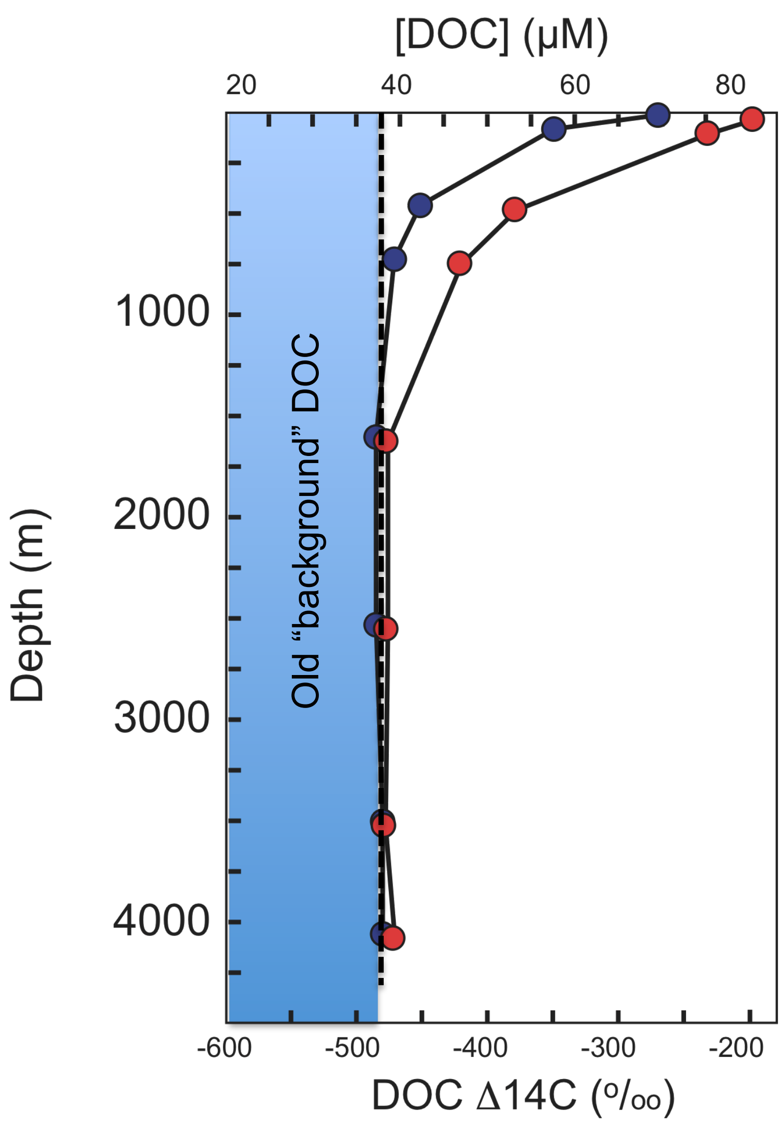
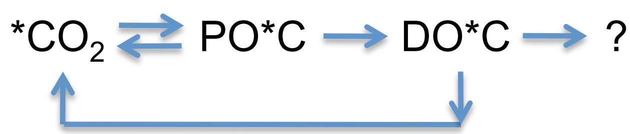
Radiocarbon based models of DOC cycling in the water column



Beaupre and Druffel 2009

[DOC] profiles show input at the surface, removal in the mesopelagic, and stasis at depth.

DOΔ^{14}C is isotopically depleted at depth and enriched In the surface.

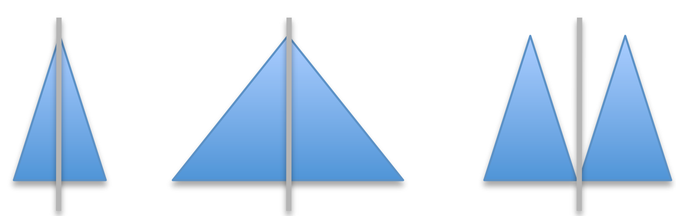


If this XΔ occurs quickly, $*CO_2$ = DO*C. If XΔ is interrupted, the two reservoirs will diverge.

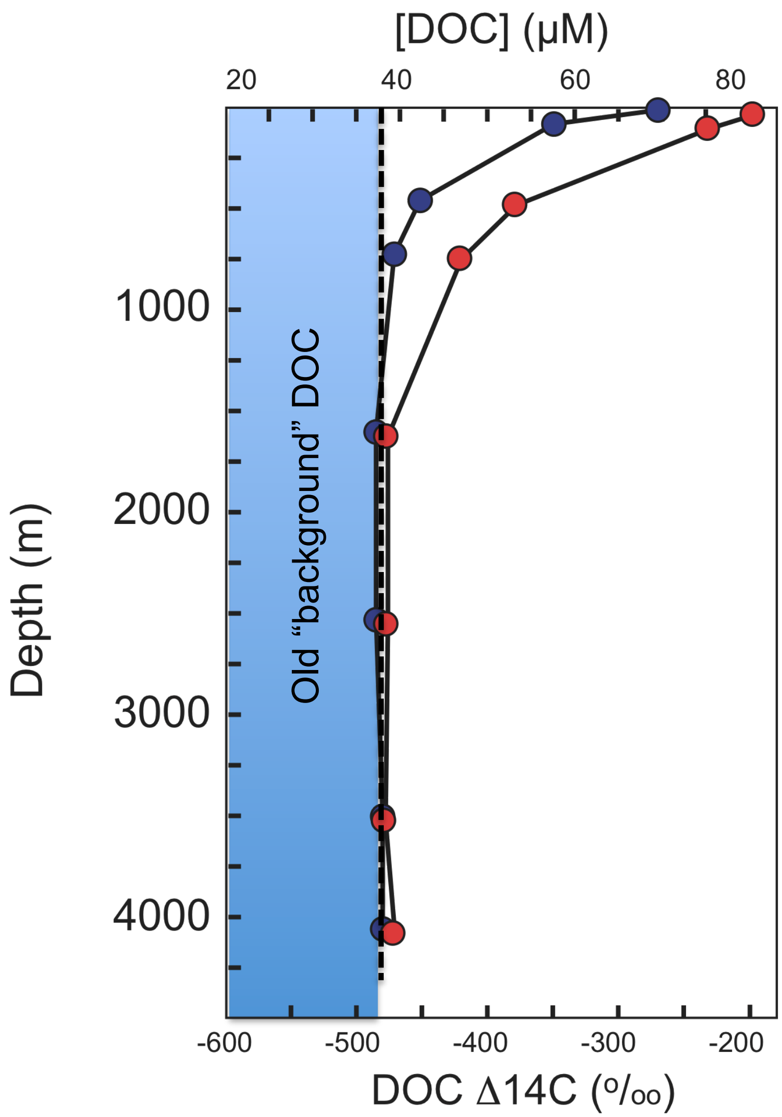
We see divergence in both surface and deep water. Deep water DIC < 1000 yr, DOC = 5000-6000 yr.

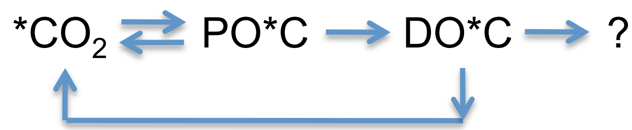
Two factors could result in old DOC in the deep ocean: DOC that survives several ocean mixing cycles, or a pre-aged source of DOC.

DO*C in the deep ocean is probably an average of deep sea DO*C values. We do not know what the range of values is.



Radiocarbon based models of DOC cycling in the water column





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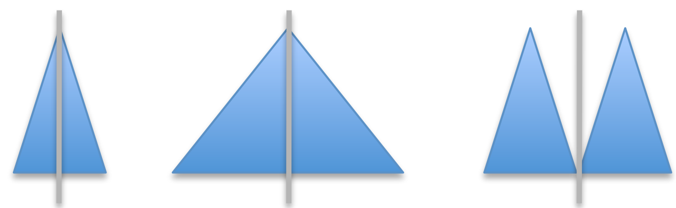
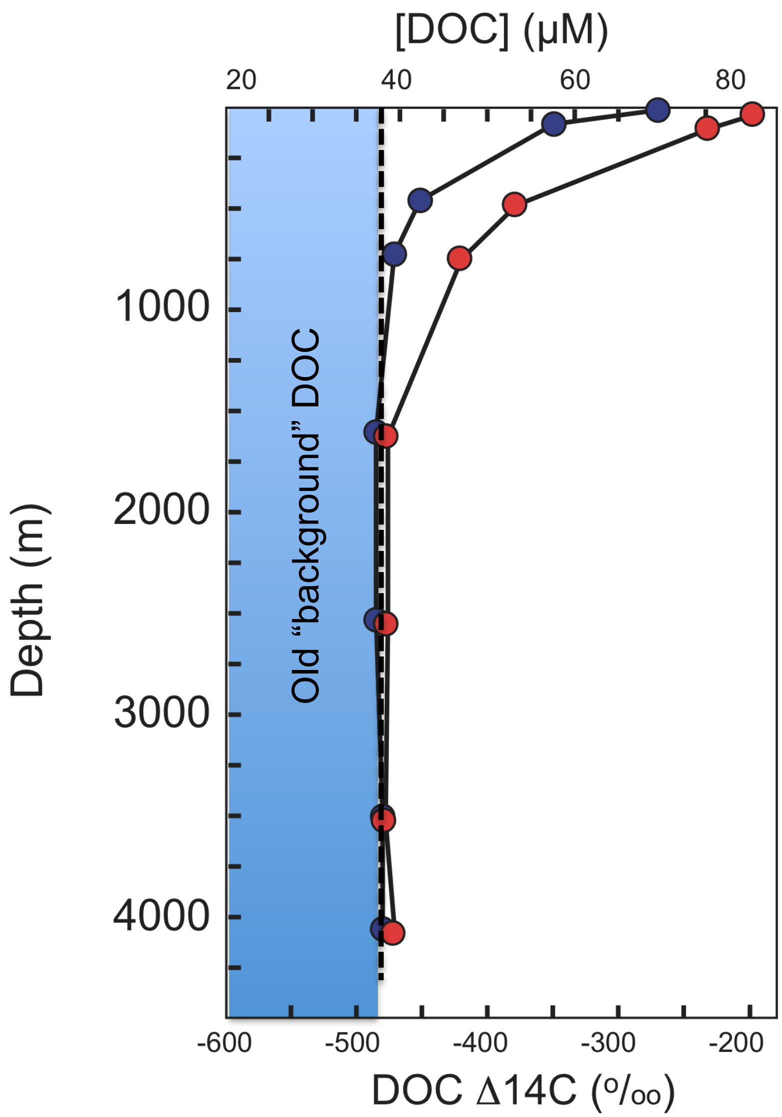


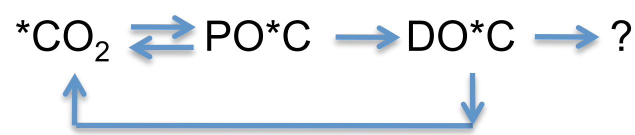
If the source of "background DOC is modern radiocarbon then the flux of C is 660 GT C/6000 yr = 0.1 GTC/yr.

If the source is "pre-aged" then the flux would be higher

Beaupre and Druffel 2009

Radiocarbon based models of DOC cycling in the water column





The surface ocean has been modeled as a two component Reservoir, with a modern and old component, such that:

$[DOC] = [DOC]_{deep} + [DOC]_{xs}$

DOC_{xs} has a modern *C value. Because the contemporary ocean is out of isotopic equilibrium with the atmosphere (bomb *C), the *C value constrains the residence time of DOC_{xs} in the surface. The more the two values diverge, the lower the flux of C through the DOC_{xs} reservior.

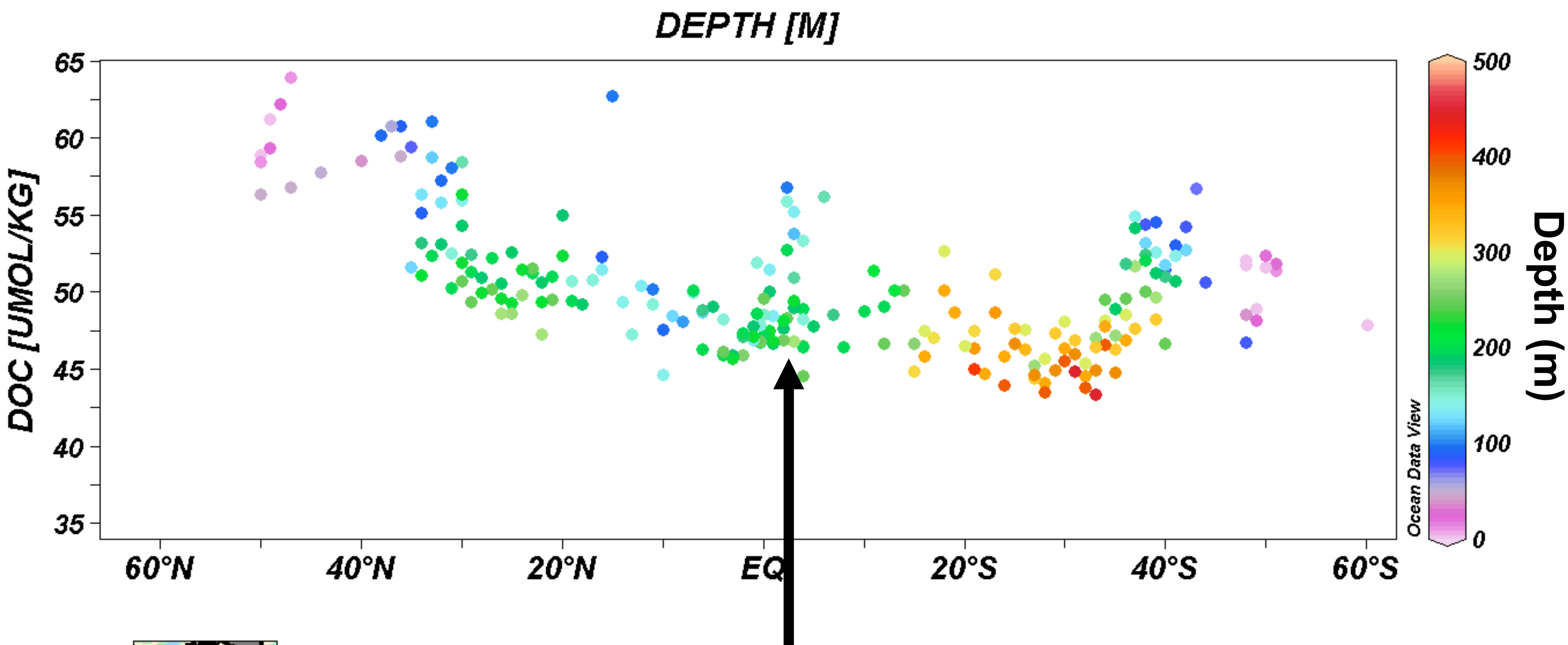
Williams and Druffel assume $DO{*}C_{xs}$ = DI*C; Mortazani and Chanton derive this from a Keeling plot and find a "modern" value with bomb radicoarbon. Both assume a constant $[DOC]_{deep}$.

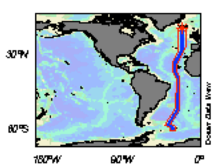
DOC_{xs} extends down into the water column several hundred meters. This is depth is more than expected for vertical mixing alone, and represents either rapid horizontal mixing or introduction of DOC through POC-DOC exchange.

The flux of carbon constrains the likely sources of DOC.

Beaupre and Druffel 2009

A16: DOC on δ_θ 26.4 – 26.7

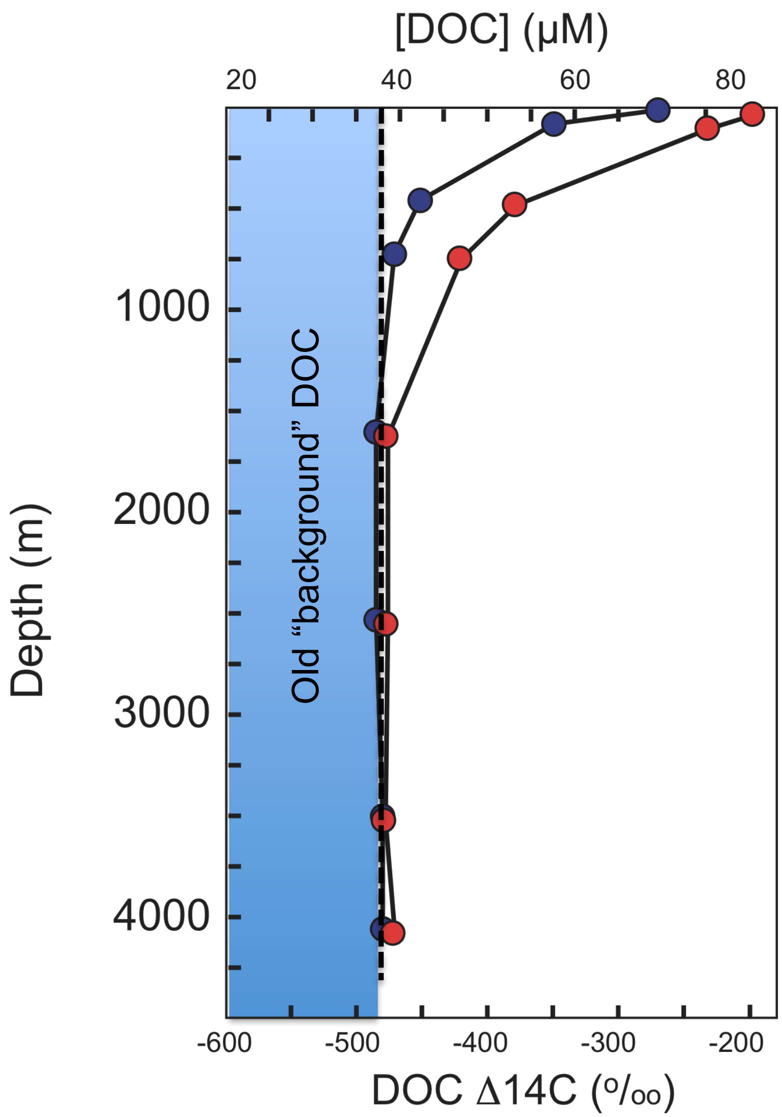




Input on the Equator
(solubilization of sinking particles
or advective input?)

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

Radiocarbon based models of DOC cycling in the water column



Beaupre and Druffel 2009

WRT the sources of DOC:

There is a source of DOC in the surface ocean (high concentrations) and a sink in the mesopelagic (low concentrations.

Deep ocean gradients in [DOC] suggest a sink for DOC in the deep sea, or non steady-state behavior.

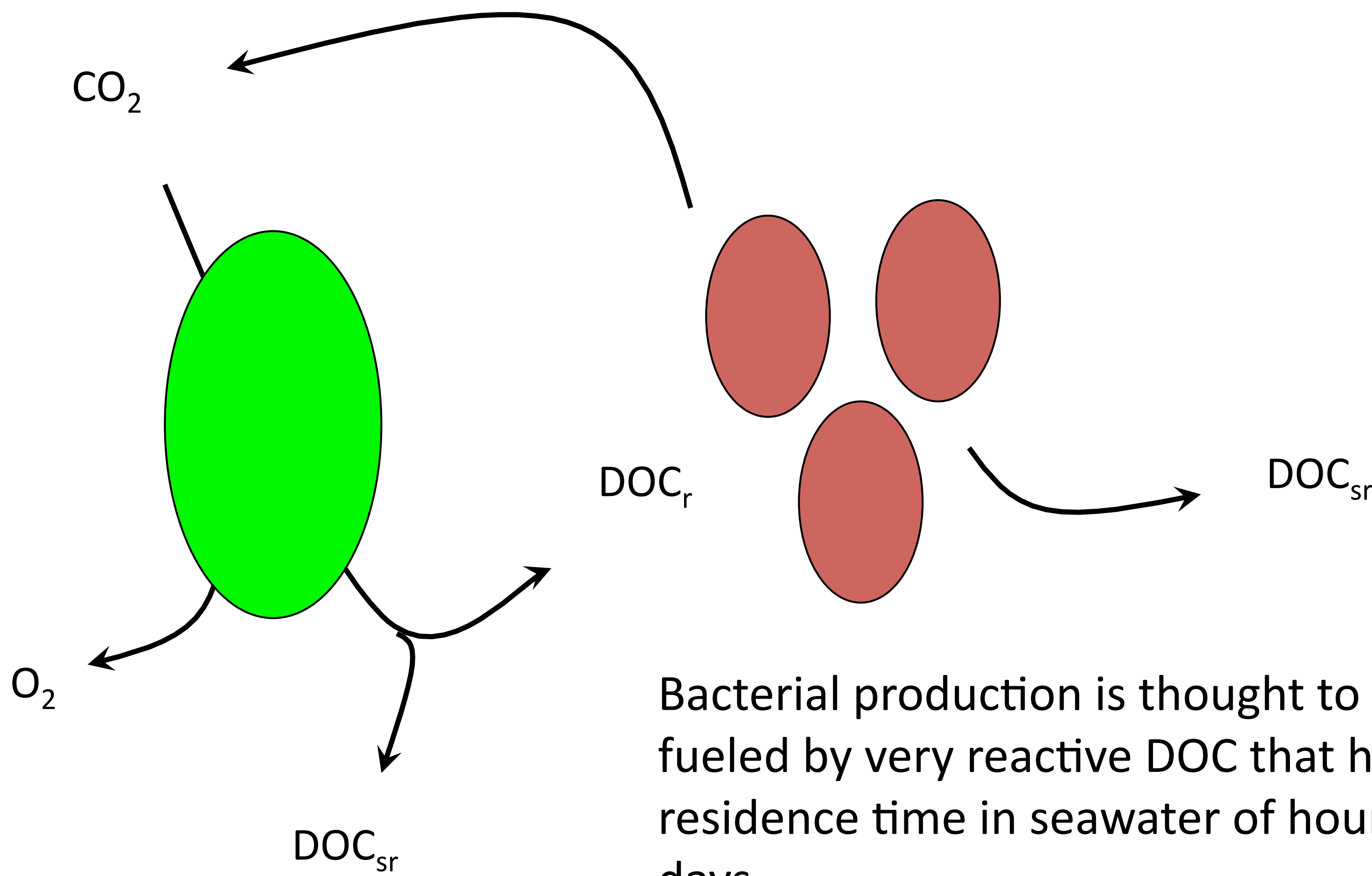
Likely sources are determined by C flux, C isotope values ^{14}C and ^{13}C, and composition. Non are definitive at this Time.

<u>Likely sources:</u>

Microbial production
Rivers/groundwater
Atmosphere (dust, rain)

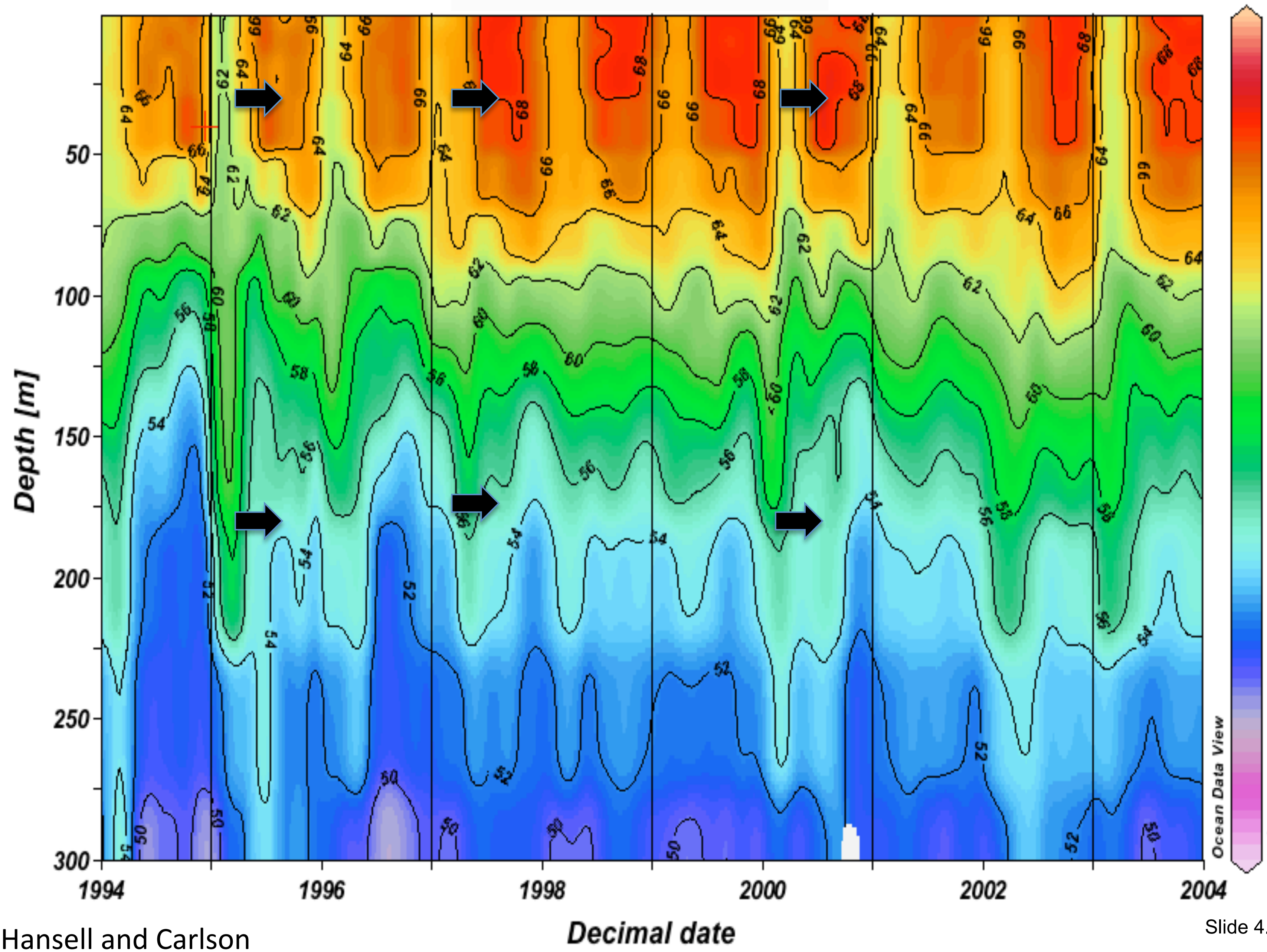
^{13}C isotopes suggest in-situ production is the source of most DOC. Marine photoautotrophs have a d13C value of -21 per mil, compared to about -27 per mil for terrestrial organic matter. DOC has a value of -22 per mil. But all likely sources contribute to marine DOC to Different degrees. ^{13}C is not definitive.

Production of very reactive and reactive DOC by phytoplankton and bacteria

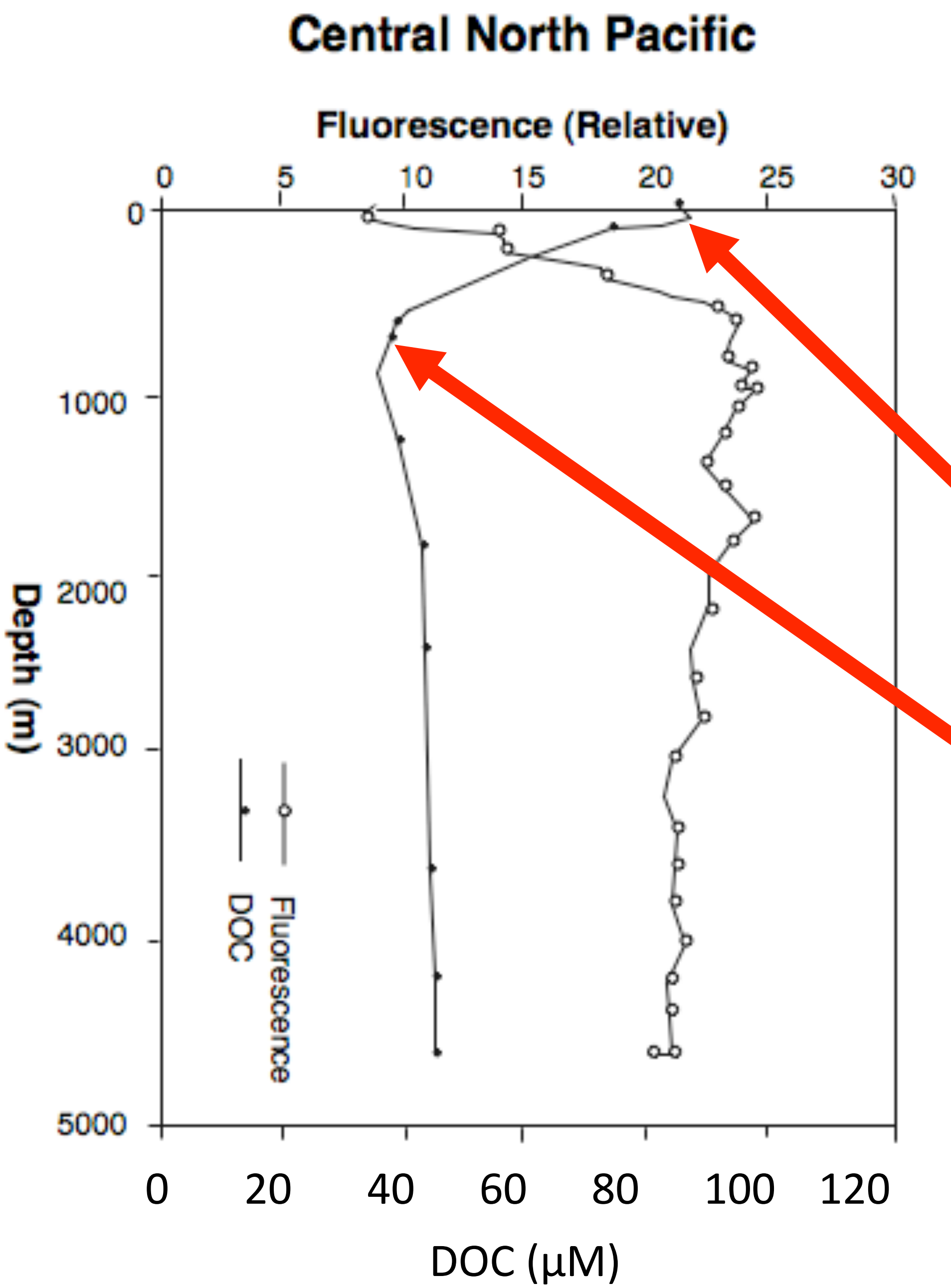


Bacterial production is thought to be fueled by very reactive DOC that has a residence time in seawater of hour to days.

BATS DOC (µM C)



Hansell and Carlson



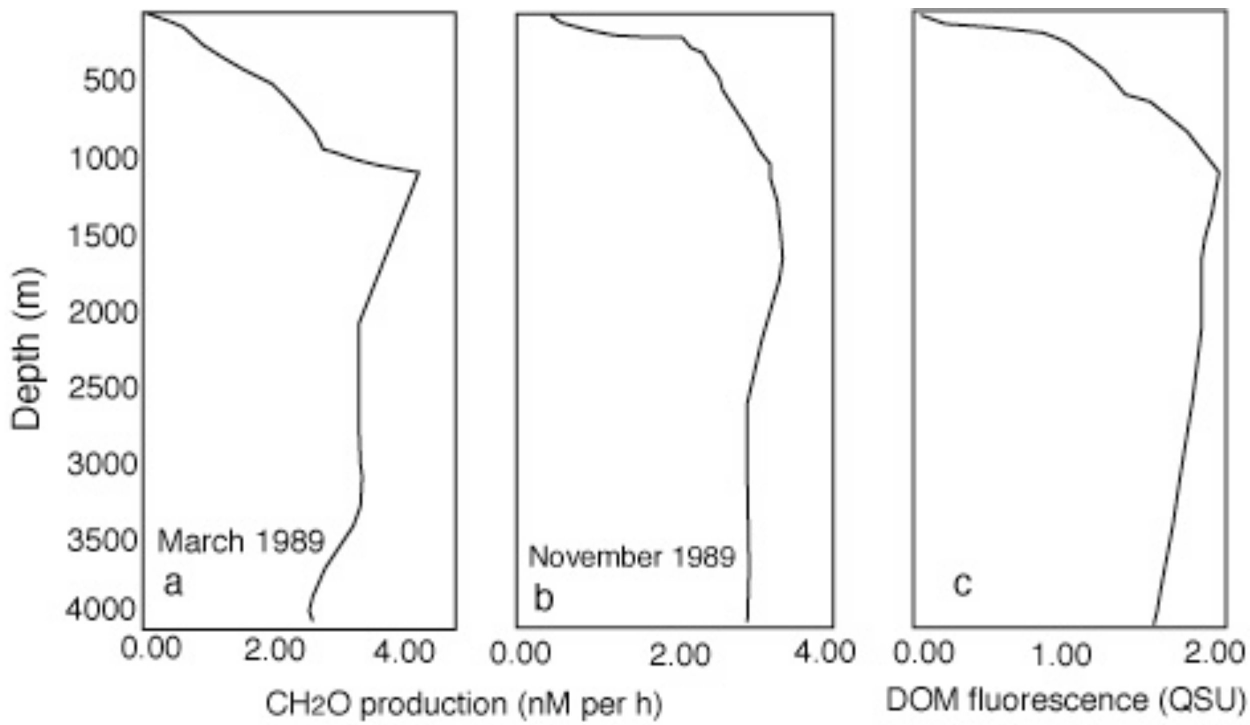
What are the sinks for DOC?

Photooxidation
Microbial consumption
Particle scavenging

DOM from surface and 900 m

Production of LMW highly oxidized DOC with depth in the ocean

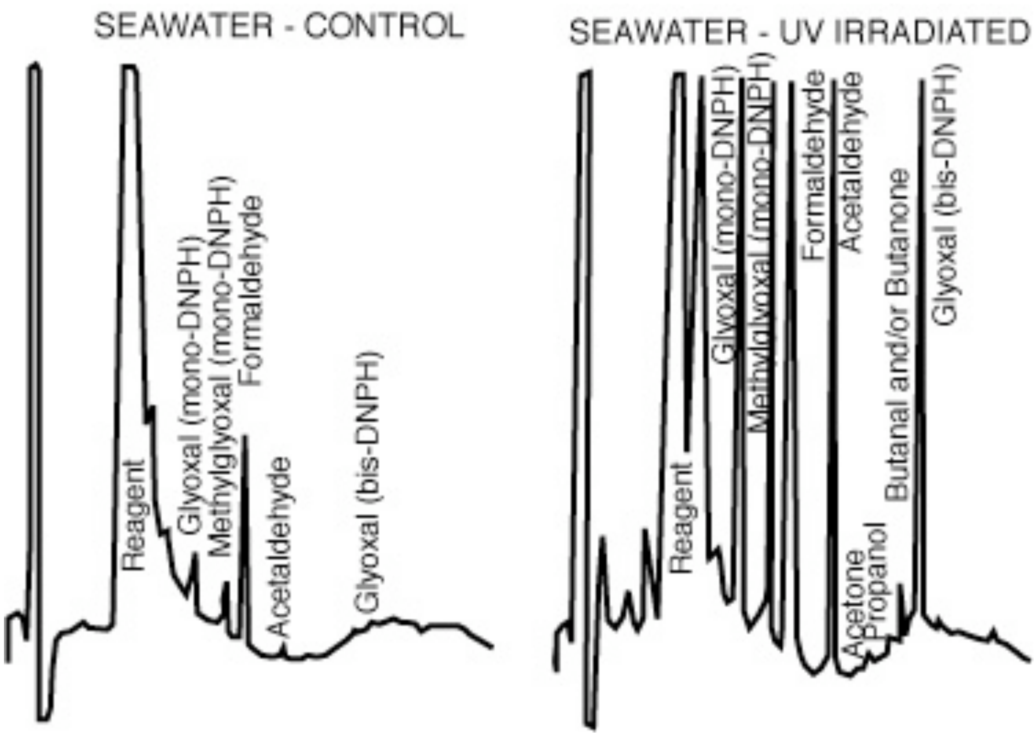
DOC + hv → LMW photo-oxidation products

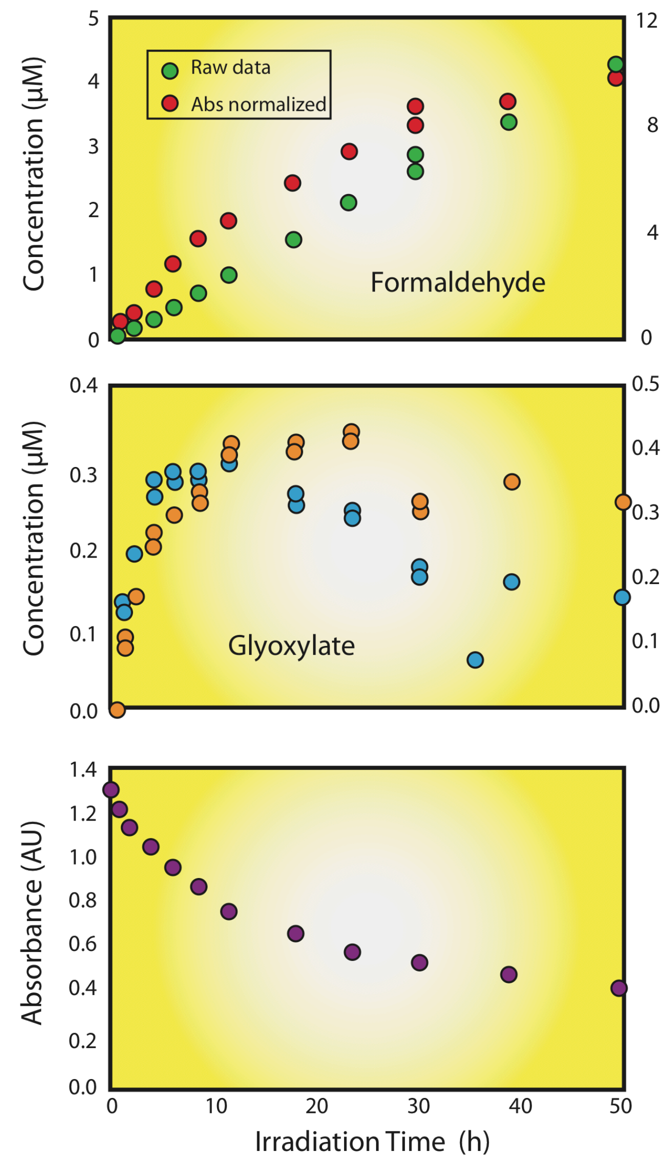


Is photochemical degradation the long term sink for recalcitrant DOM

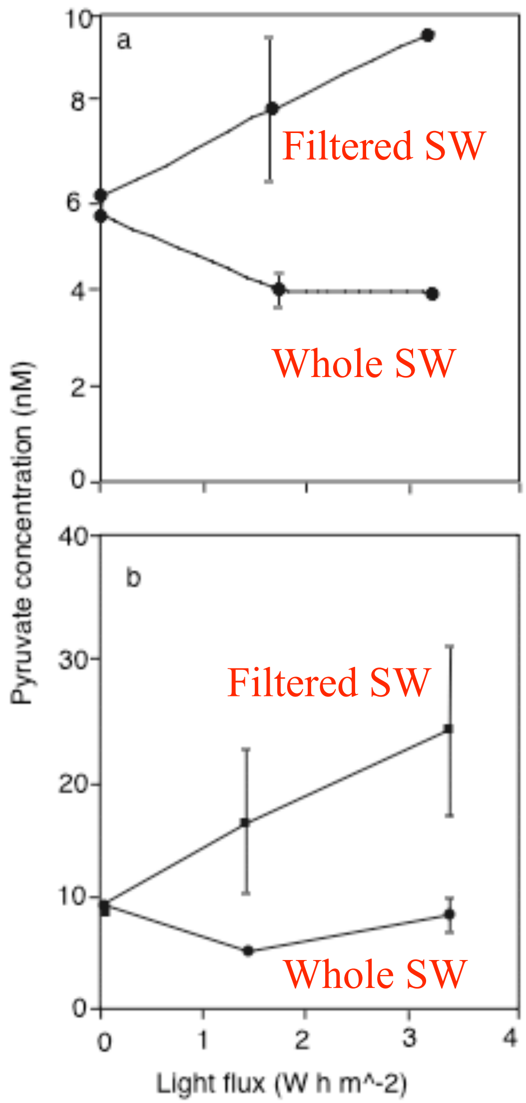
DOC + light → LMW carbonyls (C=O)

C=O + fluorophore → HPLC

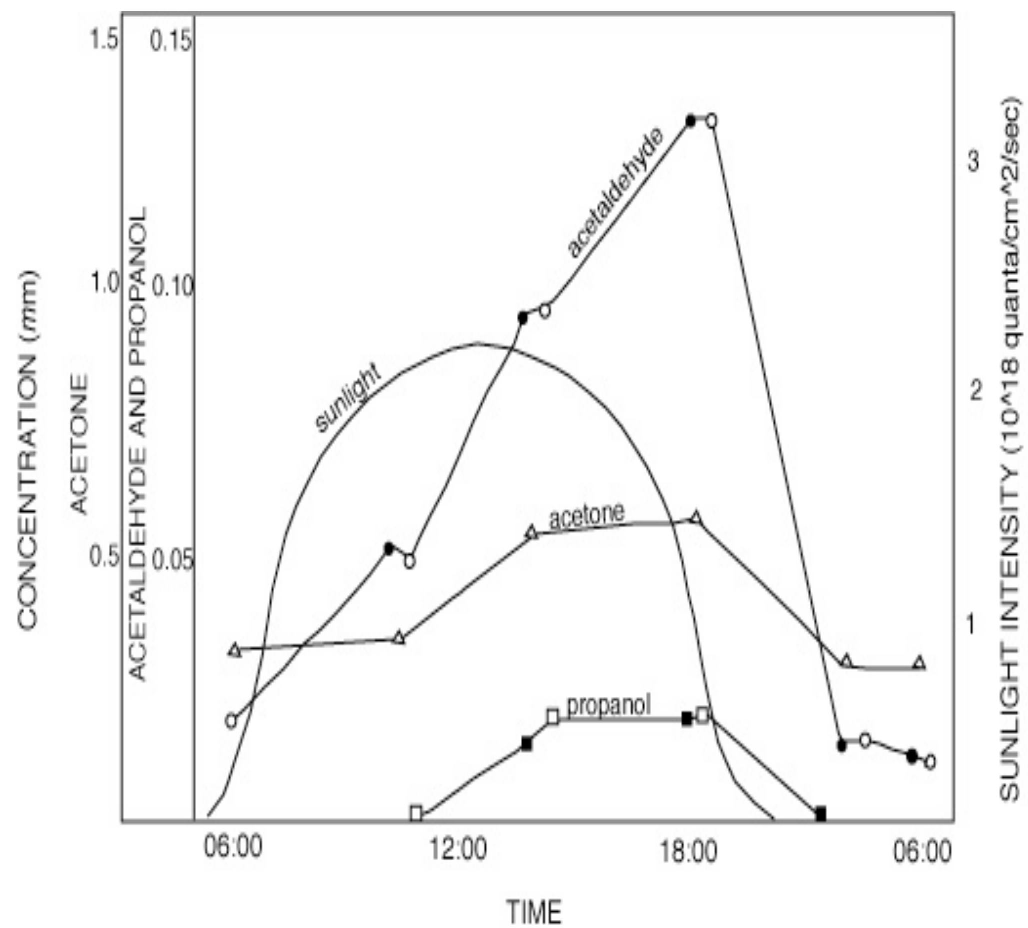




Not produced in dark controls, but are produced in sterile controls

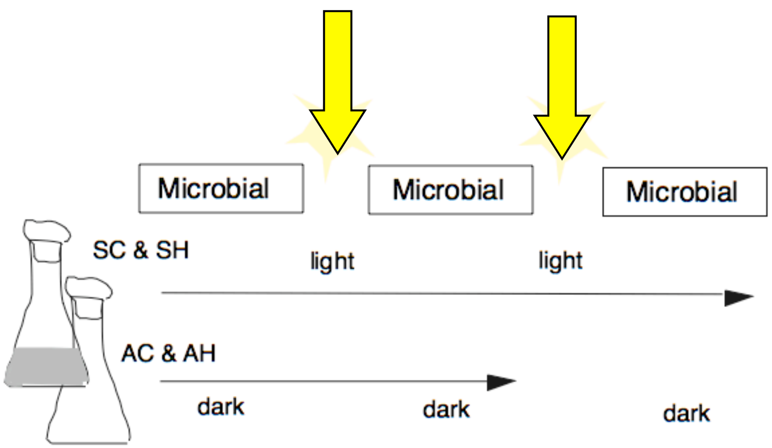


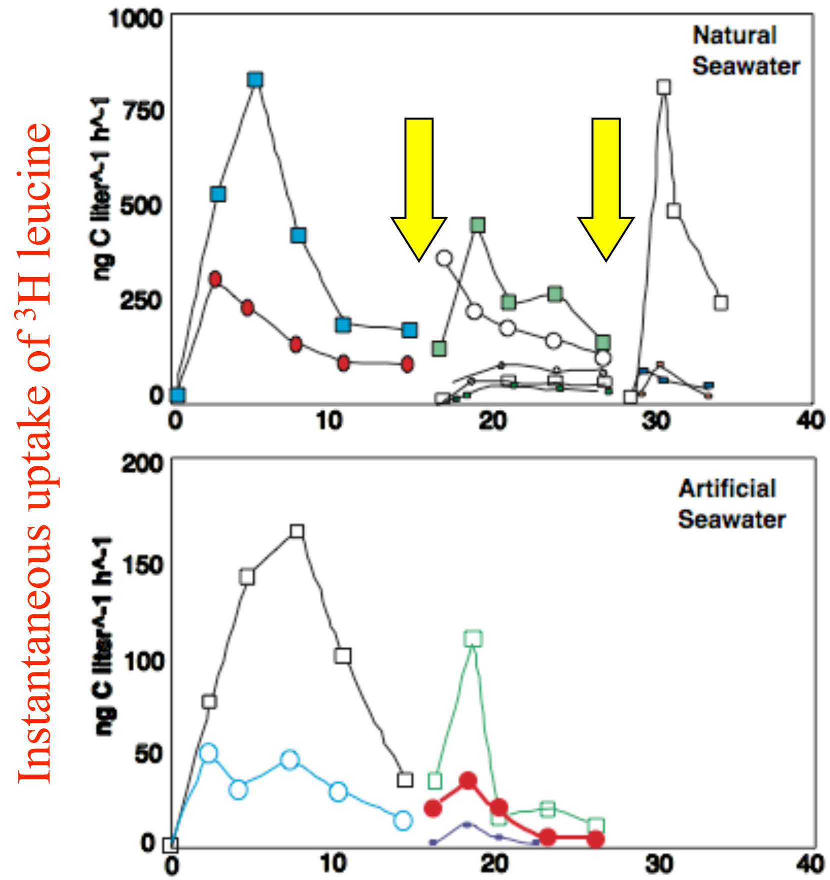
In the environment, production of LMW photooxidation products is balanced microbial respiration such that the Products of DOM photooxidation do not accumulate in The water column. This process can potentially act as A sink for old, otherwise nonreactive DOM.



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





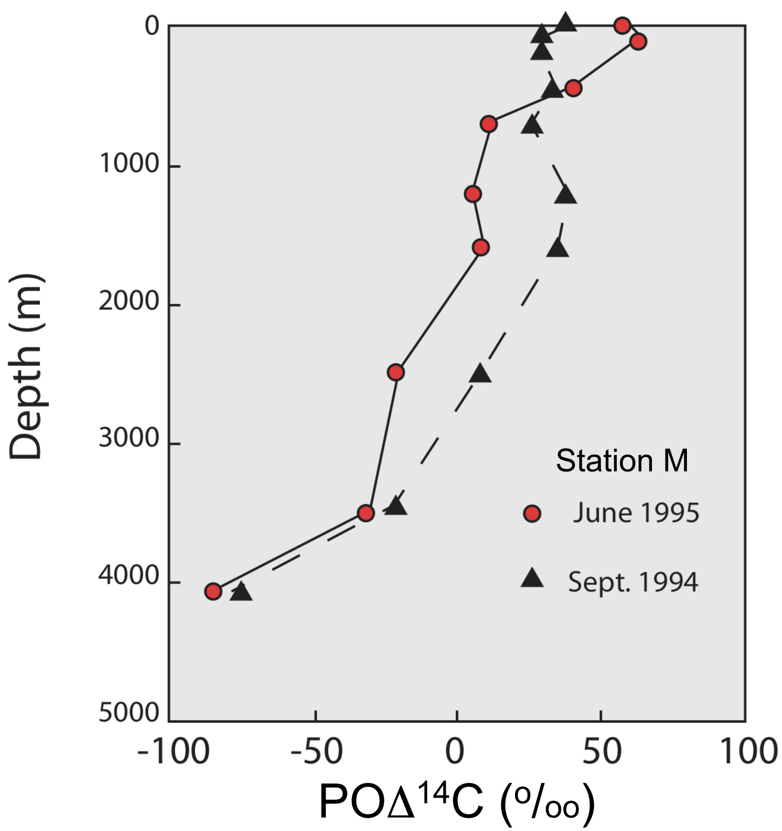
Miller and Moran L&O 1997

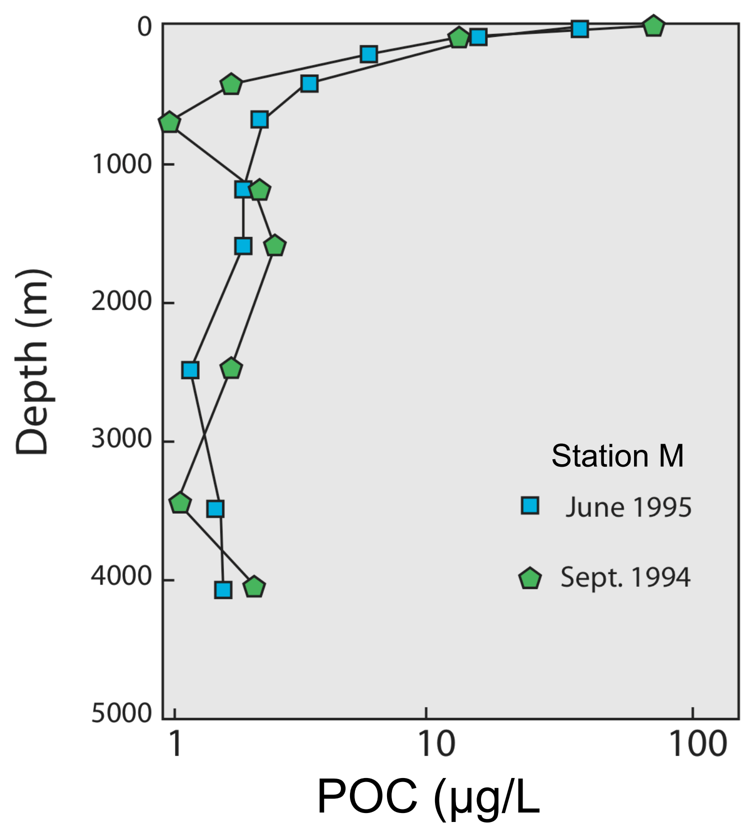
Removal of old, recalcitrant DOC by particles sinking through the water column

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

Since the particles are synthesized with a modern 14C value, Druffel concludes Old (14C 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





Slide 4.13

Druffel et al (1998) DSR v 45 p 667-687

Summary

A number of putative sources for DOM have been identified- continental organic matter from rivers, dust, and the atmosphere;prodution by marine microbes. Most DOC is depleted in radiocarbon, and the calculated residence time of DOM is on the order of 4000-6000 years with a minimum 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.

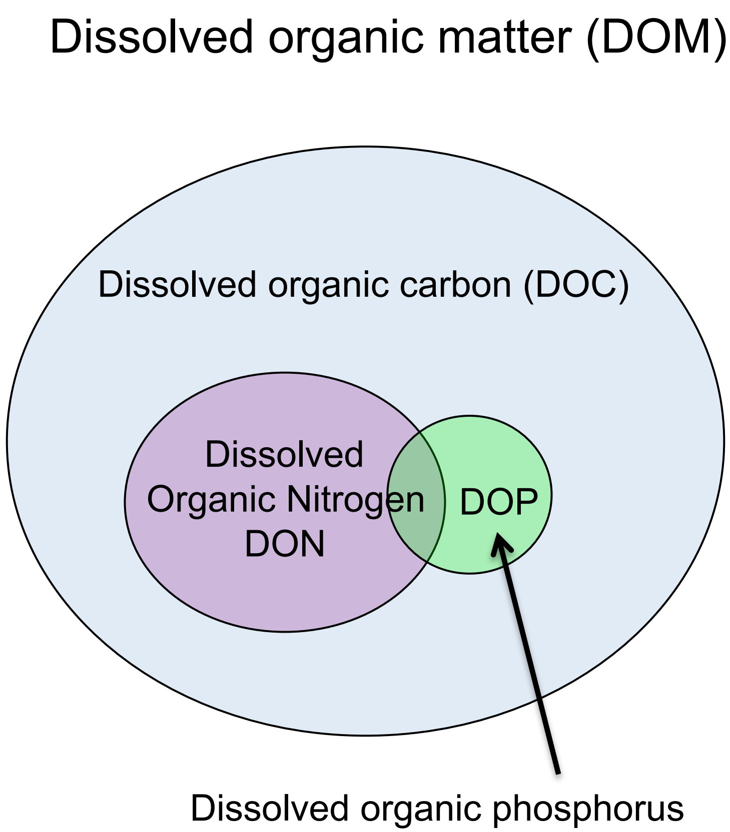
Summary *(continued)*

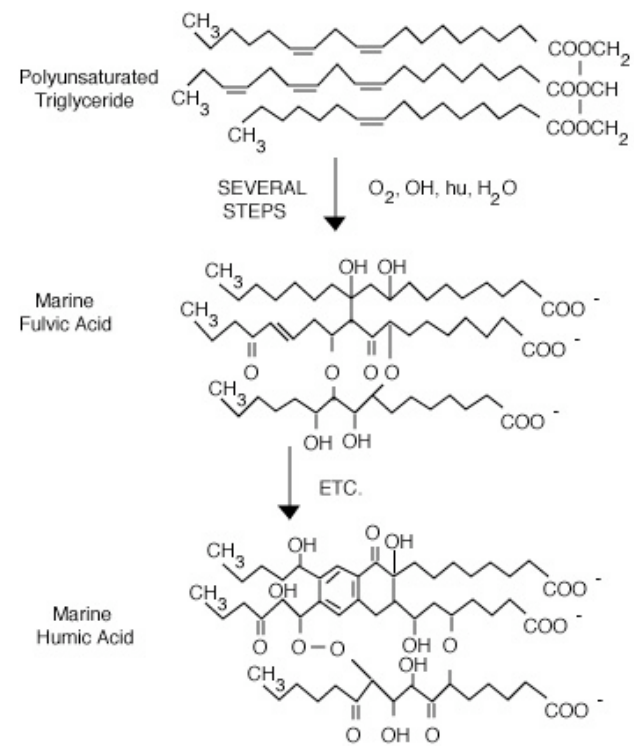
Microbial oxidation is the largest sink for DOM, and is tremendously efficient; returning 99% of (photoautotrophic) microbially produced DOC to CO_2.

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

What is the chemical composition of DOM?

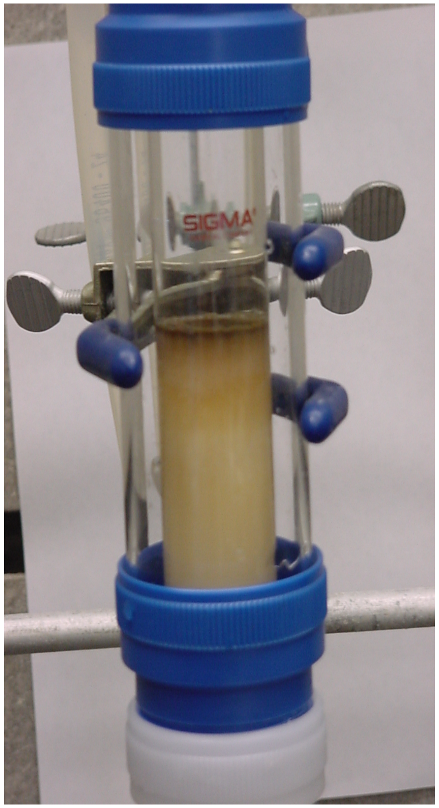
How are source, radiocarbon value and distribution linked in the ocean?
Is the reactivity (e.g the flux) and inventory of DOC affected by composition?

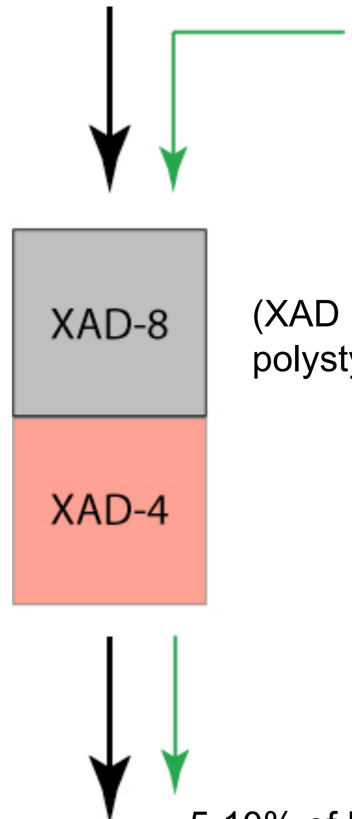


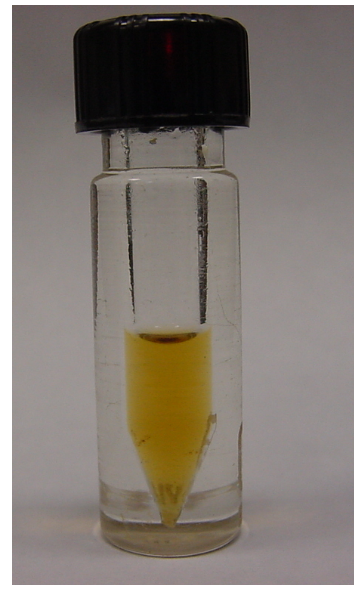


Proposed pathway to marine humic substances by oxidative crosslinking of polyunsaturated lipids catalyzed by ultraviolet light and transition metals. (Harvey et al. 1983)

Isolation of DOM by adsorption onto hydrophobic resins



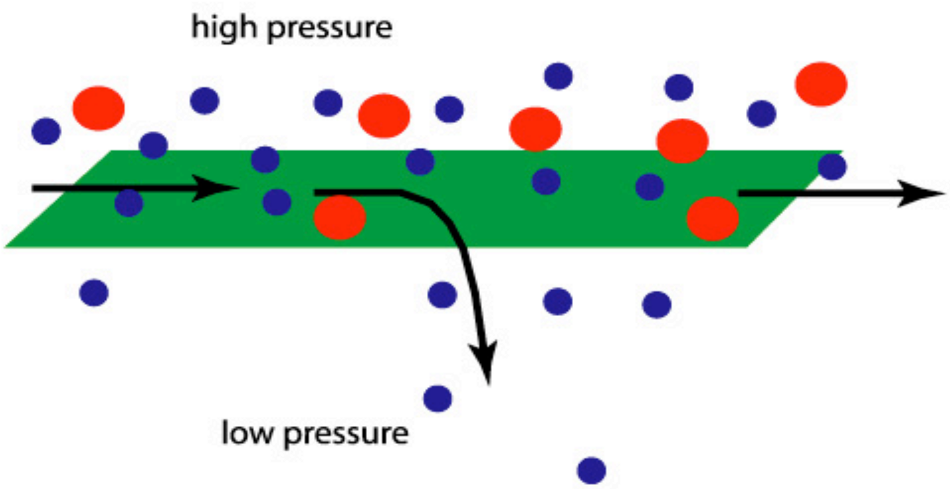




sample

Isolation is chemically selective- based on affinity for resin.
XAD selects for hydrophobic organic matter with an old radiocarbon age.

Cross or tangential flow filtration, Ultra- or nanofiltration



Separation based on size

1 nm pore @ 1 kD

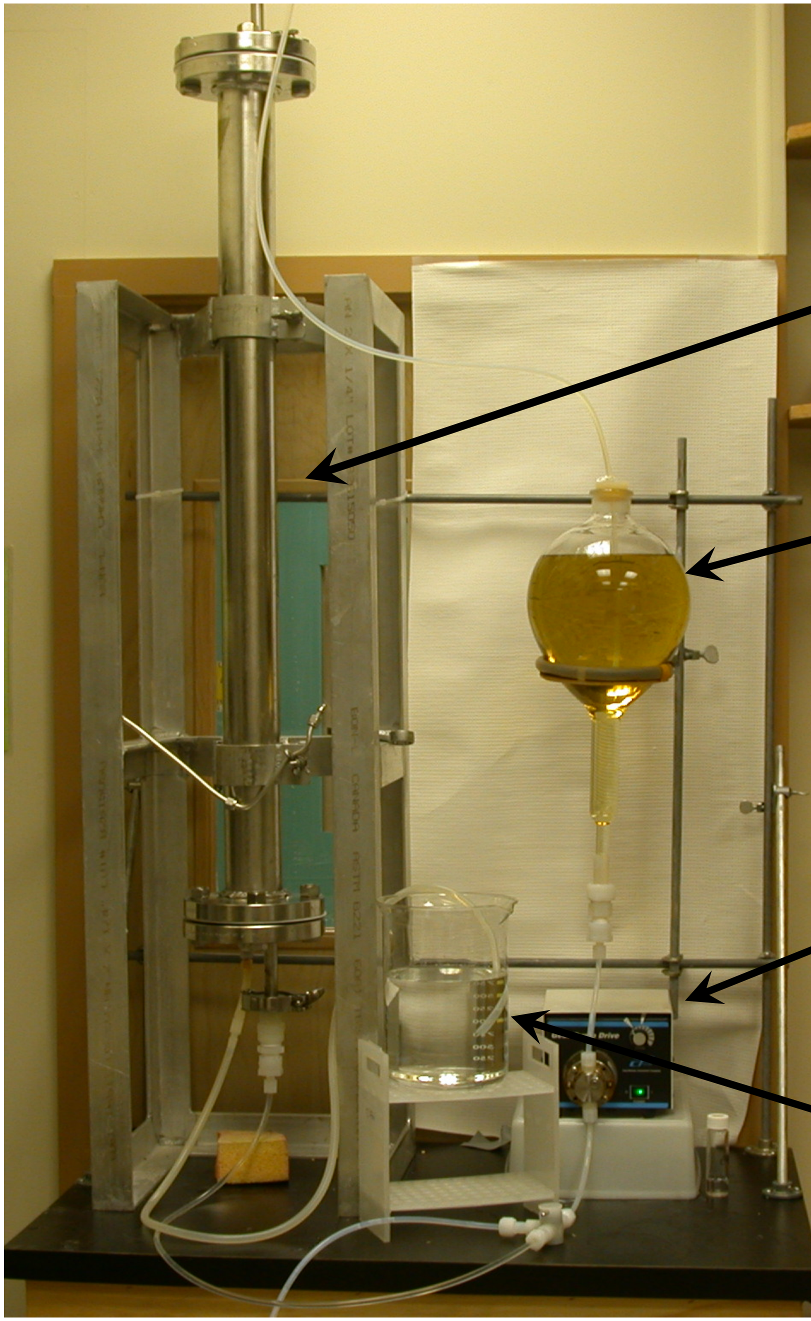
Selects for HMW fraction

about 30-35% TOC (now up to 80% using electrically assisted UF)

C/N = 15-16
C/P = 150 to > 500 (*f(z)*)

Membrane effects what is collected

DOC sampling



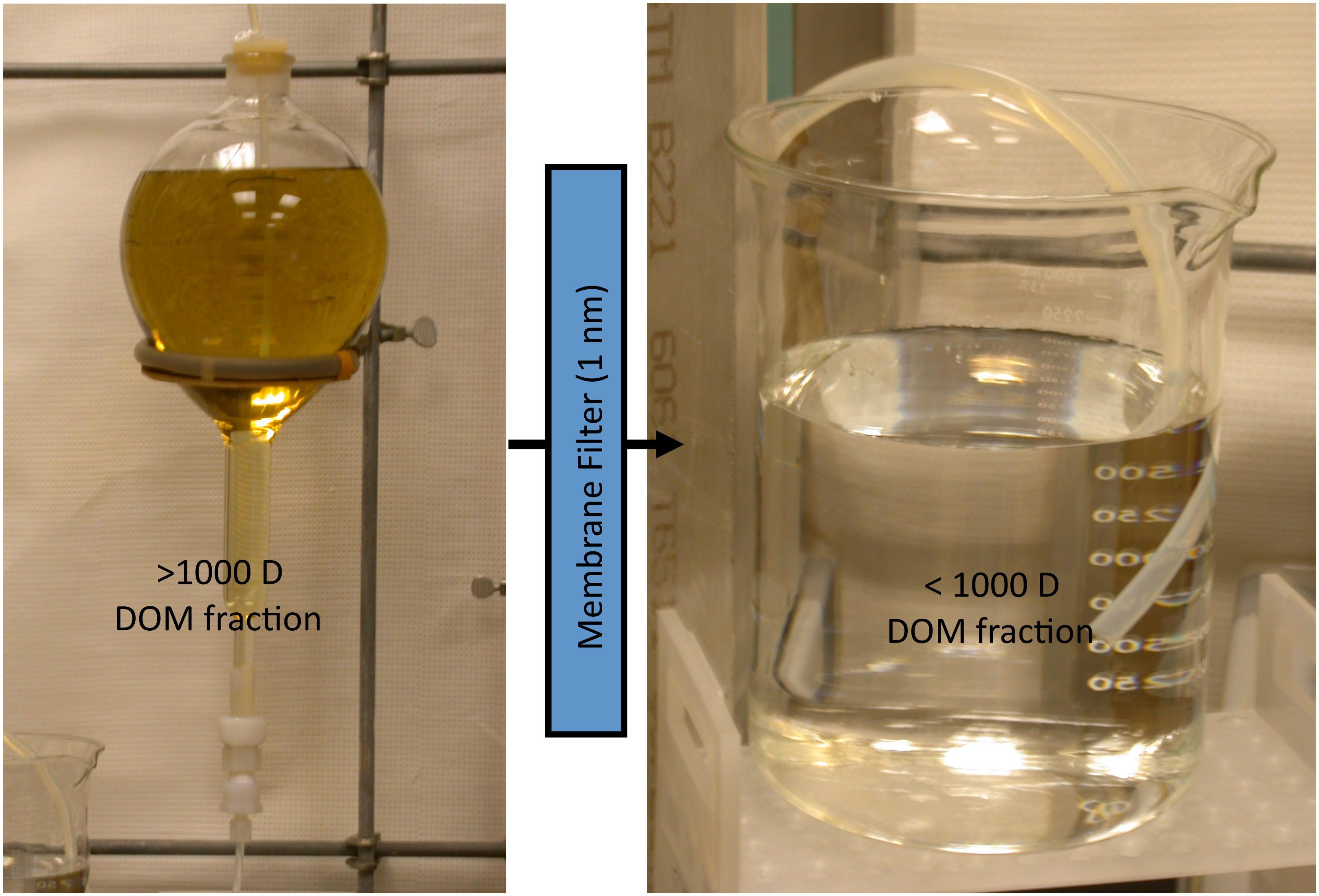
filter (1 nm)

sample concentrate (> 1000 MW)

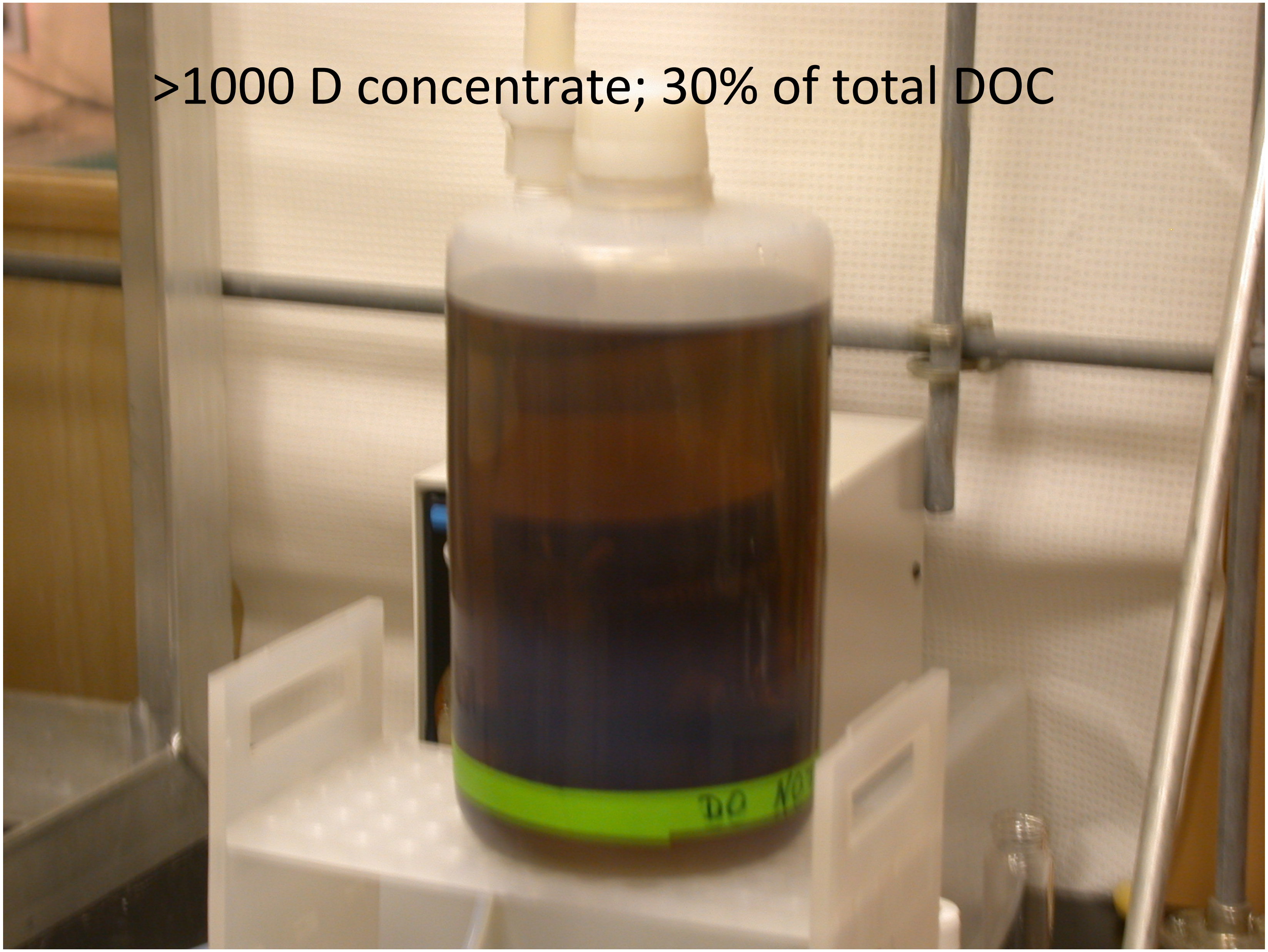
pump

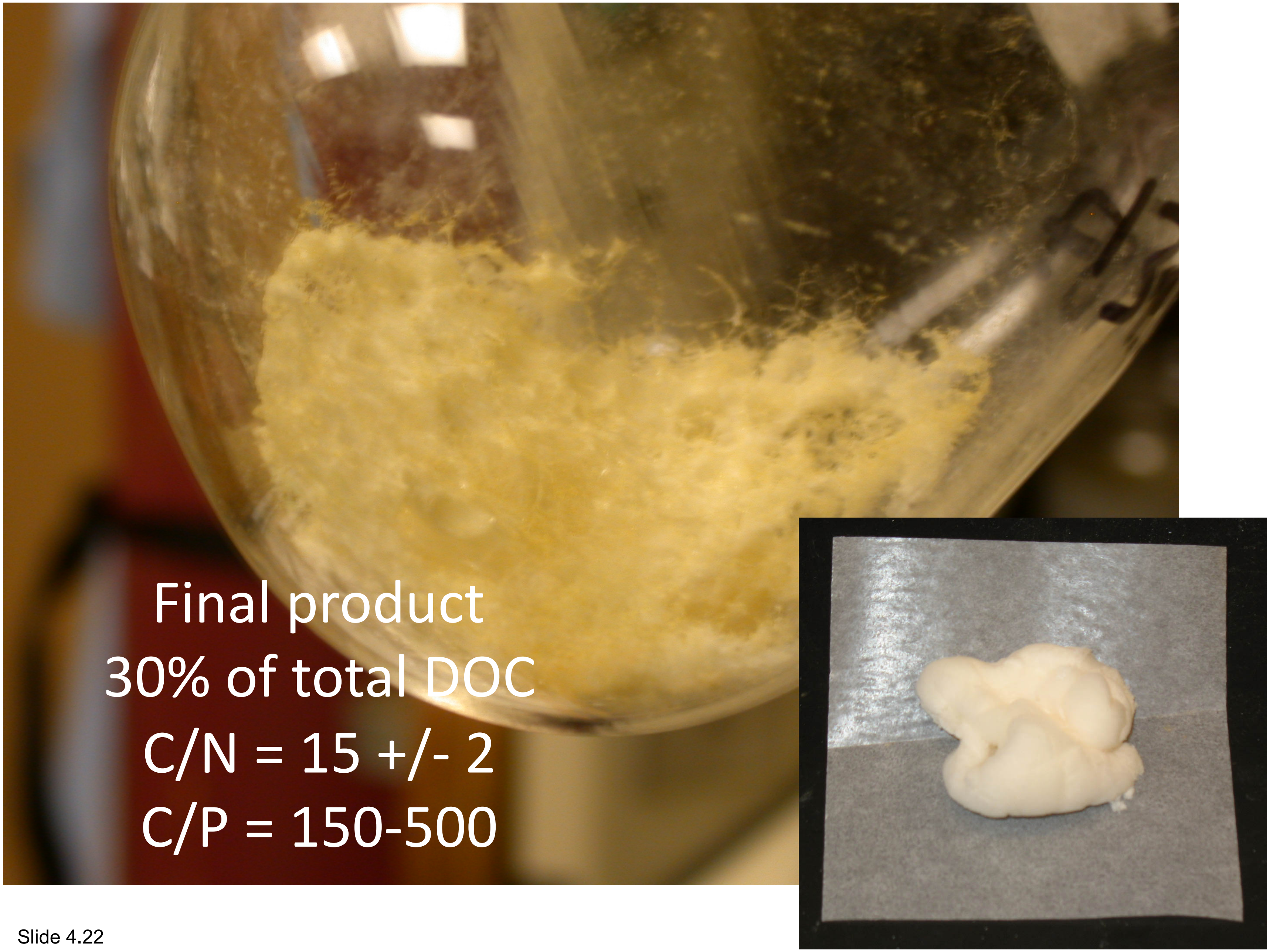
filtrate (< 1000 MW)

Ultrafiltration of high molecular weight DOM (HMWDOM)



>1000 D concentrate; 30% of total DOC





Slide 4.22

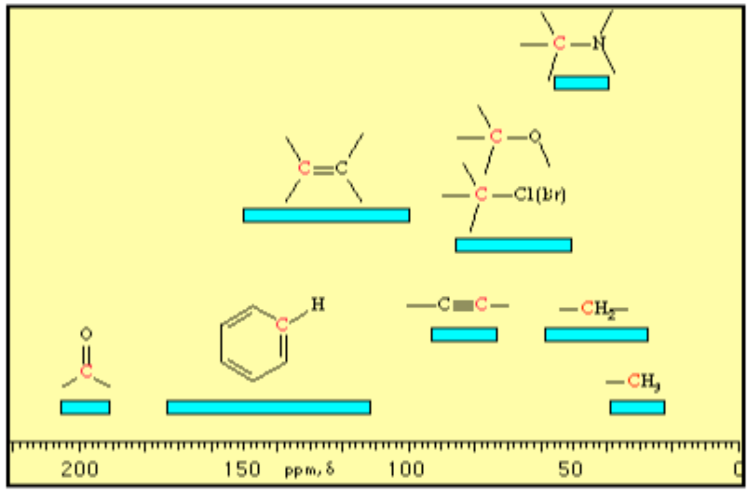
Nuclear Magnetic Resonance
Spectroscopy (NMR)

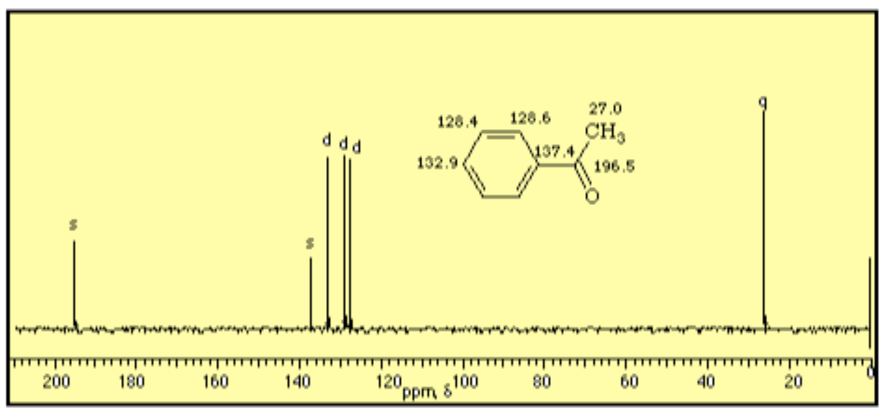
Can be tuned to different
Nuclei of interest (C,N,P…).

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

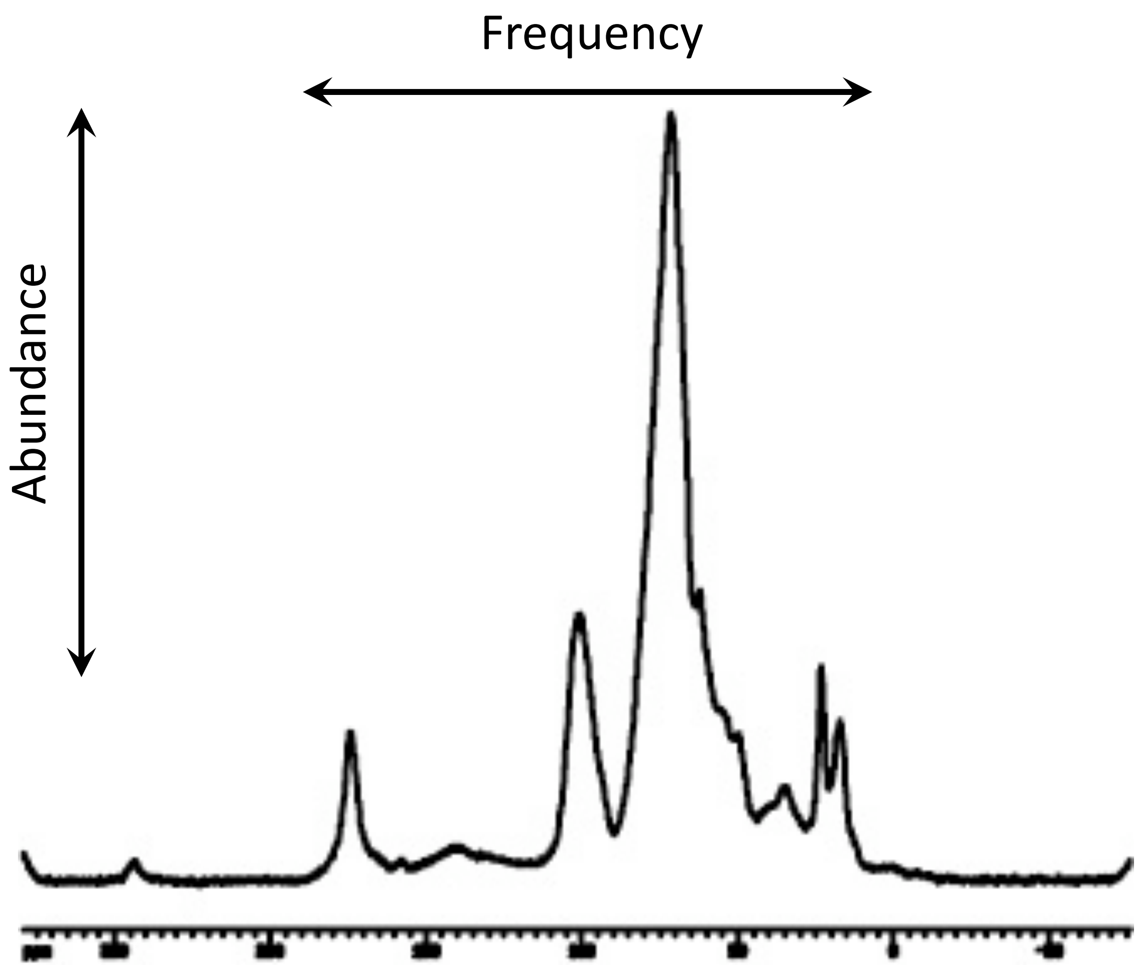
Internally quantitative.

Carbon 13 Nuclear Magnetic Resonance Spectroscopy





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



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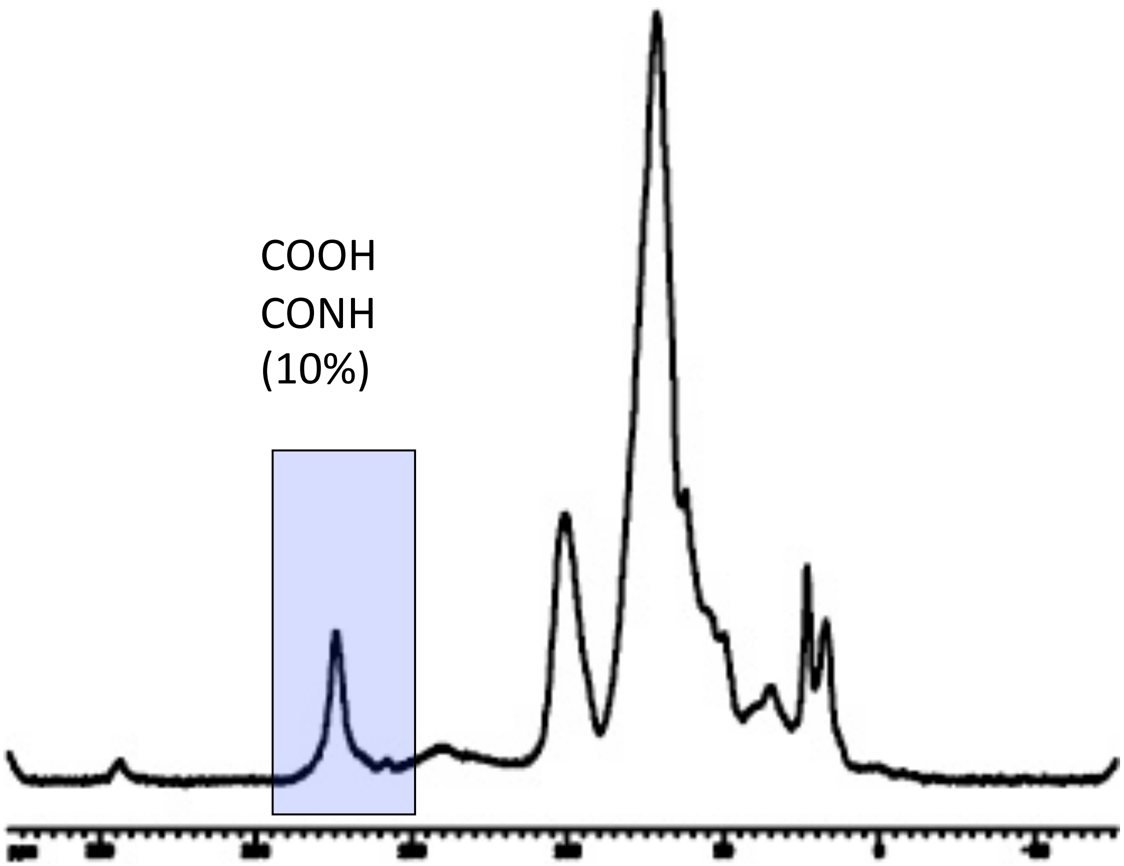

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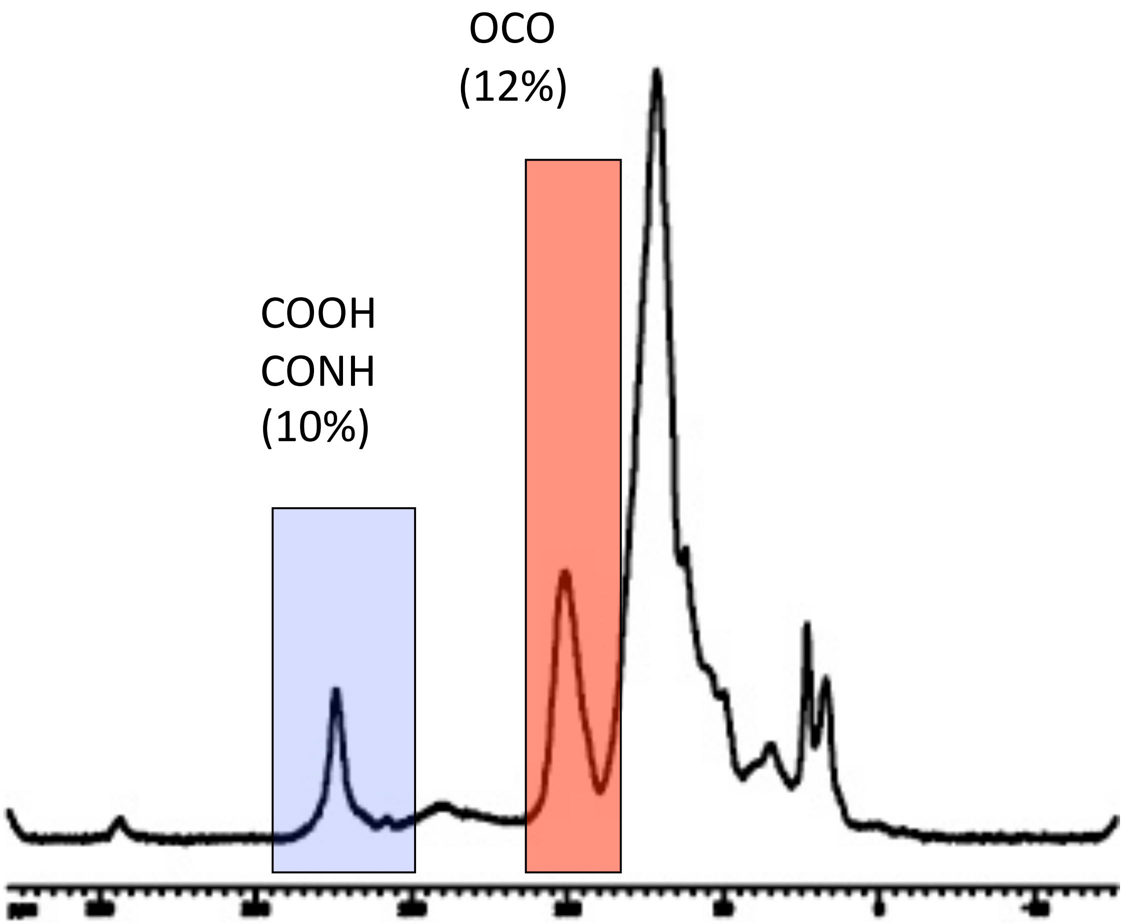

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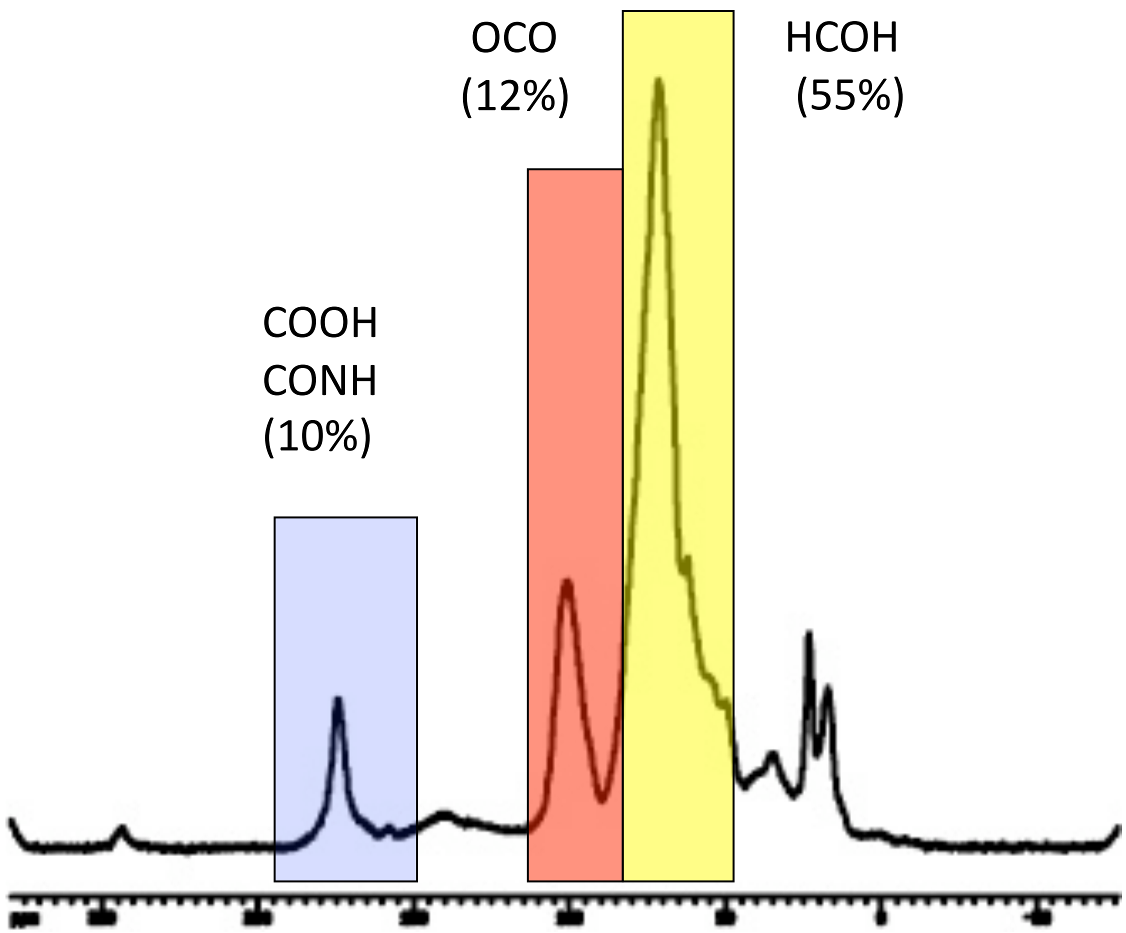

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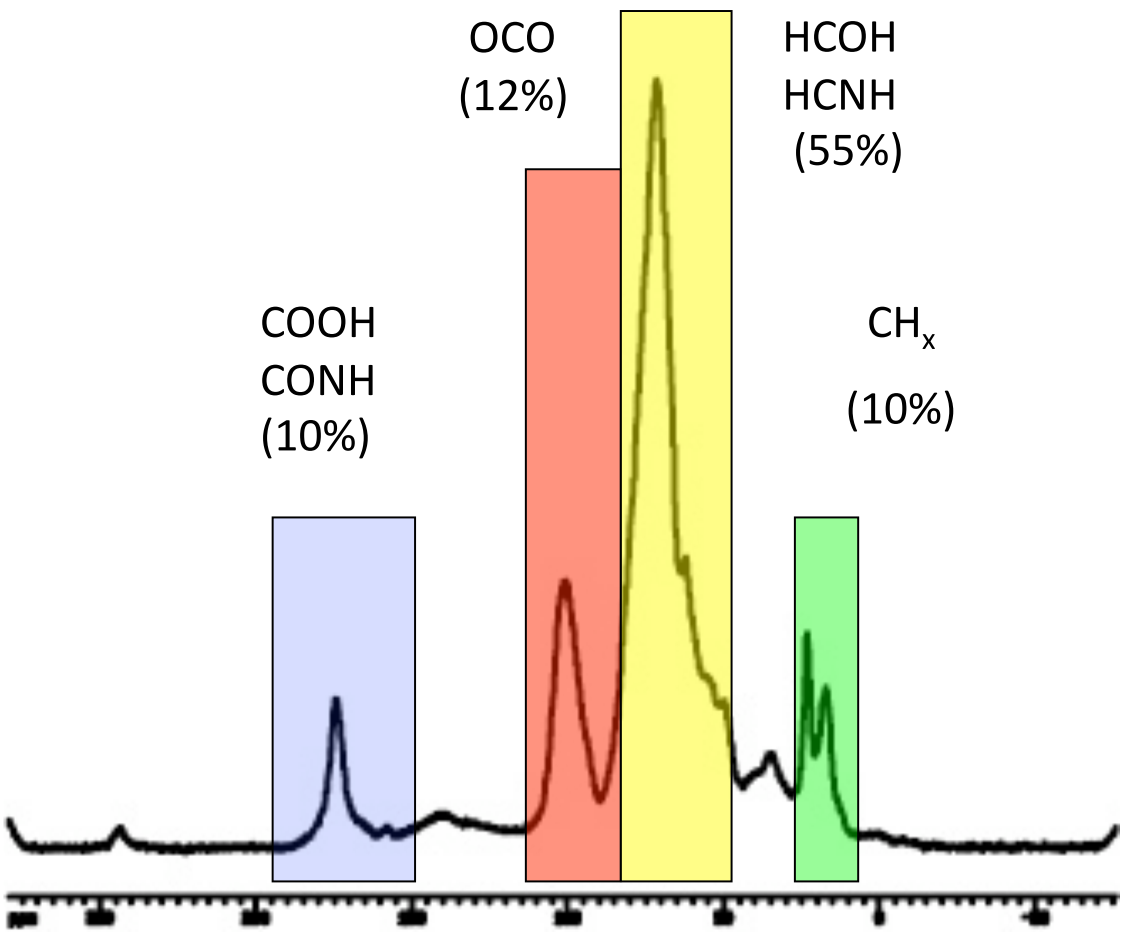
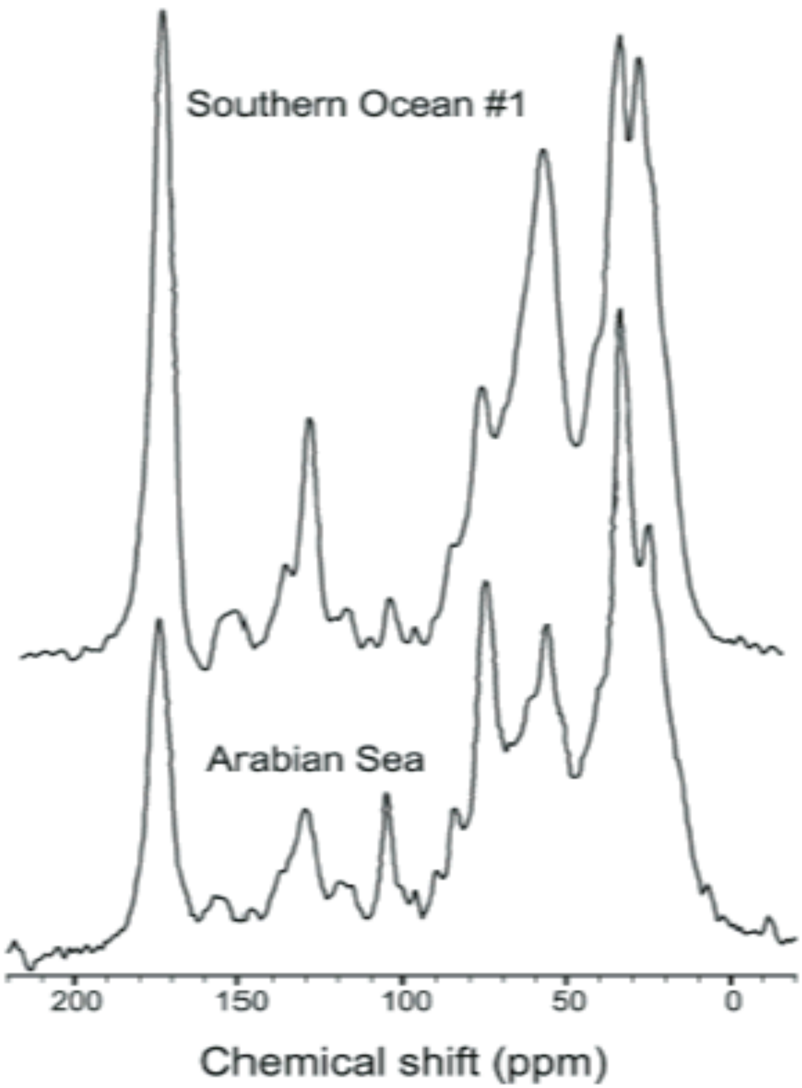


Proximate analysis of algal cells

Chlorophyceae	**Protein**	**Carbohydrate**	**Lipid**	**Ash**
(green algae)				
Tetraselmis maculata	72	21	7	(24)
Dunaliela salina	58	33	10	(8)
Chrysophyceae				
(golden brown algae)				
Monochrysis lutheri	53	34	13	(6)
Syracosphaera carterae	70	23	7	(37)
Bacillariophyceae				
(brown algae, diatoms)				
Chaetoceros sp.	68	13	16	(28)
Skeletonema costatum	58	33	10	(39)
Coscinodiscus sp.	74	16	10	(57)
Phaeodactylum tricornutum	49	36	14	(8)
Dynophyceae				
(dinoflagellates)				
Amphidinium carteri	35	38	23	(14)
Exuriella sp.	37	44	20	(8)
Average	**57**	**29**	**13**	

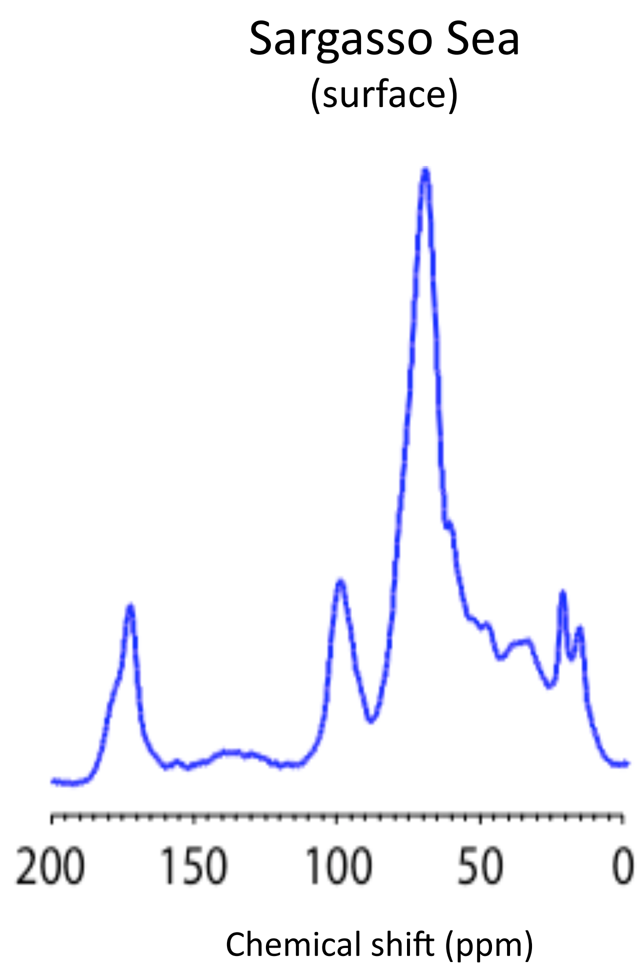
Most POM is protein, and this is probably a large fraction of reactive DOM
Dissolved “free” amino acids have been measured in seawater at 10’s nM

^{13}CNMR of plankton tows



Hedges et al GCA 2001

^{13}CNMR of HMWDOM



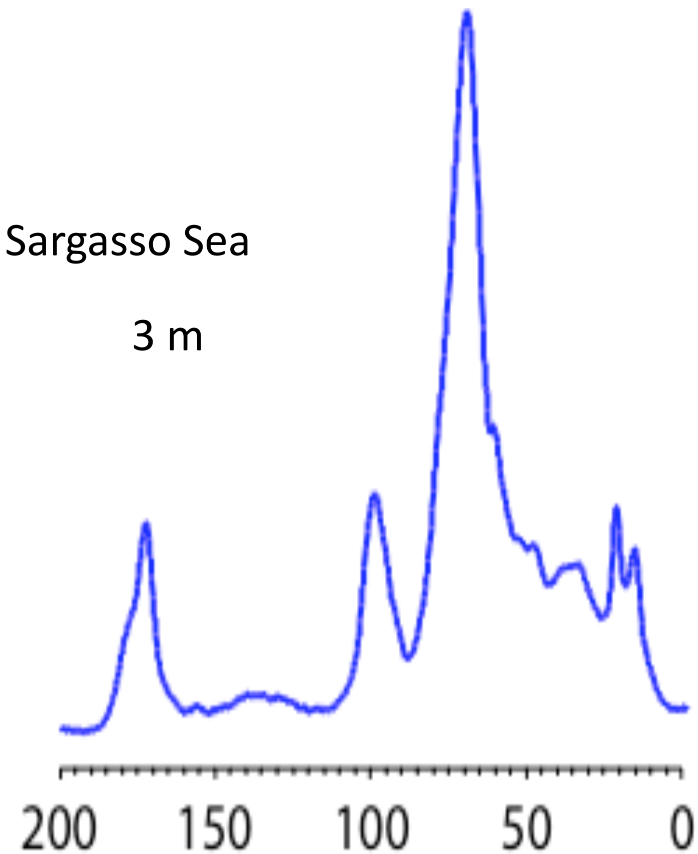
What are the biochemical ingredients of HMWDOM?

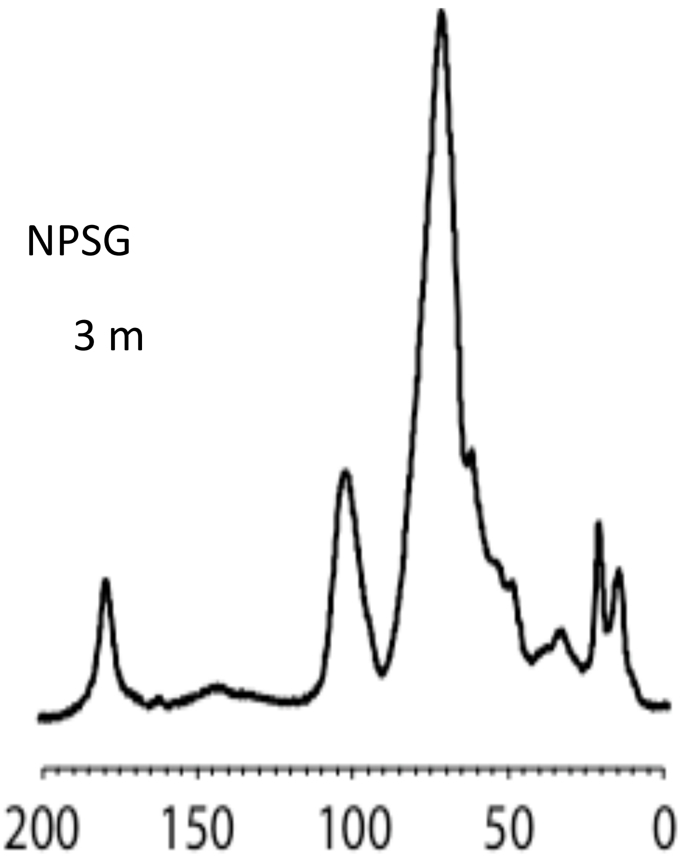
From our knowledge of cell biochemicals…
C/N….COOH:OCO:HCOH:CH_x…

HMWDOM	C/N = 15	CHx:HCOH:OCO:COOH =1:5.5:1.2:1
Proteins	C/N = 4,	CH_x(O):CON = 3:1
Carbohydrates	C maybe N	OCO:HCOH = 1:5
Lipids	C only	CH_x:COOH = 2-18 CH_x:COH = 2-30

unsolved mysteries #1…Carbohydrates are thought to be easily degraded by microbes, so why is the ocean filled with carbohydrate?

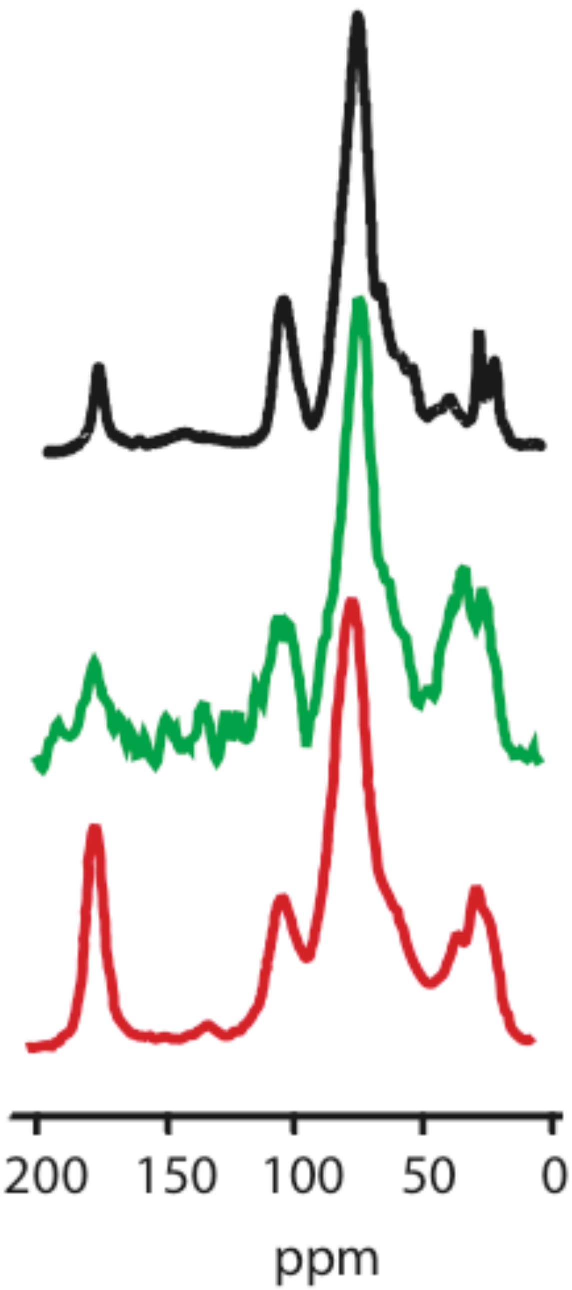
^{13}CNMR spectra of HMWDOM





unsolved mysteries #2…if the source of DOC is marine plants, and plants change with location, why is the ocean filled with the same type of carbohydrate everywhere?

HMWDOM in different aquatic environments



NPSG

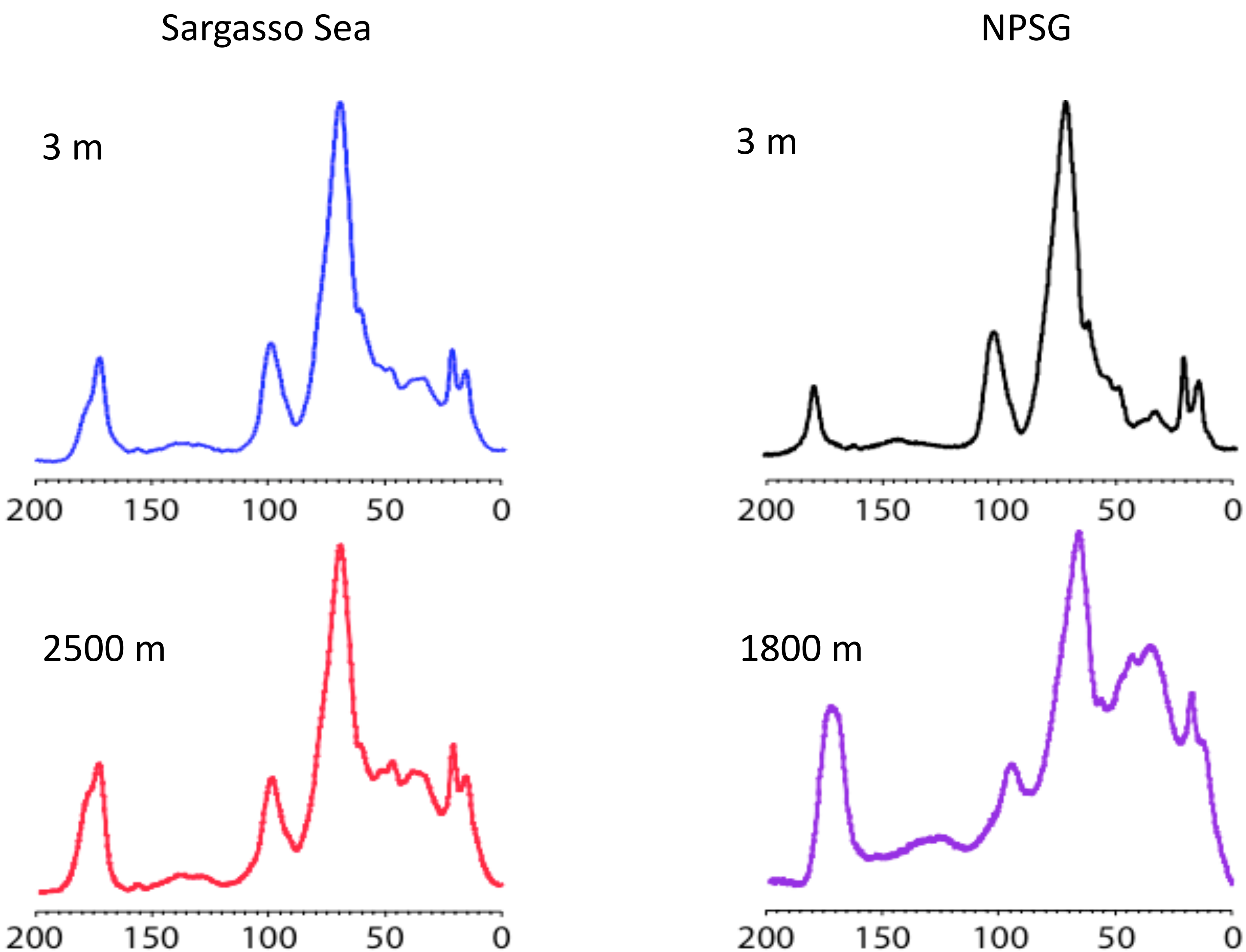
Andrews Creek

+3500 m in Rocky Mountains National Park

Great Salt Lake

Diane McKnight et al, BGC 1997; Jim Leenher, BGC 2004

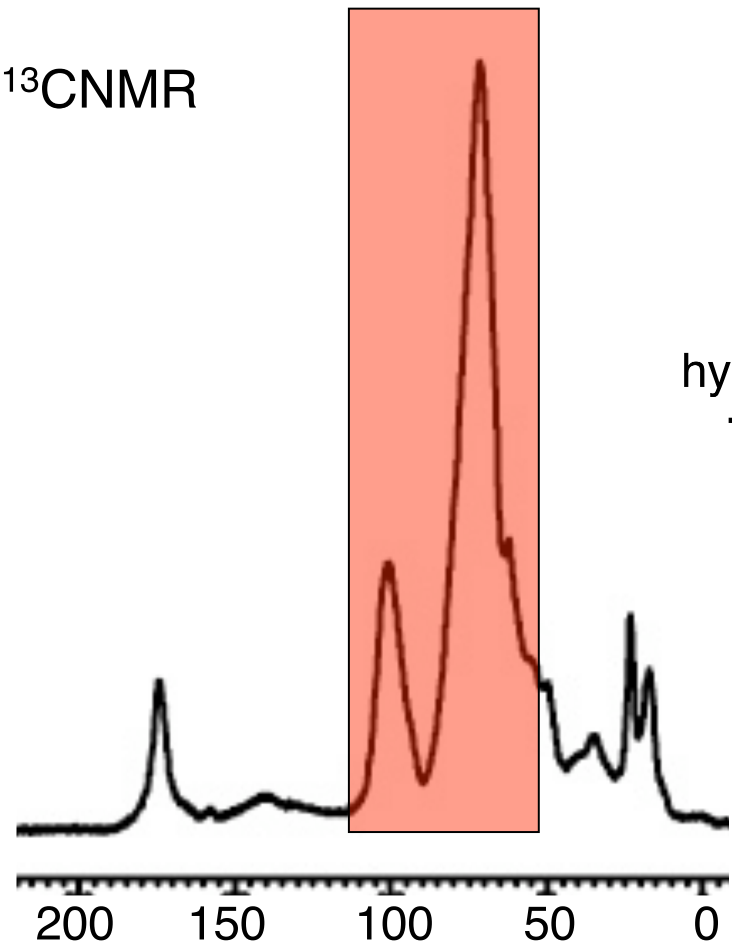
HMWDOM in the deep sea



Spectral and chemical analyses of HMWDOC

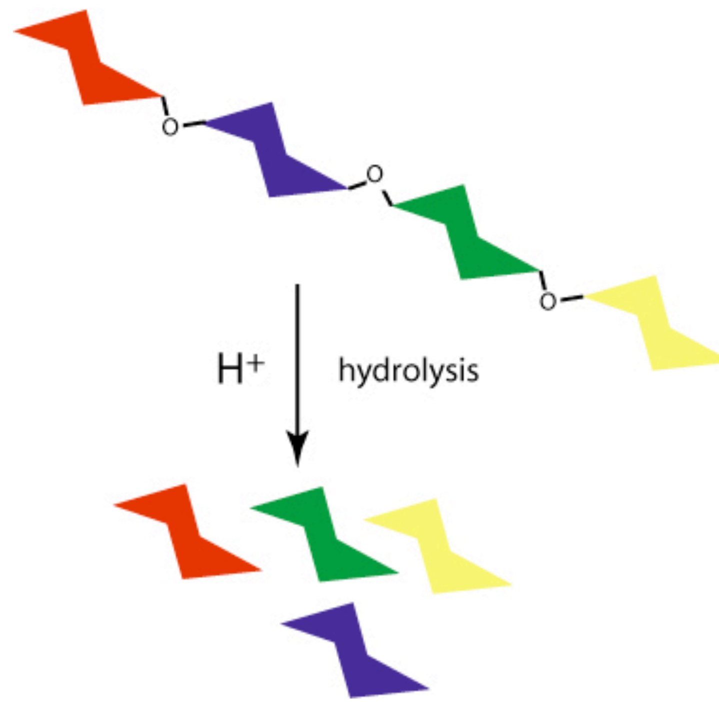
Carbohydrate
70-90% of surface water HMWDOC

^{13}CNMR

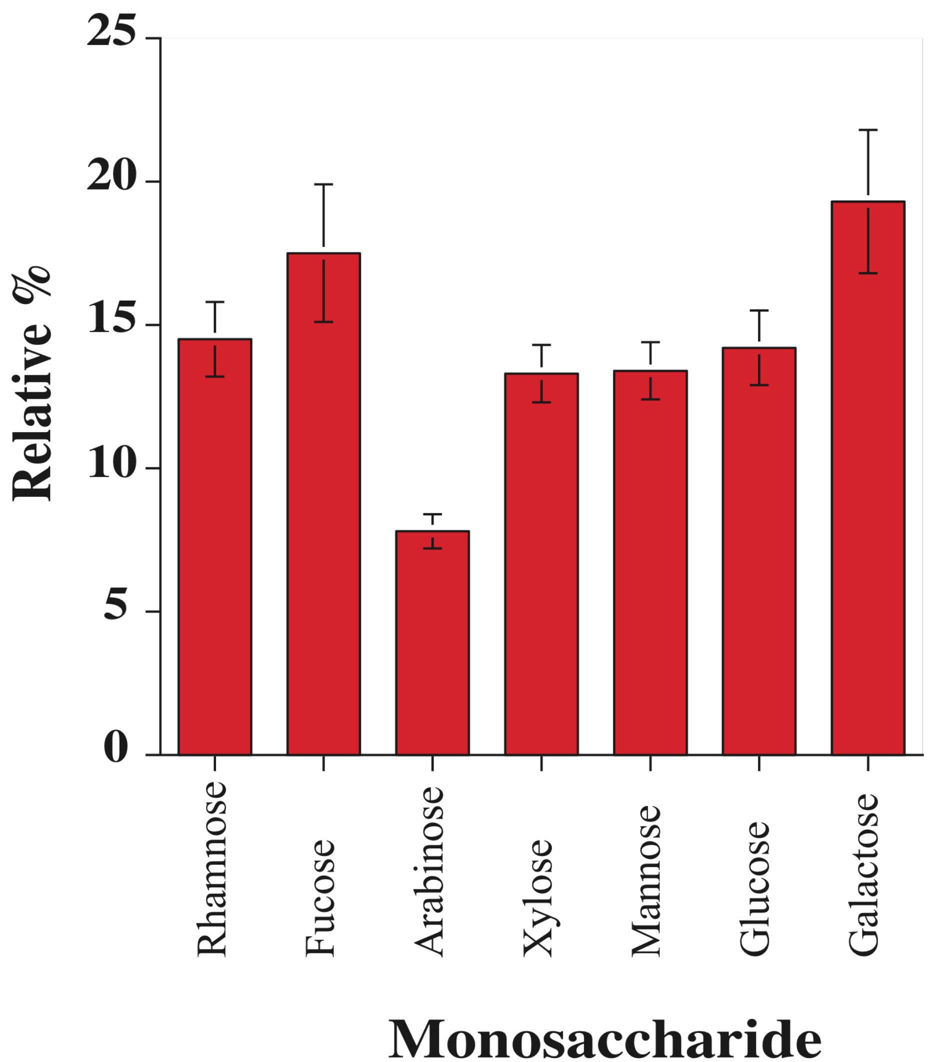


Acid hydrolysis →

Acid hydrolysis followed by
Monosaccharide analyses
yields 7 major neutral sugars
that represent 10-20% of HMWDOC
in surface water



Relative abundance of sugars in HMWDOC

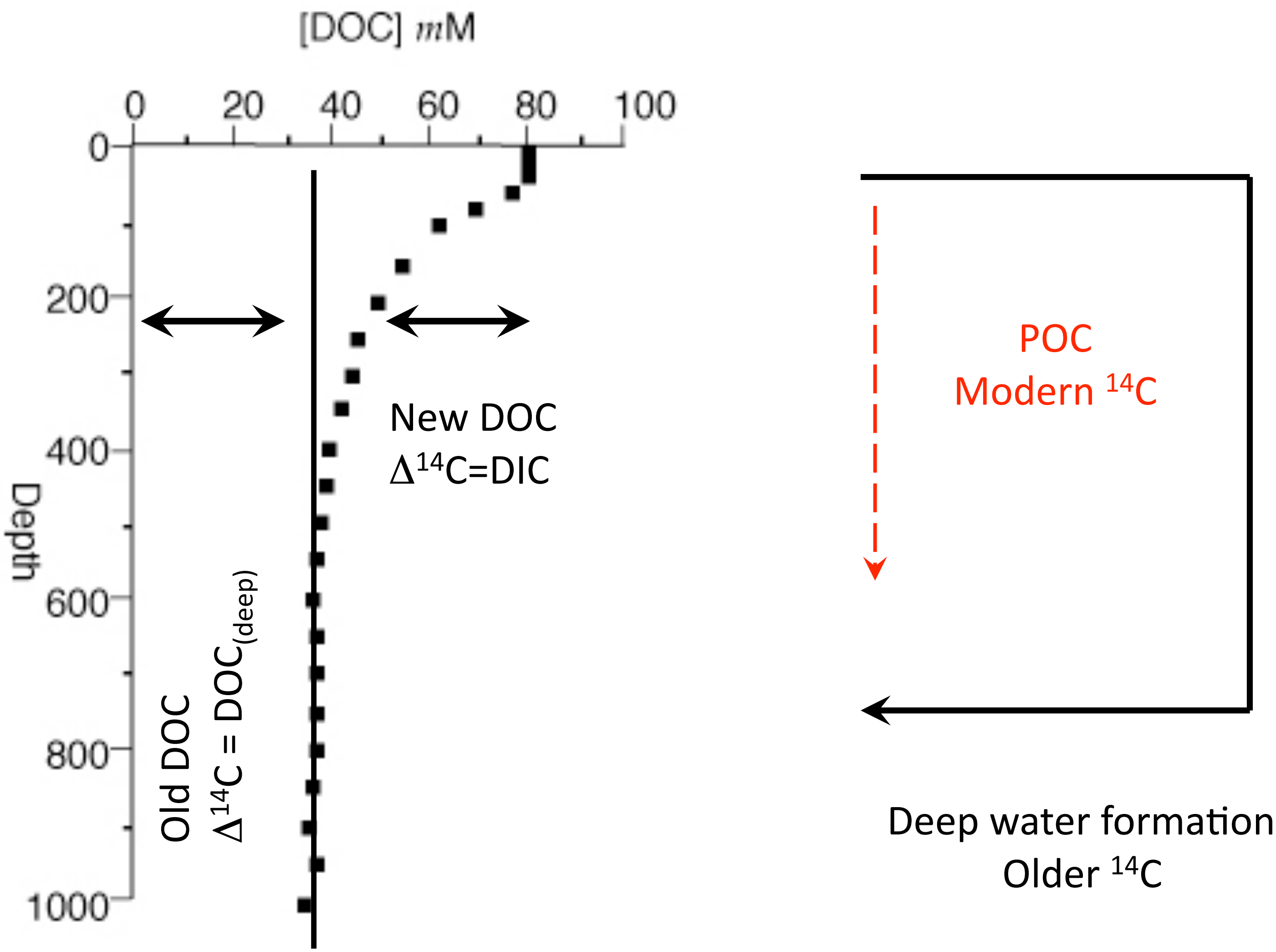


A good number of HMWDOM samples have been analyzed after hydrolysis for simple sugars or monosaccharides. In every case, hydrolysis yields seven major neutral sugars. Samples include HMWDOM from the North Pacific, North and South Atlantic, near shore, estuary, and open ocean water; surface and deep.

The mixture of neutral sugars found in HMW-DOM is not typical of polysaccharides, which tend to have a narrower range of sugars, and a few dominant sugars. HMWDOM has a large number of sugars in about equal amounts.

The small range in relative % composition suggests that these sugars are linked into a common macromolecular structure, and is not a mixture that can vary spatially and temporally.

Sequestration of DOC in the deep sea



Radiocarbon analyses of HMWDOC carbohydrates in surface water

Sample	Hawaii	NPSG
DIC	72±7‰ (n=4)	89±7‰*
Glucose	47, 58	79
Galactose	67	103
Mannose	65	99
Xylose	52, 58	94
Arabinose	63	ND
Fucose	49, 52	69
Rhamnose	40, 57	57
Average sugar	56±6‰	89±13‰

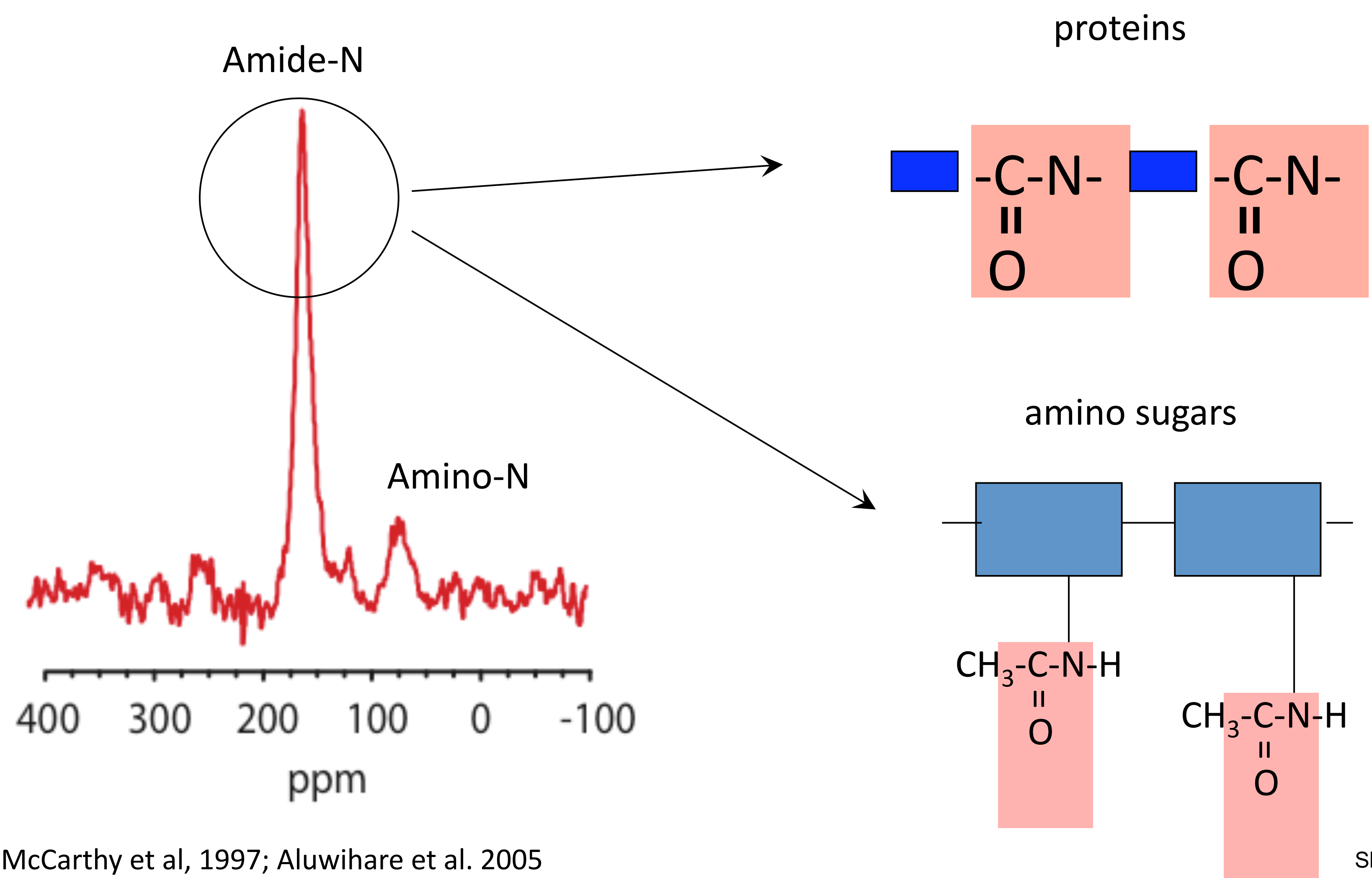
*data from Ellen Druffel

Enrichment of $\Delta^{14}C$ in deep sea HMWDOM carbohydrate

	DIC$\Delta^{14}C$(‰)	HMWDOC$\Delta^{14}C$	sugars $\Delta^{14}C$
Surface	89$\pm$7	46	84$\pm$17
600m	-155$\pm$7	-259	-122$\pm$18
3600m	-240$\pm$7	-381	-145$\pm$23

What else is in HMWDOM ?

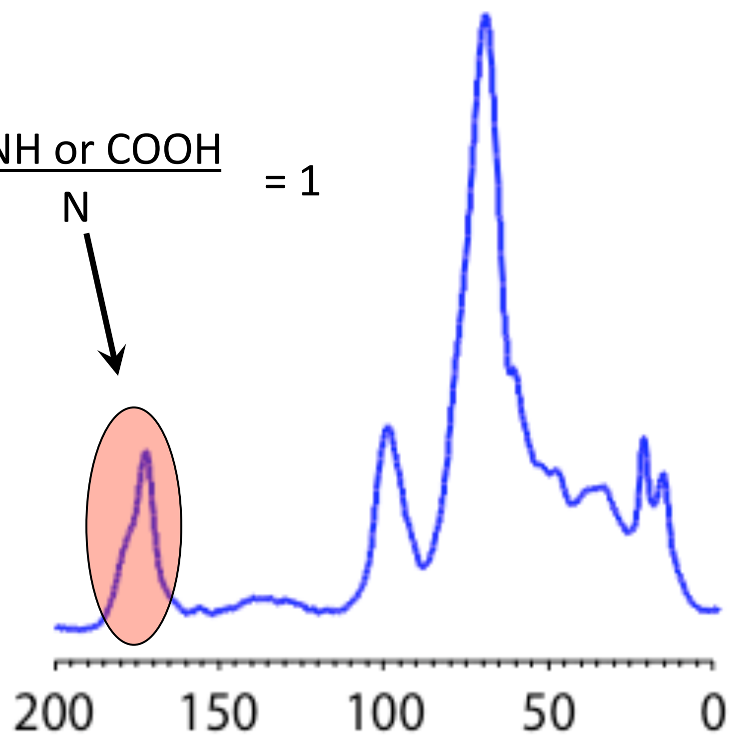
^{15}N NMR



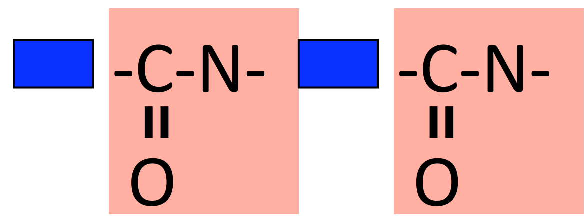
McCarthy et al, 1997; Aluwihare et al. 2005

C/N = 15, if all N is amide, then
CON should be about 7% of the total
C, which it is....

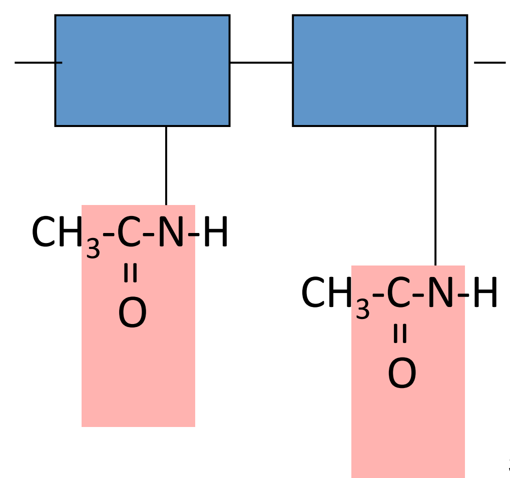
$$\frac{\text{CONH or COOH}}{\text{N}} = 1$$



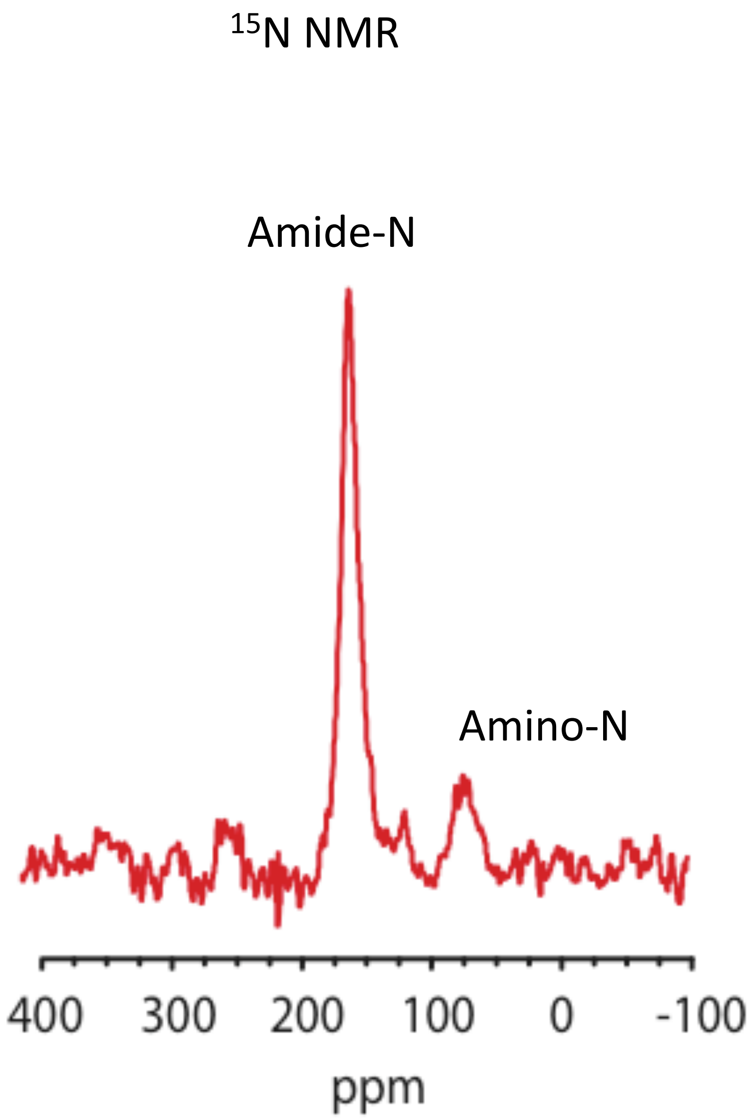
proteins

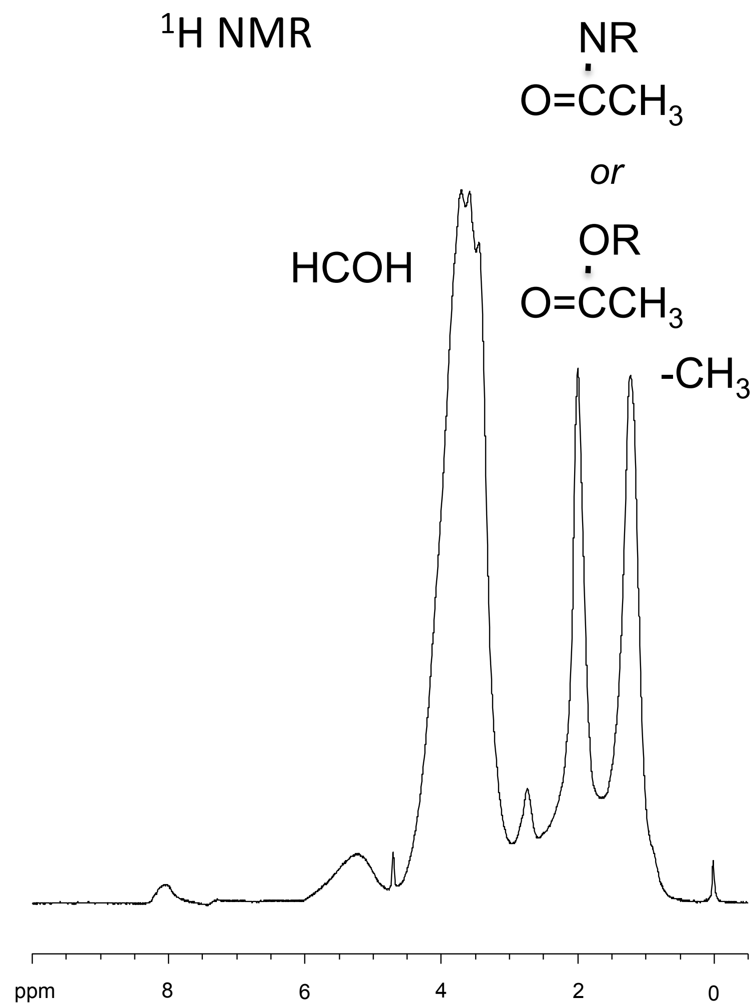


amino sugars



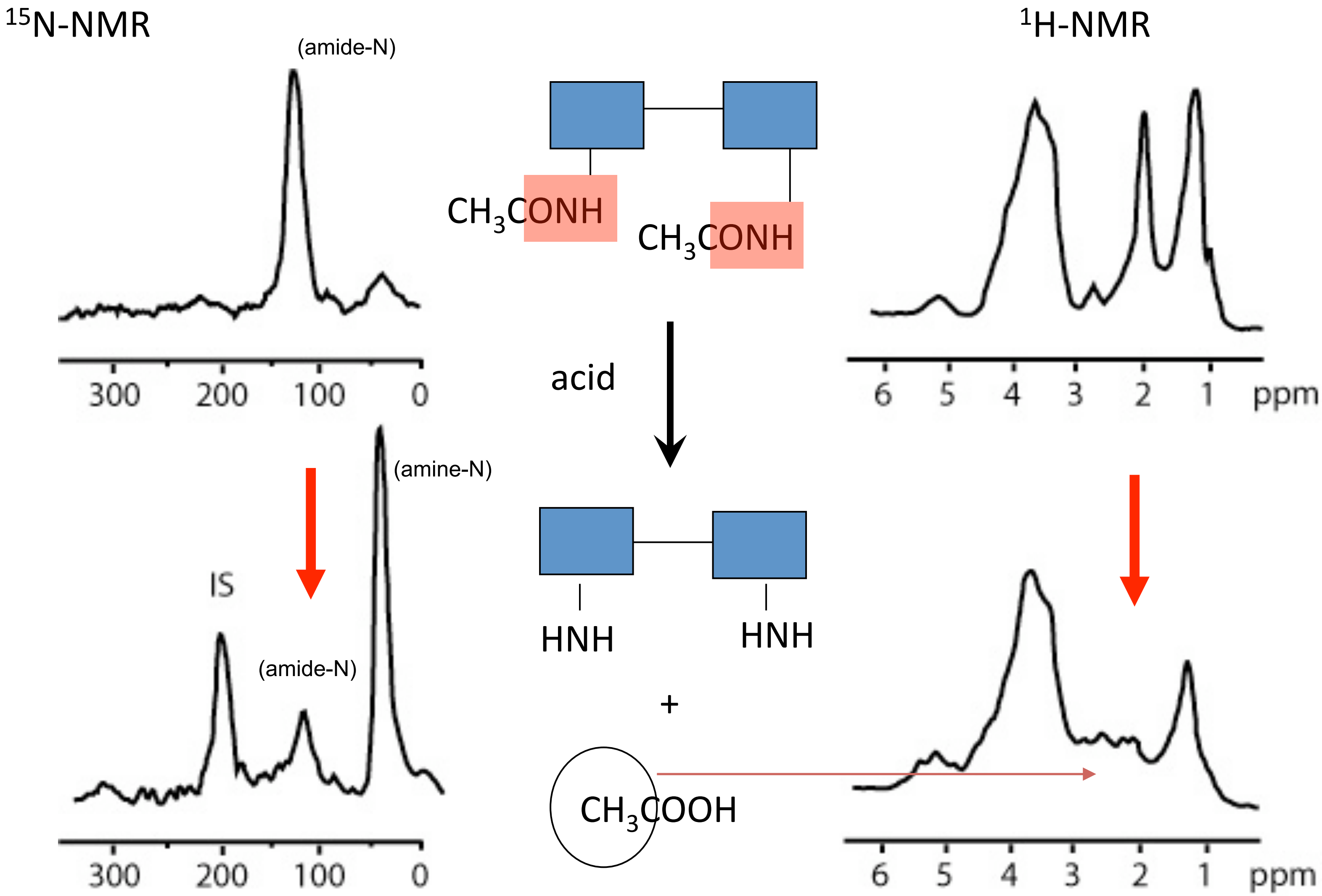
What else is in HMWDOM ?



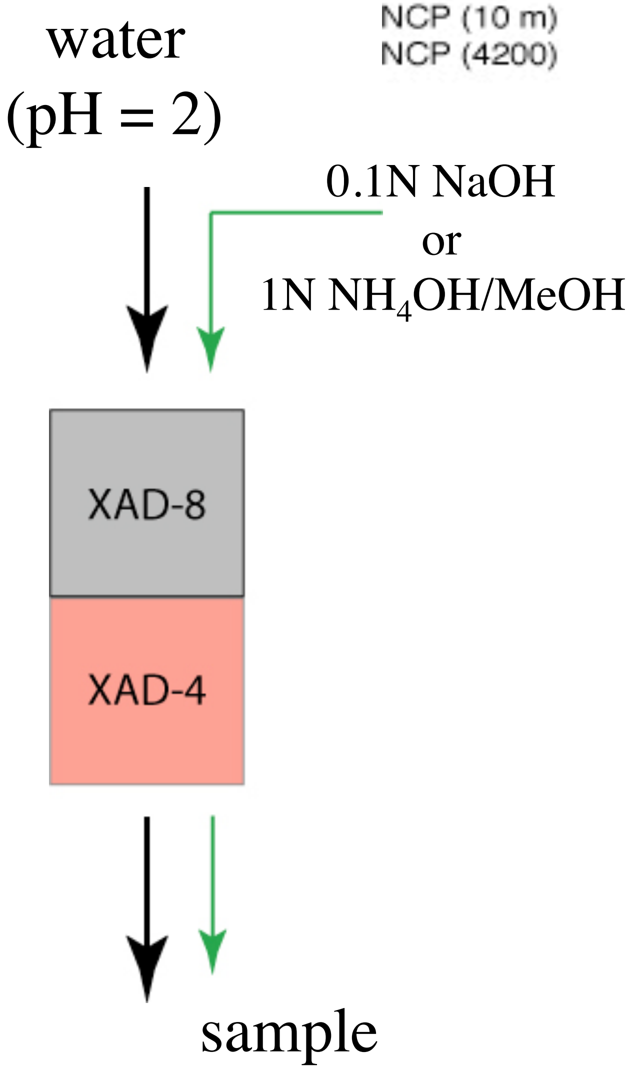


McCarthy et al, 1997; Aluwihare et al. 2005

Is a large fraction of HMWDOC and HMWDON from amino sugars?

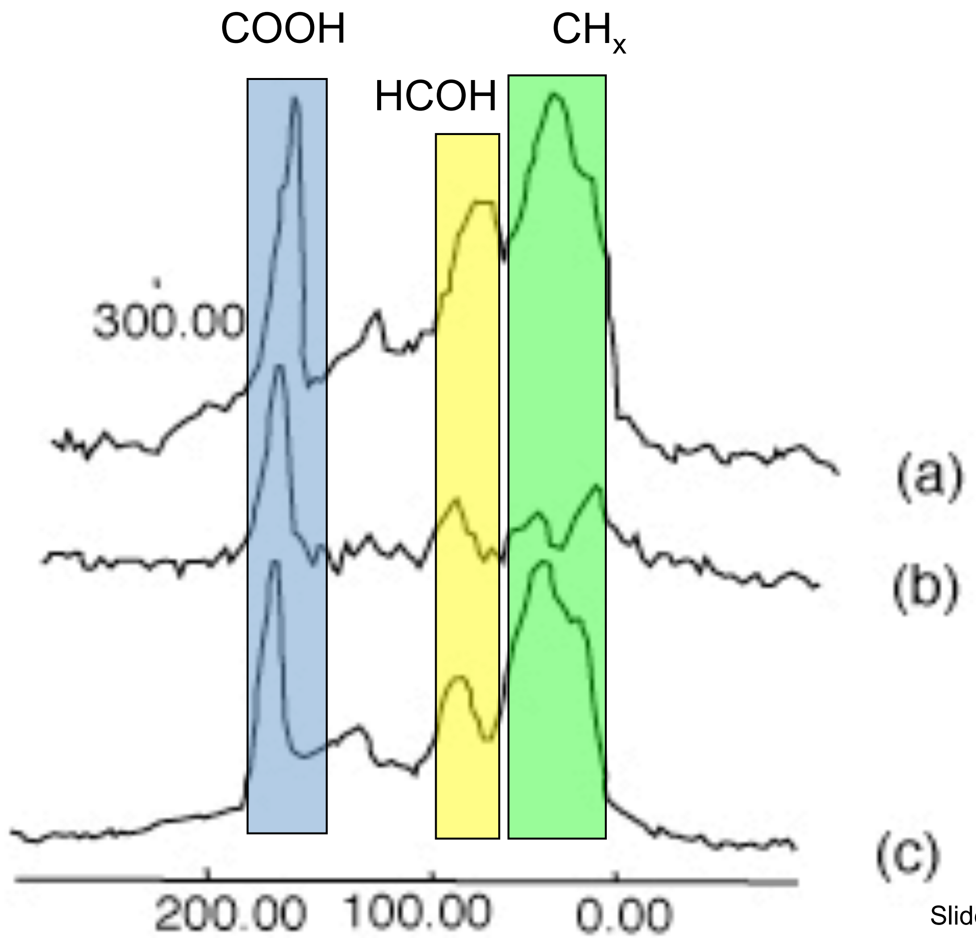


Hydrophobic (XAD collected) DOM in North Pacific Ocean

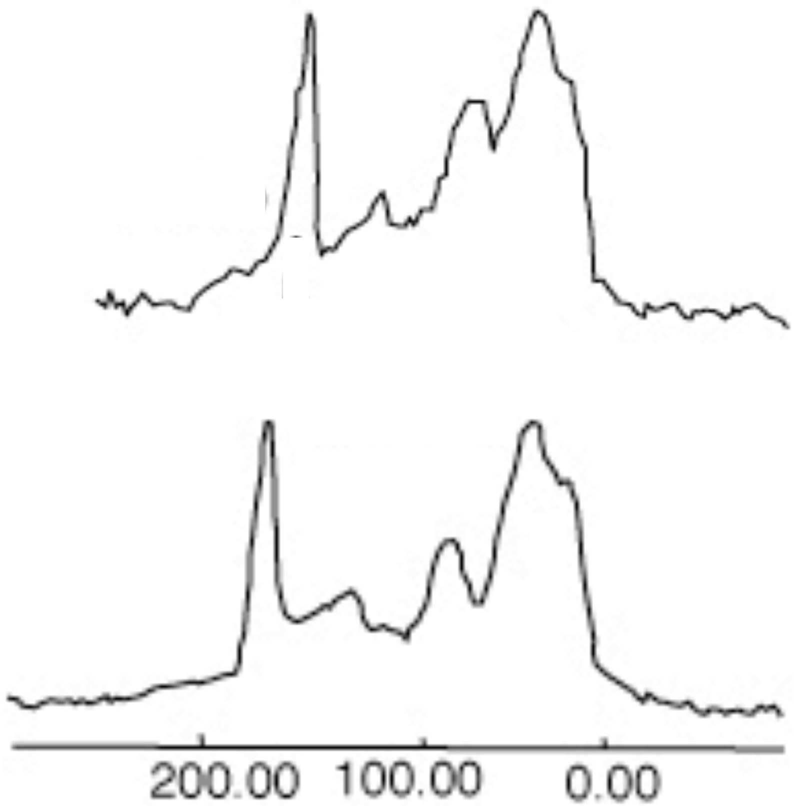


Pacific Ocean samples

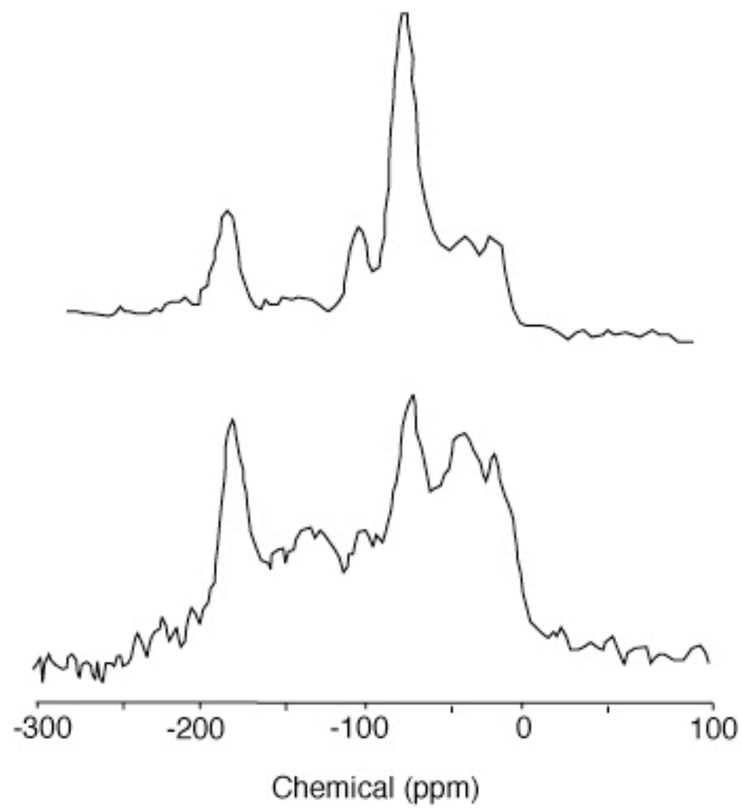
EEP (5 m)	51	36	1.6	45	18	18	15	5	-22
NCP (10 m)	48	46	1.2	44	20	20	16	ND	-22
NCP (4200)	50	43	1.2	46	17	19	15	3	-22



A comparison of ^{13}CNMR spectra of XAD and ultrafiltration collected DOM in surface (top) and 4200 m (bottom) Pacific seawater



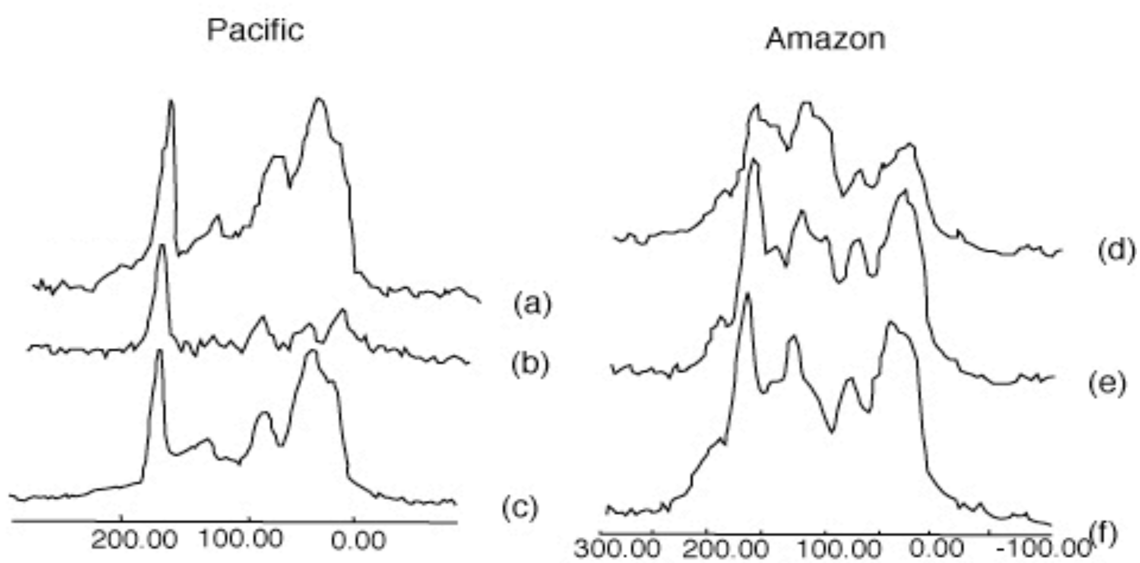
XAD DOM



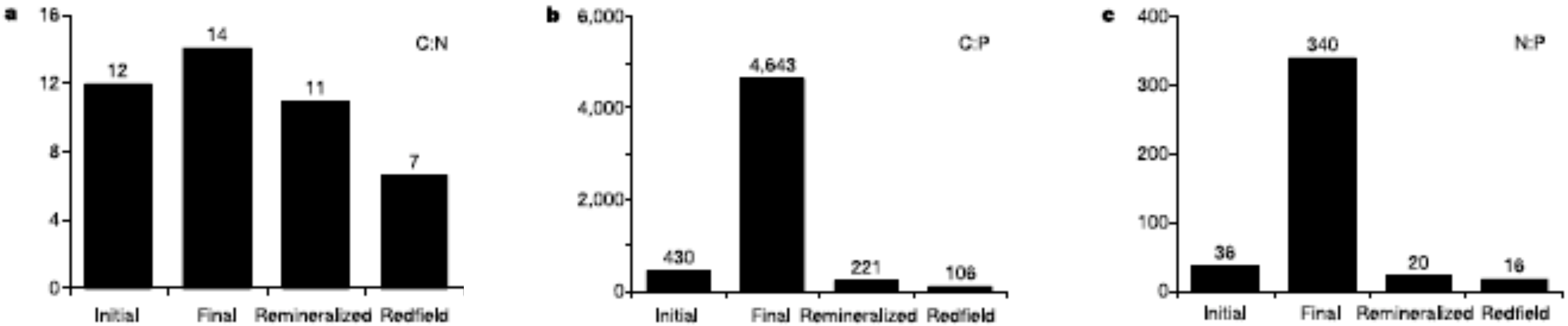
HMWDOM

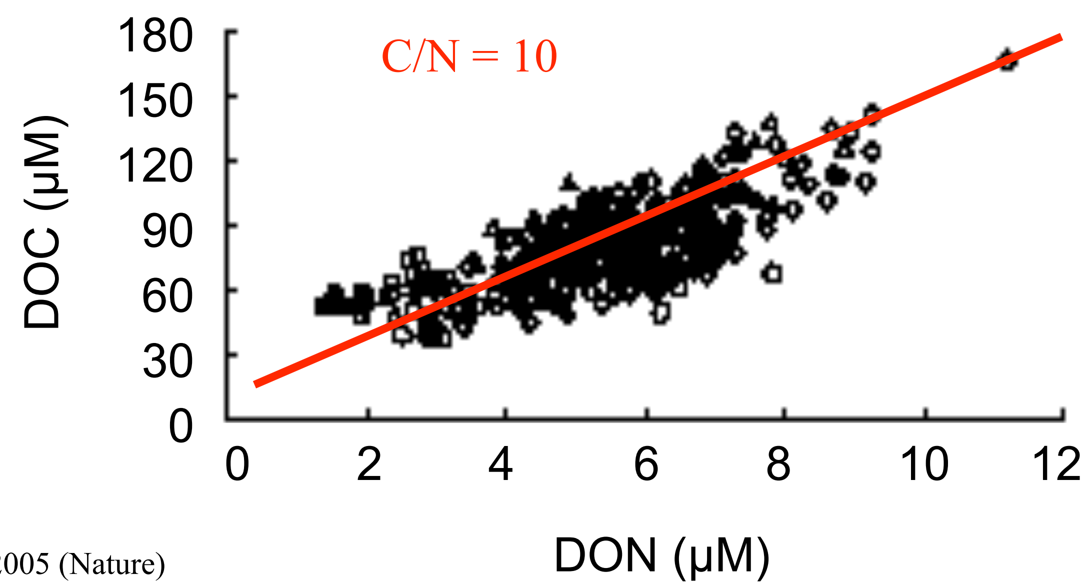
The composition of humic substances in the Amazon River and North Pacific Ocean

Sample	%OC	C/N	H/C	CHx	HCOH	C=C	COO	HC=O	C-13
				Amazon River samples					
Rio Negro FA	52	85	0.95	32	15	33	16	4	-29.0
Rio Negro HA	52	58	0.79	27	9	41	18	6	-29.2
main branch FA	51	60	1.00	32	13	31	17	7	-29.0
				Pacific Ocean samples					
EEP (5 m)	51	36	1.6	45	18	18	15	5	-22
NCP (10 m)	48	46	1.2	44	20	20	16	ND	-22
NCP (4200)	50	43	1.2	46	17	19	15	3	-22



What is the degradation stoichiometry of recalcitrant DOC ?





Hopkinson and Vallino 2005 (Nature)

Summary

DOM is isolated from seawater using either adsorption onto hydrophophic resin or ultrafiltration (molecular filtration). Adsorptive techniques selects DOM that has a high affinity for the adsorption media, while ultrafiltration relies on the hydrodynamic diameter of the organic matter.

Adsorptive techniques select for DOM that is depleted in radiocarbon, while ultrafiltration selects for "HMWDOM" that is enriched in radiocarbon.

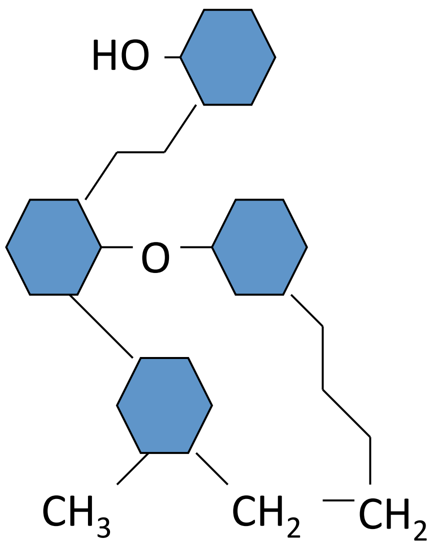
NMR analysis of HMWDOM shows it to have a remarkably uniform distribution of functional groups that is conserved across ocean basins. Carbohydrates are the dominant biochemical class present in HMWDOM. Chemical hydrolysis Only recovers 10-20% of carbohydrate as neutral sugars, characterized by seven major neutral sugars (rhamnose, fucose, arabinose, mannose, glucose, xylose, galactose). These data suggest that the HMWDOM is a biopolymer with a specific composition.

Nitrogen occurs primarily as a amide, linked through N-acyl amino sugars.

The old, hydrophobic fraction of DOM is relatively more enriched in aliphatic carbon And highly oxidized, with a high COOH/CHx ratio.

Composition, reactivity, flux and distribution of DOM

Non-reactive DOM



"Humic" substances

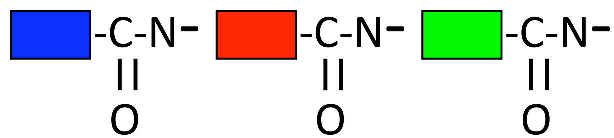
Concentration 40 μM

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

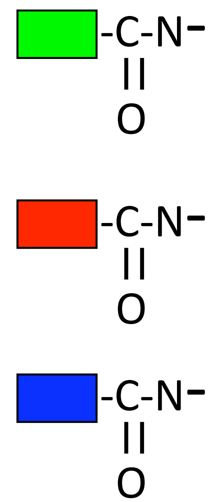
Inventory = 10-20 GT C

$\Delta^{14}C$= 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