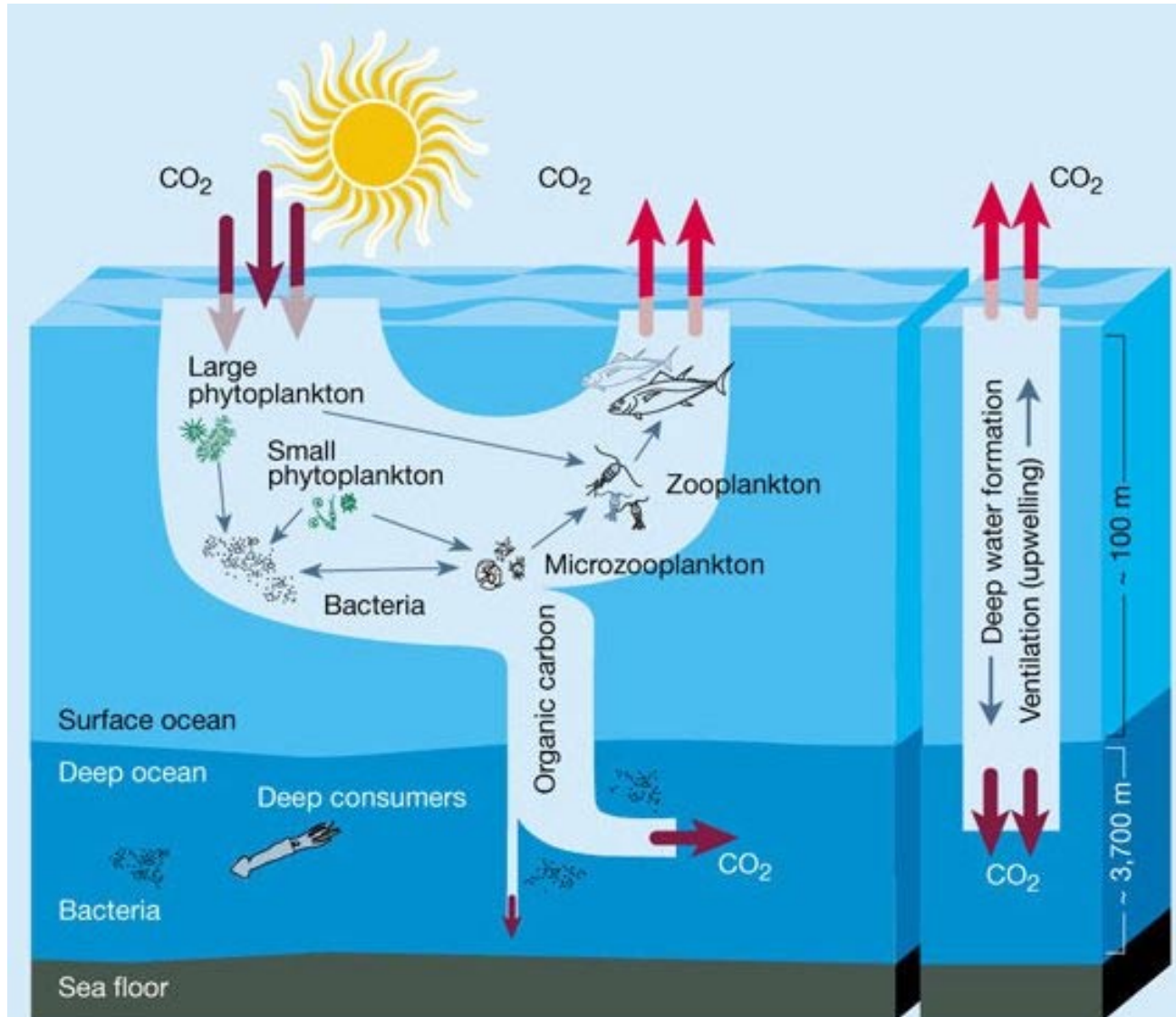
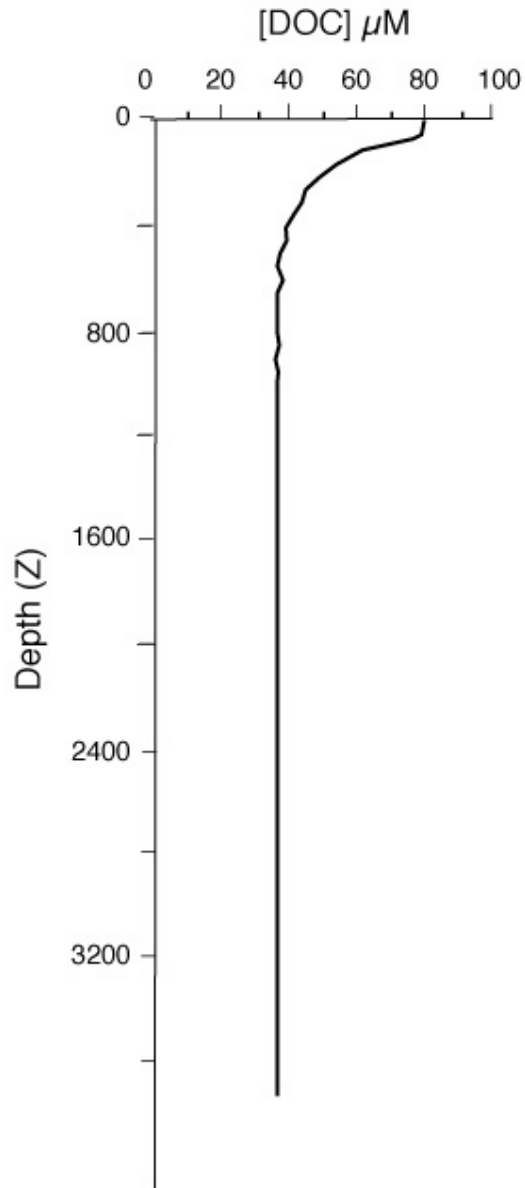


# Biogeochemical cycling of dissolved organic C and nutrients



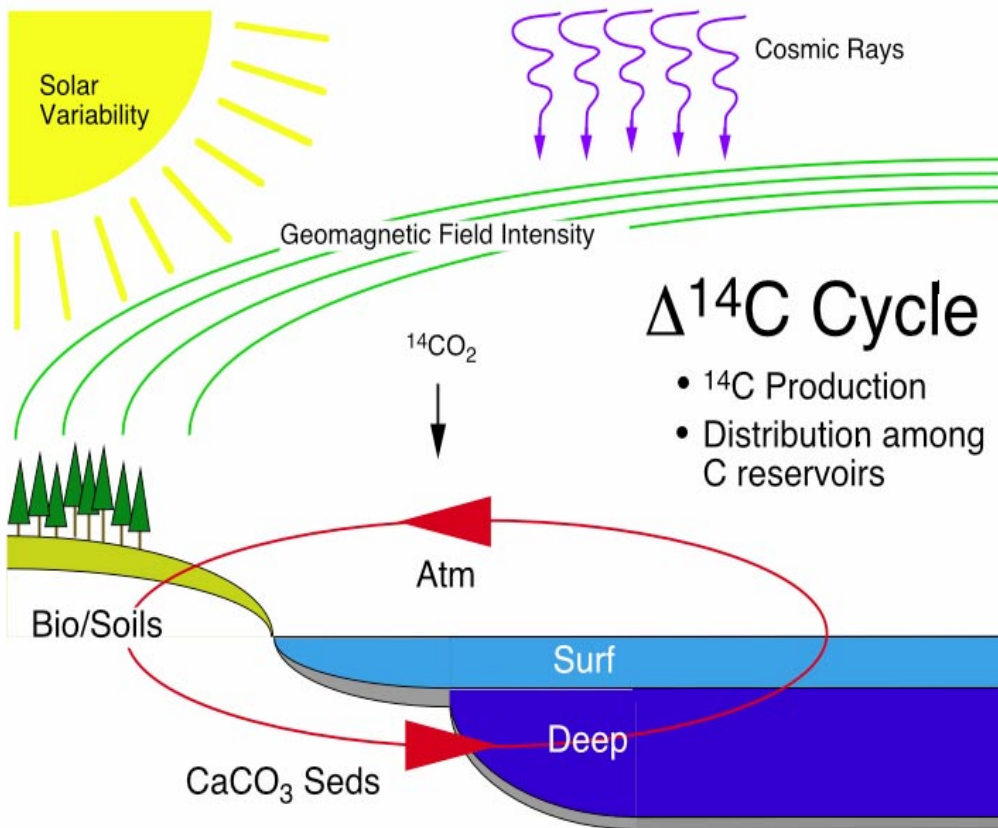


## The profile of [DOC] With depth in the ocean

1. Measured by HTCO or wet chemical oxidation
2. Surface values are 60-80 $\mu\text{M}$  C  
deep sea values are 40  $\mu\text{M}$  C
3. Deep sea values are nearly constant  
(implies some tight feedback/control)
4. Global inventory is 680 GT C. Most Resides in the deep ocean!

# Why 40 $\mu\text{M C}$ ?

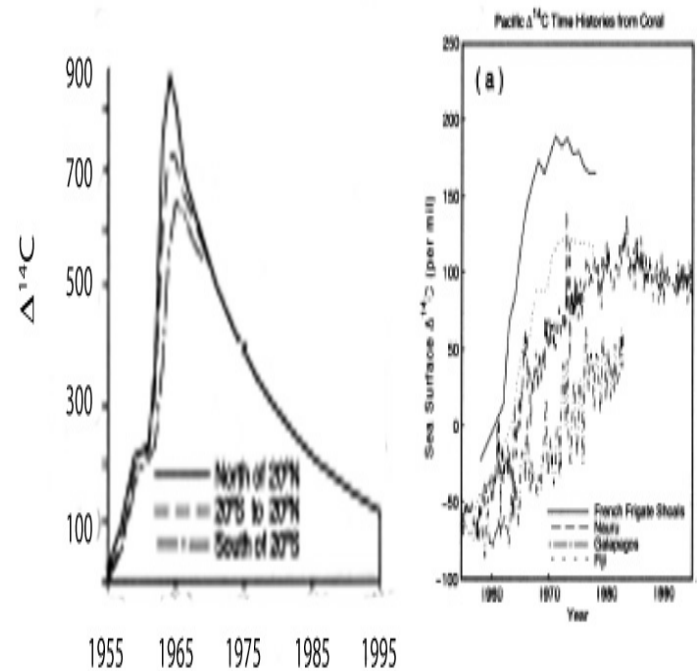
## What processes set the global inventory of marine organic carbon?



**$\Delta^{14}\text{C}$  Cycle**

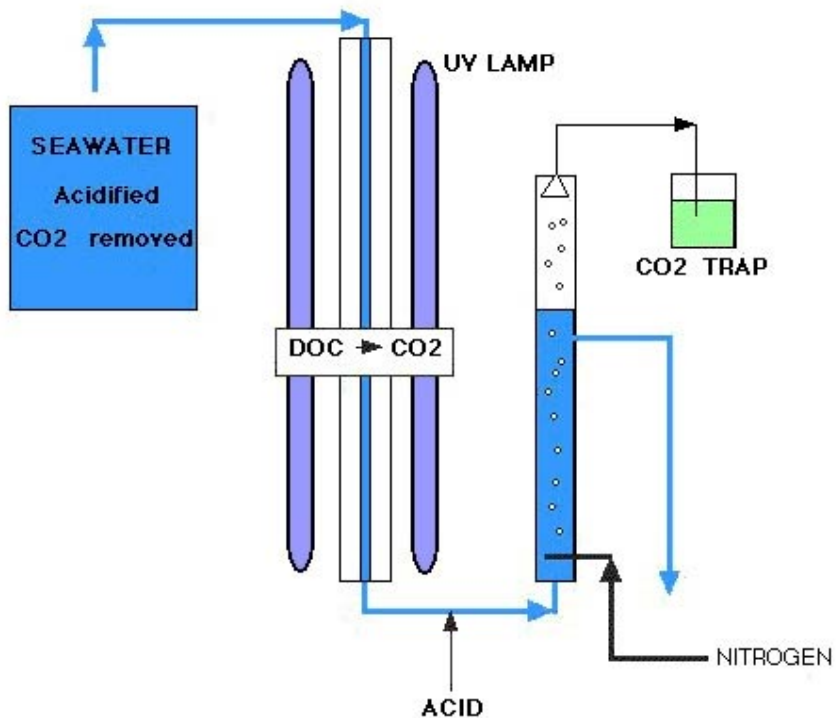
- $^{14}\text{C}$  Production
- Distribution among C reservoirs

Bomb radiocarbon in the atmosphere and ocean



year

□ Radiocarbon Age of Dissolved Organic Carbon



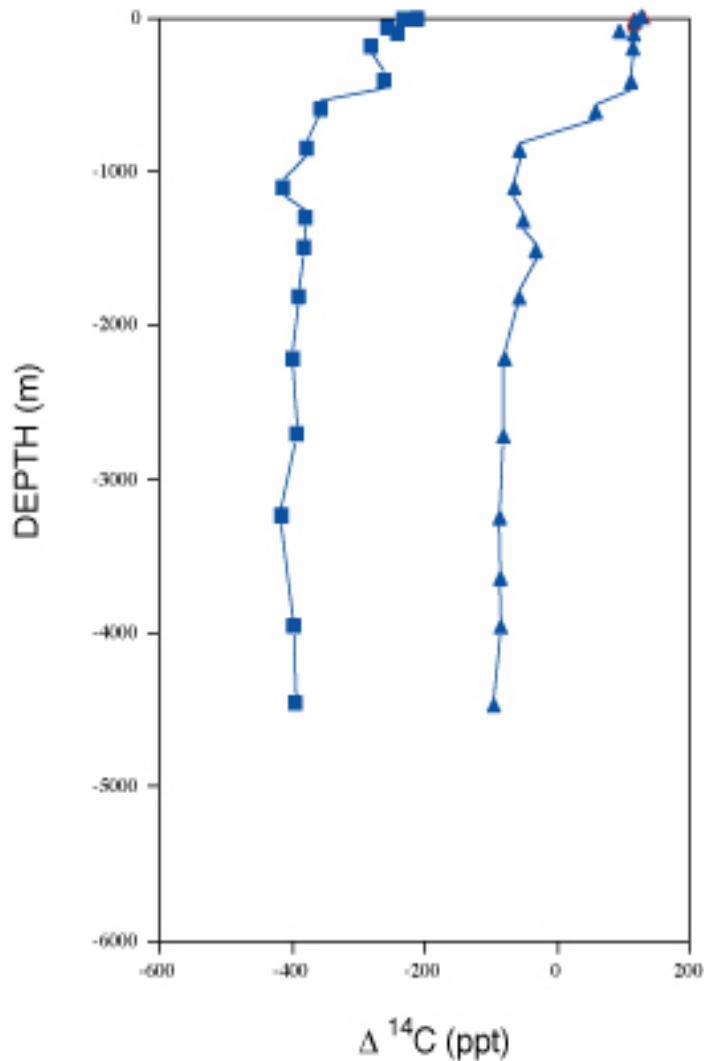
Pioneered by Pete Williams  
At SIO.

Contamination is a  
big problem!!!

Does UV get it all ?

Pre AMS 1g C (1m<sup>3</sup>)  
Now about 1mg C (1L)

# Radiocarbon in DOC and DIC



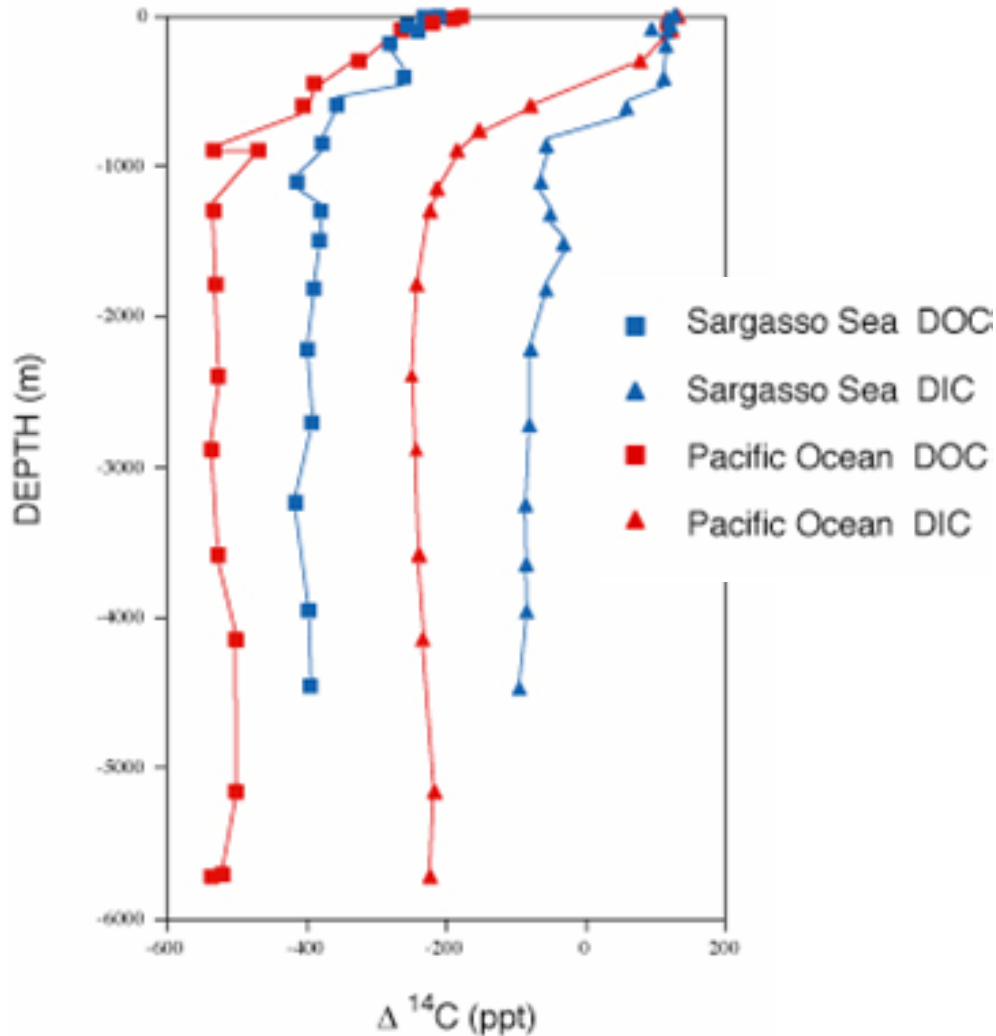
CO<sub>2</sub>->DIC->POC->DOC

DOC is depleted (older)  
than DIC at all depths

There is a source of new  
DOC in the surface ocean

The  $\Delta\Delta^{14}\text{C}$  between DIC  
and DOC is not the same  
at all depths (greater at the  
Surface)

# Radiocarbon in the Atlantic and Pacific Oceans



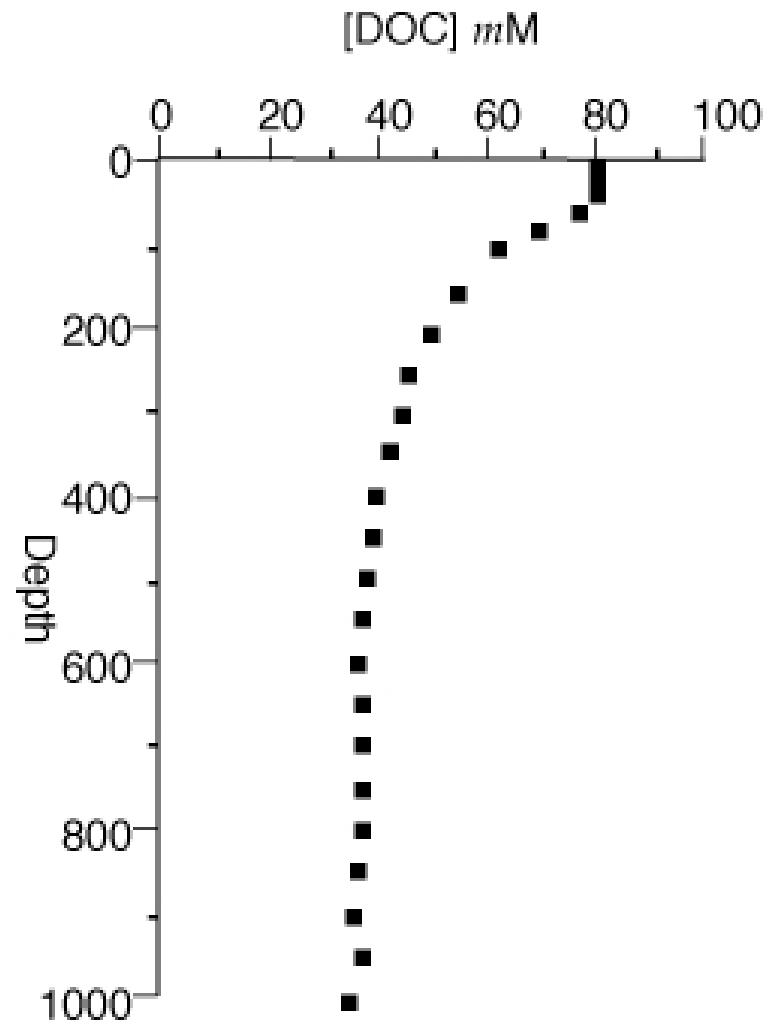
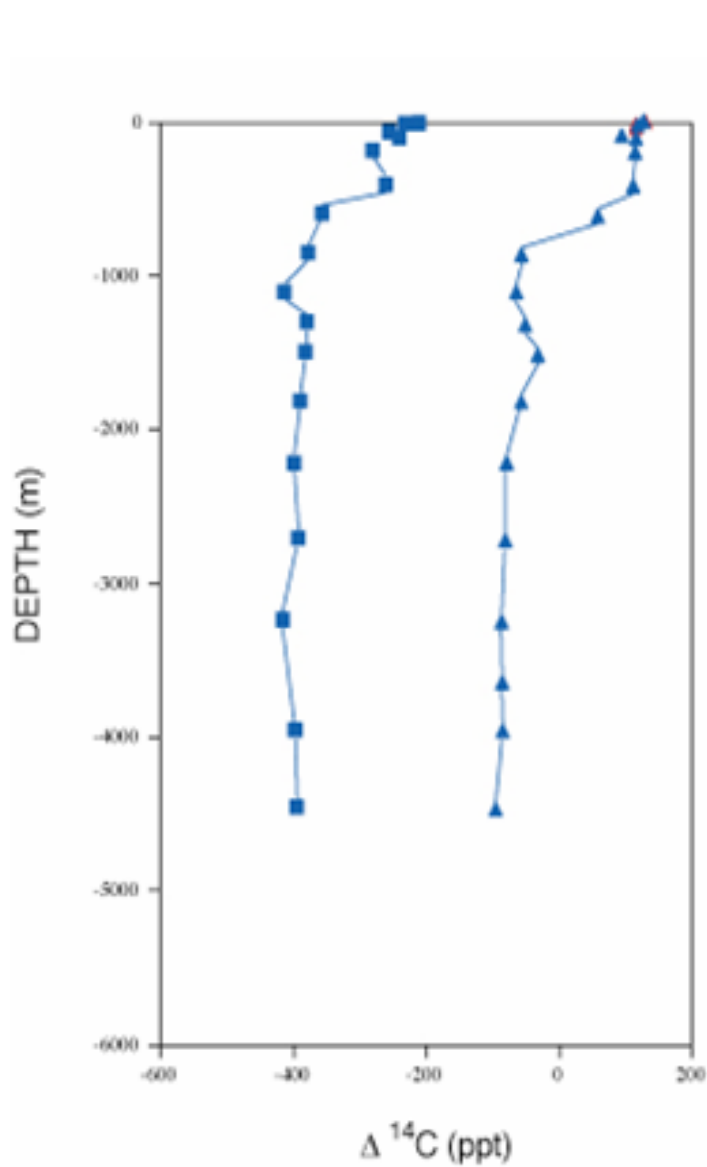
DIC  $^{14}\text{C}$  has the same Value in the Atl and Pac

$\Delta\Delta^{14}\text{C}$  of DIC and DOC is about the same in the deep Atl and Pac oceans

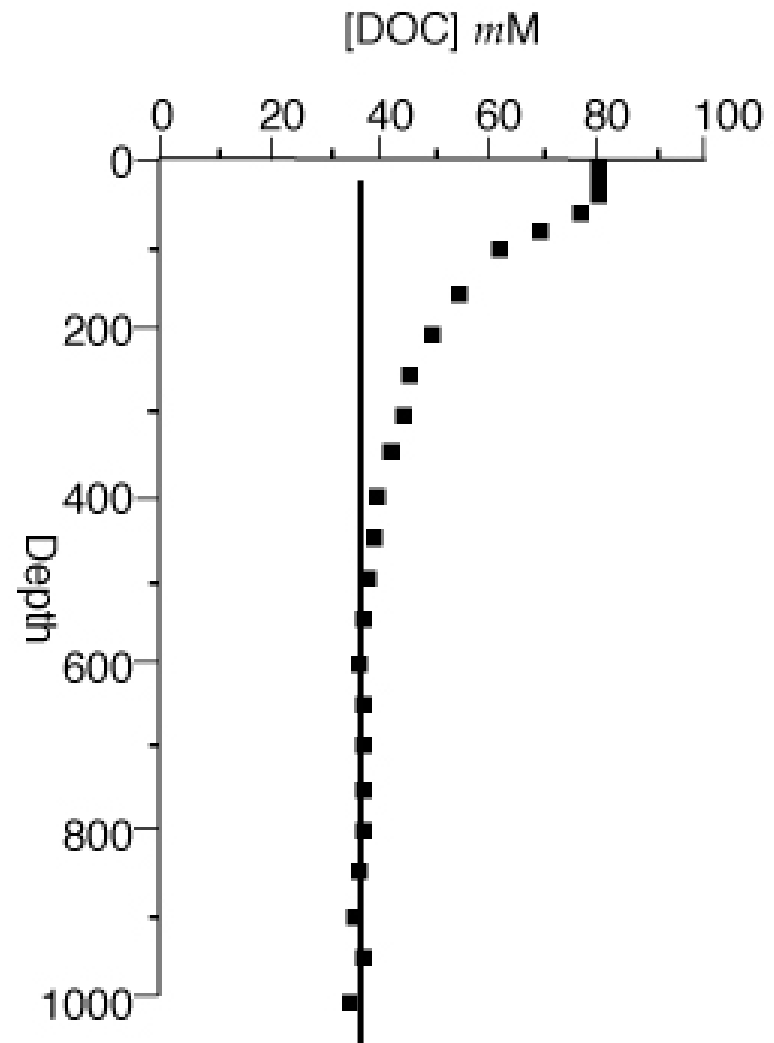
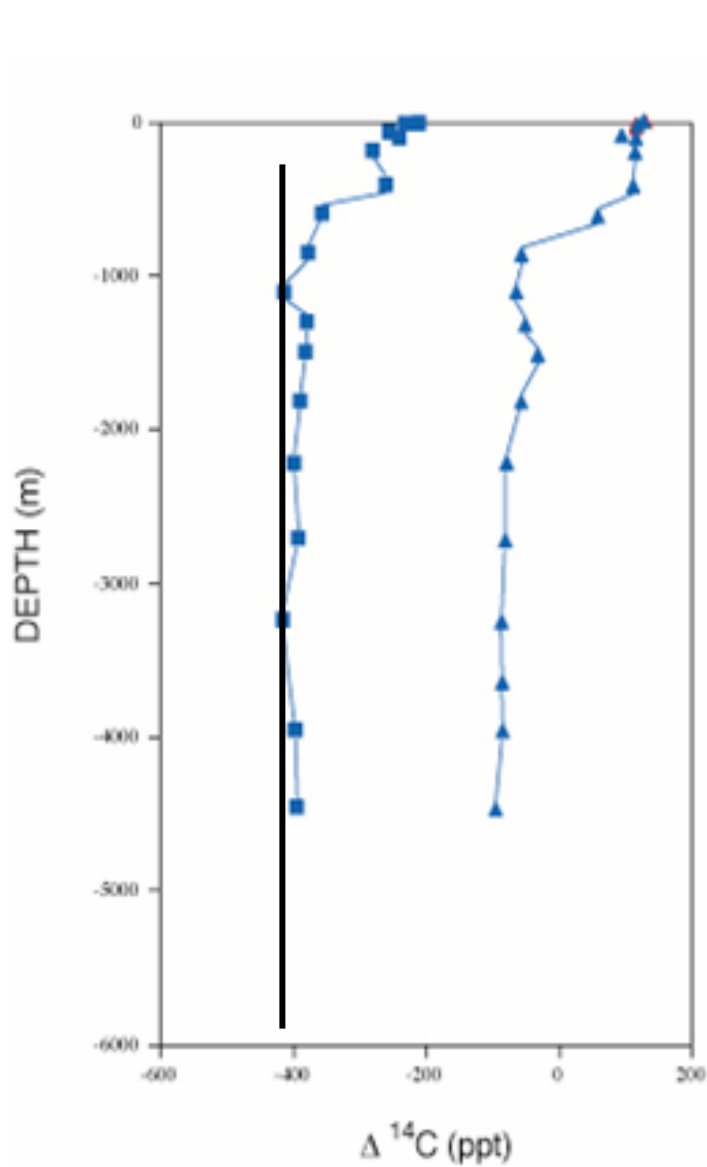
Deep ocean values are equal to a RC age of Several 1000's years

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

# Why is DOC old in surface water?

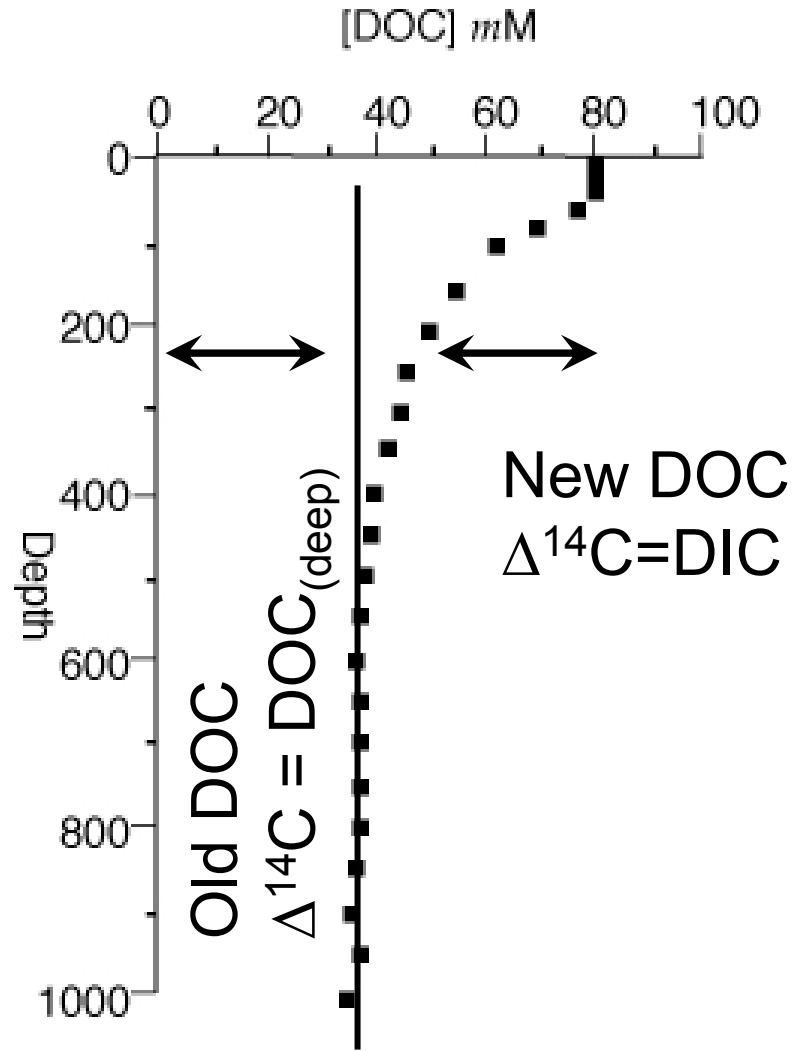
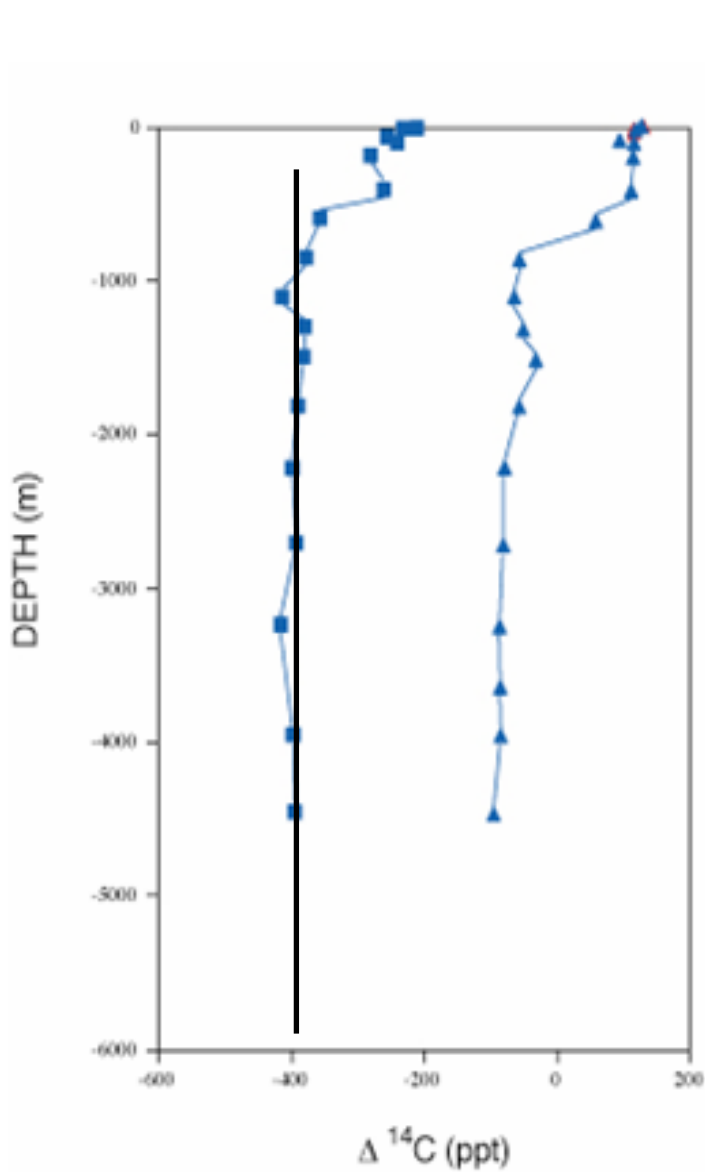


# Why is DOC old in surface water?

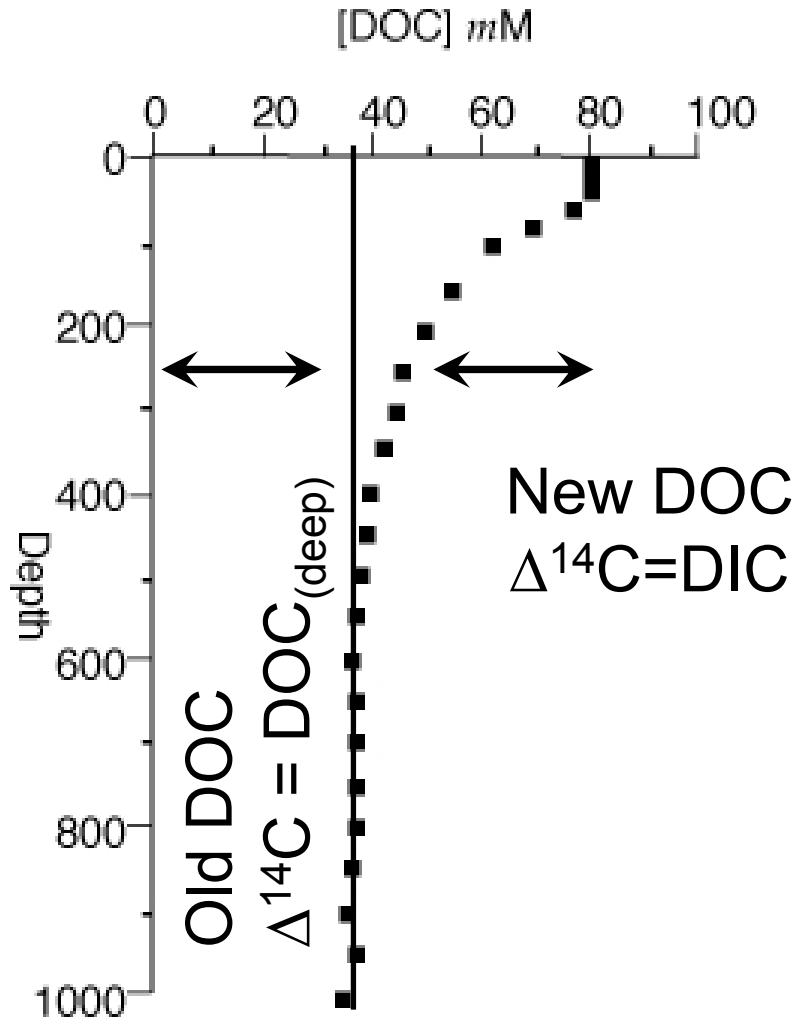




# Why is DOC old in surface water?



# Why is DOC old in surface water?



Atlantic surface water

$$^{14}\text{C}_{\text{calc}} = -120 \text{ ‰}$$

$$^{14}\text{C}_{\text{obs}} = -127 \text{ ‰}$$

Pacific surface water

$$^{14}\text{C}_{\text{calc}} = -147 \text{ ‰}$$

$$^{14}\text{C}_{\text{obs}} = -148 \text{ ‰}$$

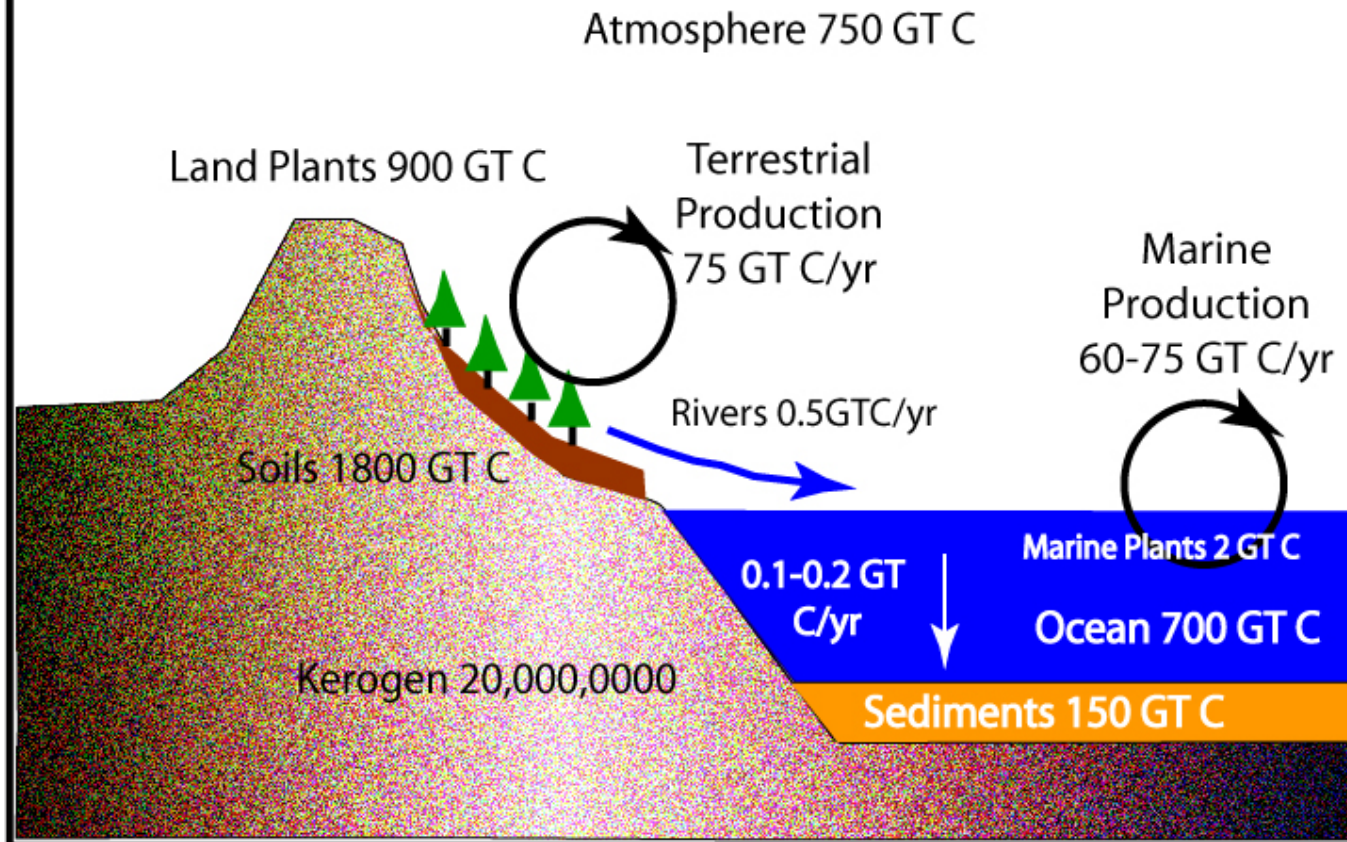
What flux of carbon is needed to maintain the marine DOC reservoir?

Global inventory/residence time = annual flux

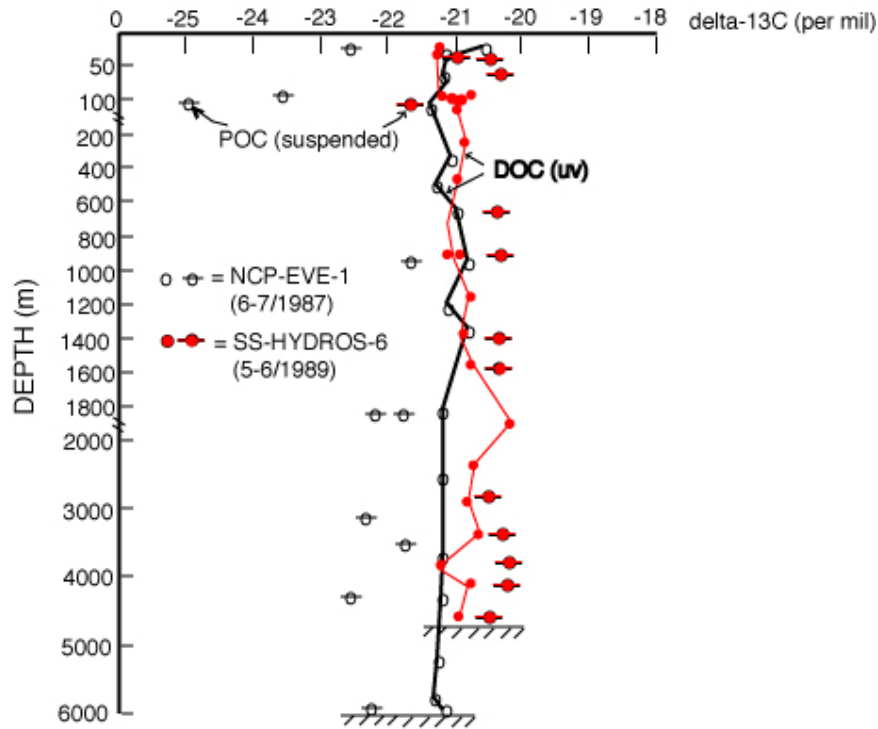
680 GT C/ 5000-6000 yr = 0.11-0.14 GT C/yr !!!

How does this compare with other C fluxes?

# Major Carbon Reservoirs



# What is the source of Marine DOC ?



Stable C isotopes

Marine C -21‰

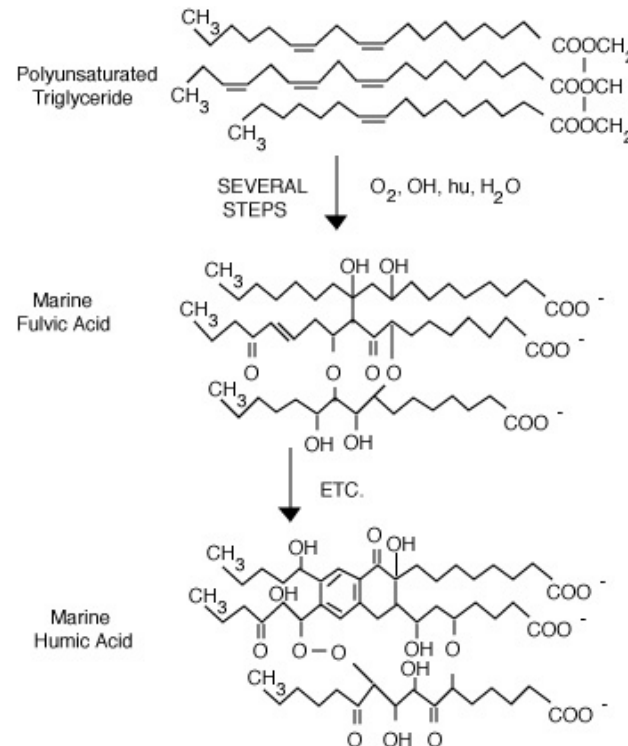
Terrestrial C

C3 plants -27‰

C4 plants -15‰

A comparison of the stable isotope ratio measurements for DOC uv and suspended POC for the North Atlantic (Hydros-6) and the NCP (Eve-1) site.

# Hard problems in oceanography- what is DOC and why is it so old??



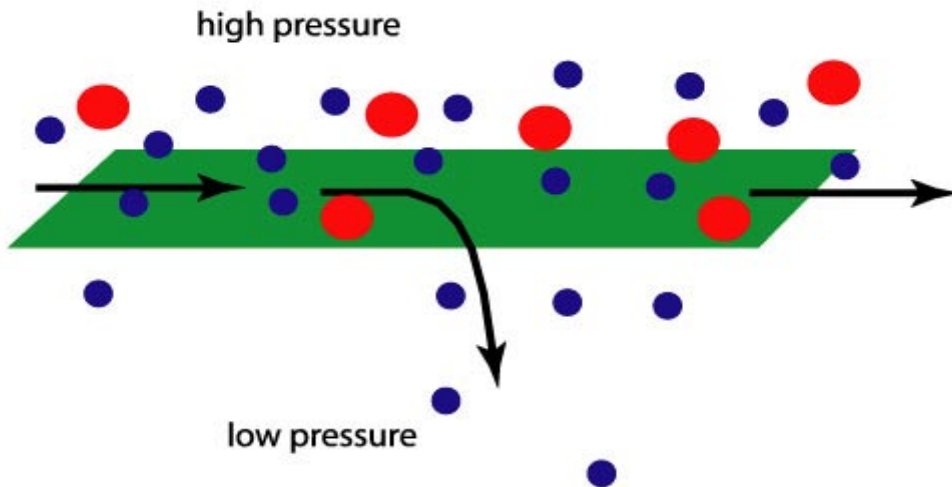
Proposed pathway to marine humic substances by oxidative crosslinking of polyunsaturated lipids catalyzed by ultraviolet light and transition metals. (Harvey et al. 1983)

**DOC = humic substances**

# Sampling DOC is hard to do...

DOC = 1mg/L C    Salt = 35g/L

## Cross Flow Filtration



Separation based on size

1 nm pore @ 1 kD

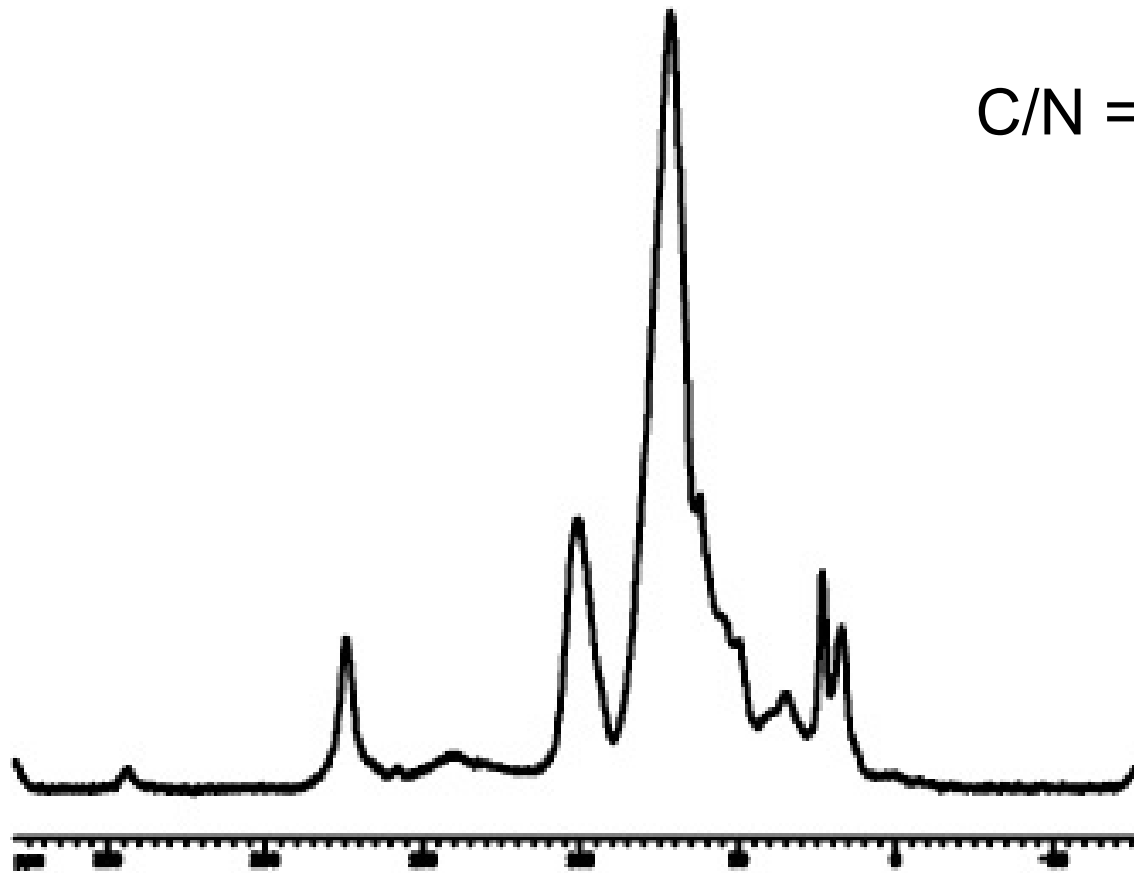
Selects for HMW fraction

about 30-35% TOC

Membrane effects what  
is collected

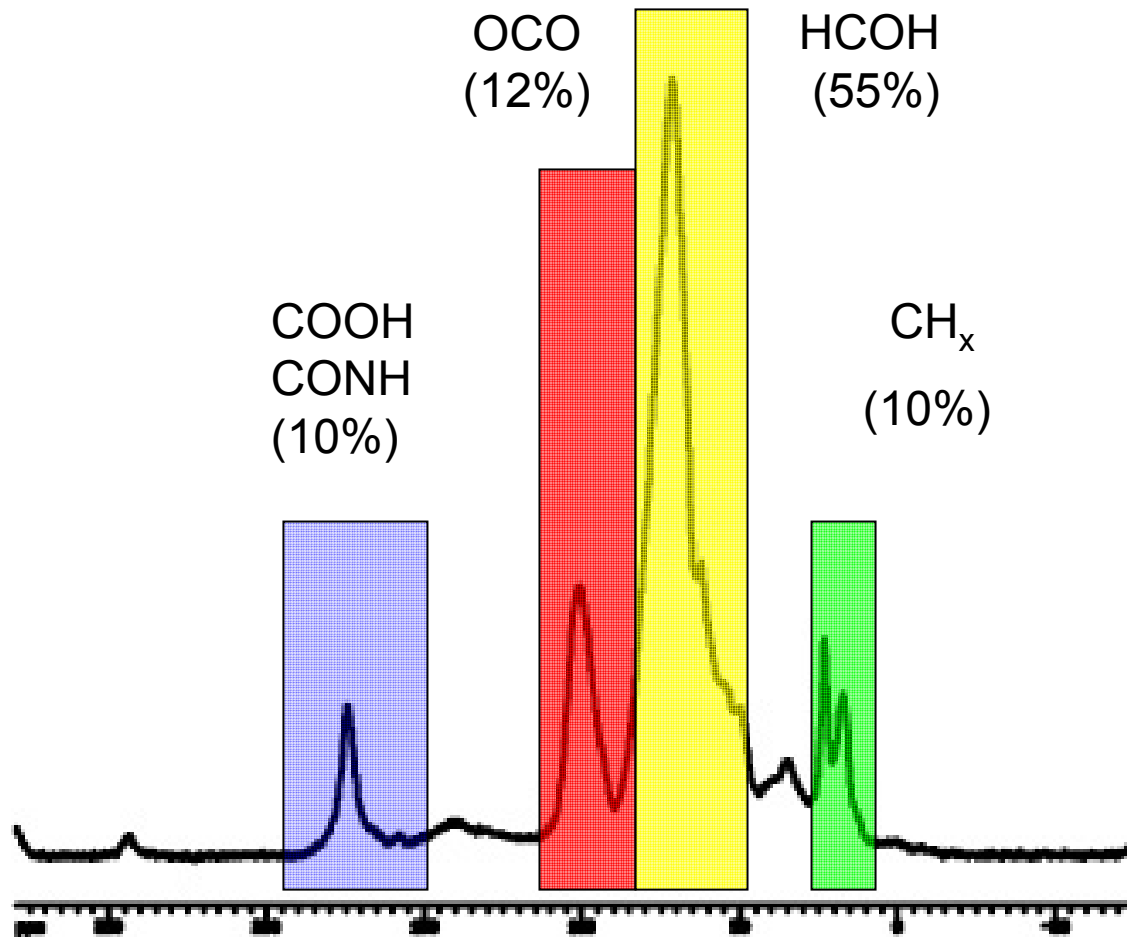
Some salts collected too!

$^{13}\text{C}$  Nuclear Magnetic Resonance Spectrum  
of high molecular weight dissolved organic matter

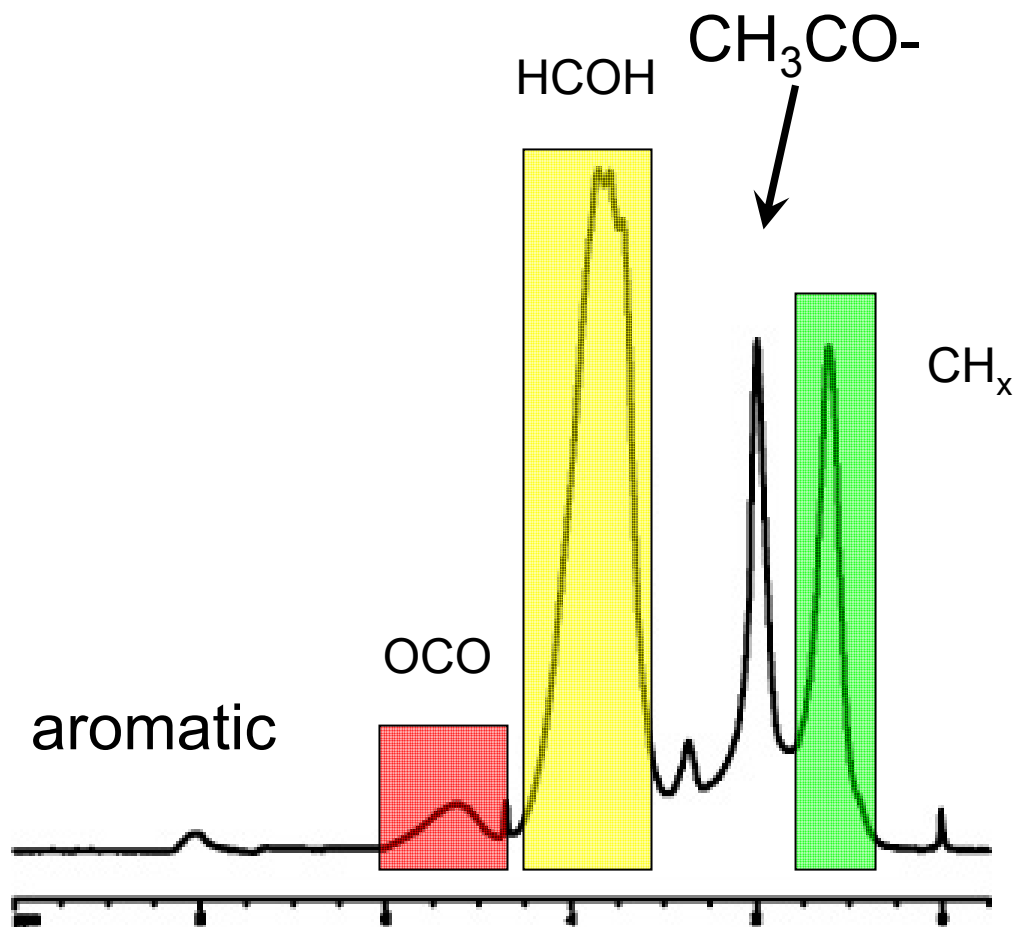




# $^{13}\text{C}$ Nuclear Magnetic Resonance Spectrum of high molecular weight dissolved organic matter



# $^1\text{H}$ NMR of high molecular weight DOC



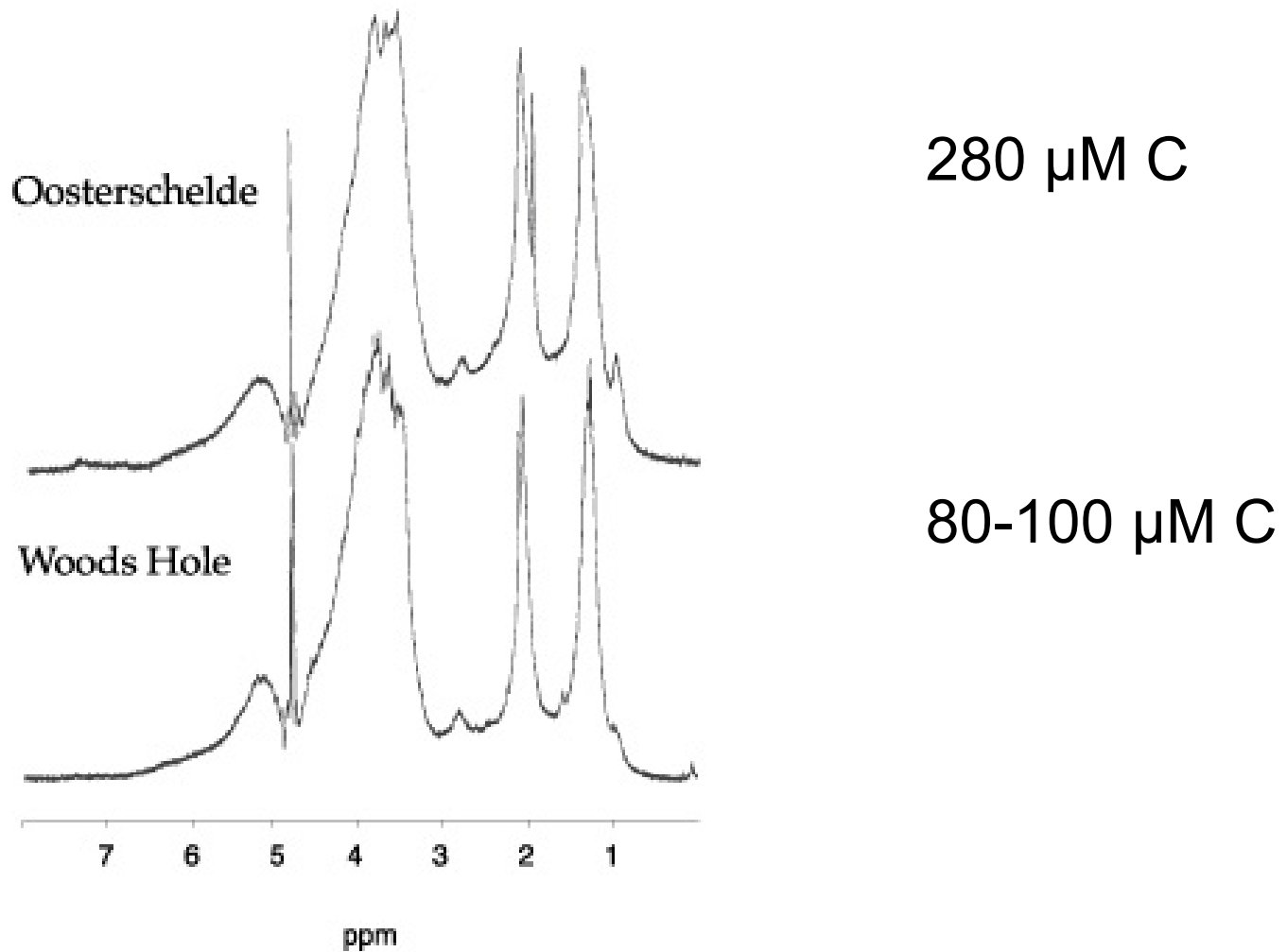
# HMWDOC, what could it be?

From our knowledge of cell biochemicals...

Proteins	C/N = 4,	$\text{CH}_x(\text{O}):\text{CON} = 3:1$
Carbohydrates	C only ?	$\text{OCO}:\text{HCOH} = 1:5$
Lipids	C only	$\text{CH}_x\text{COOH}$ $\text{CH}_x\text{COH}$

.....looks to be mostly (50-70%) carbohydrate !

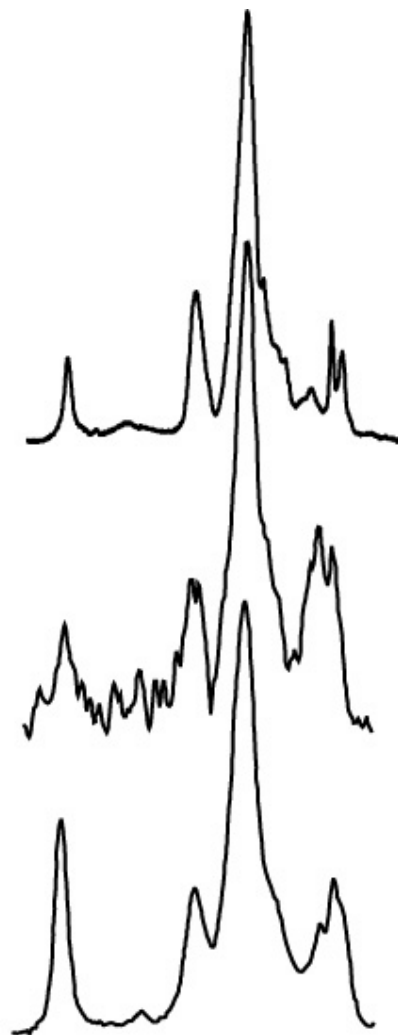
# Chemical characterization of UDOM in seawater



# Relative abundance of major biochemicals in HMWDOC

Sample	DOC	Carbon (relative %)		
		Carbohydrate	Acetate	Lipid
<b>Atlantic Ocean</b>				
Georges Bank-1	80	81	11	4
Georges Bank-2	76	76	9	14
Mid Atlantic Bight-1	95	73	10	15
Mid Atlantic Bight-2	116	84	6	10
Mid Atlantic Bight-3	99	75	9	16
Mid Atlantic Bight-4	97	77	10	14
Woods Hole-1	102	86	10	4
Woods Hole-2	102	77	15	7
Oosterschelde	260	84	11	4
<b>Pacific Ocean</b>				
Scripps Pier	ND	81	12	6
Peru coast	ND	81	13	6
Hawaii	ND	85	7	8
Average		80±4	10±2	9±4

# HMWDOC in freshwater and marine environments

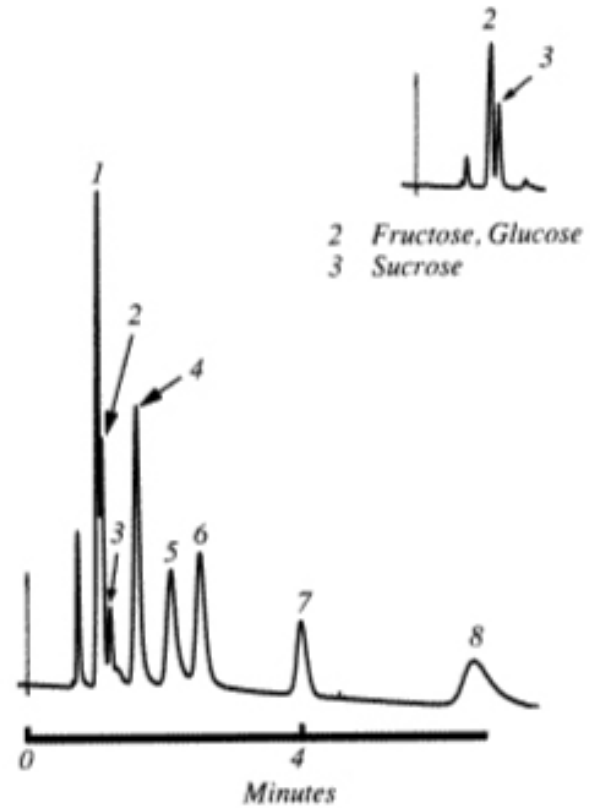
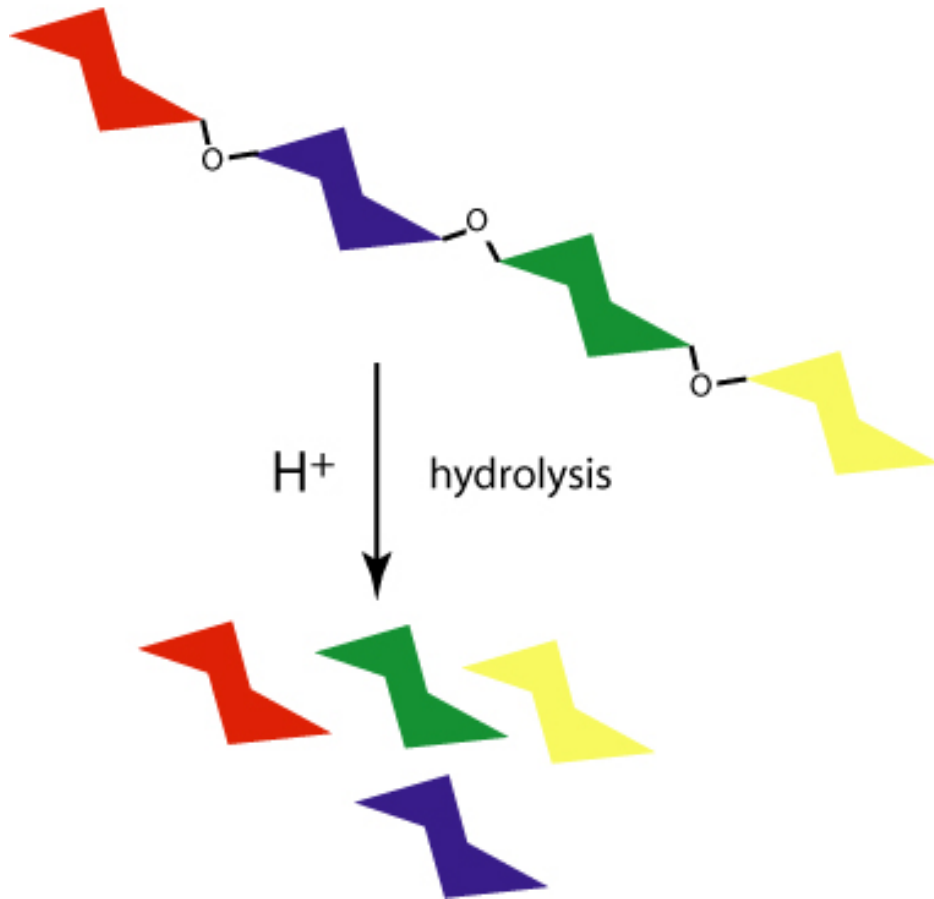


NPSG

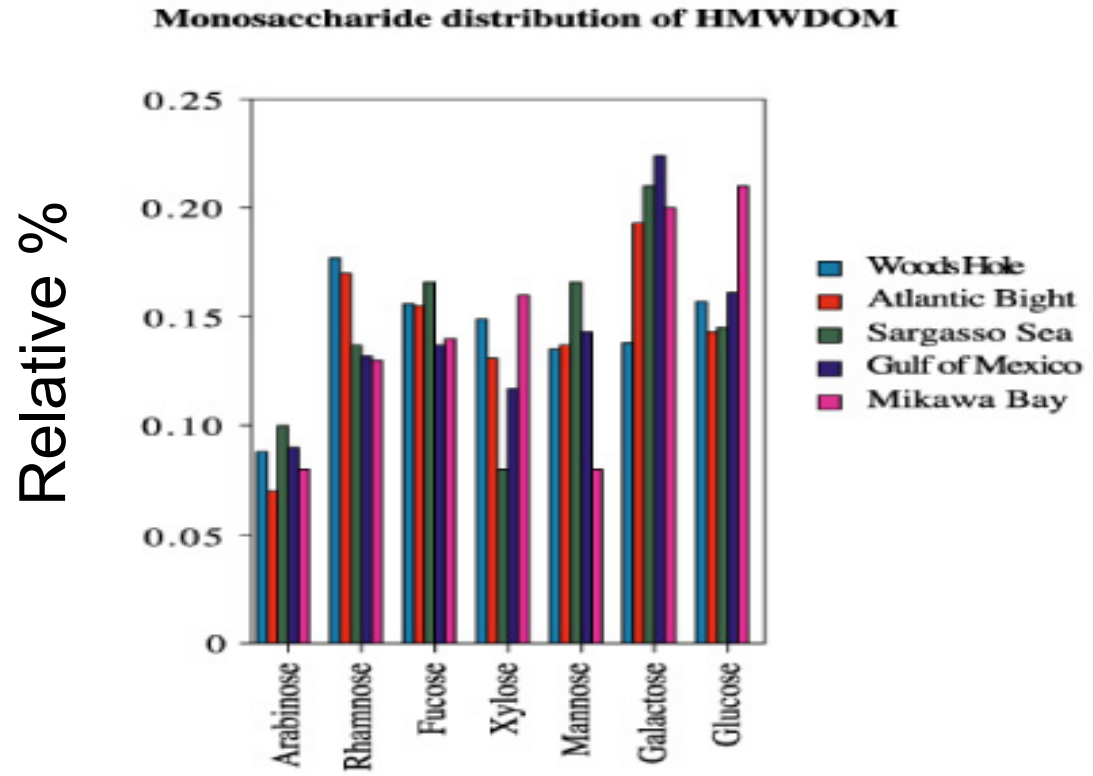
Andrews Creek  
RMNP 3400M

Great Salt Lake (UT)

# Polysaccharide analysis

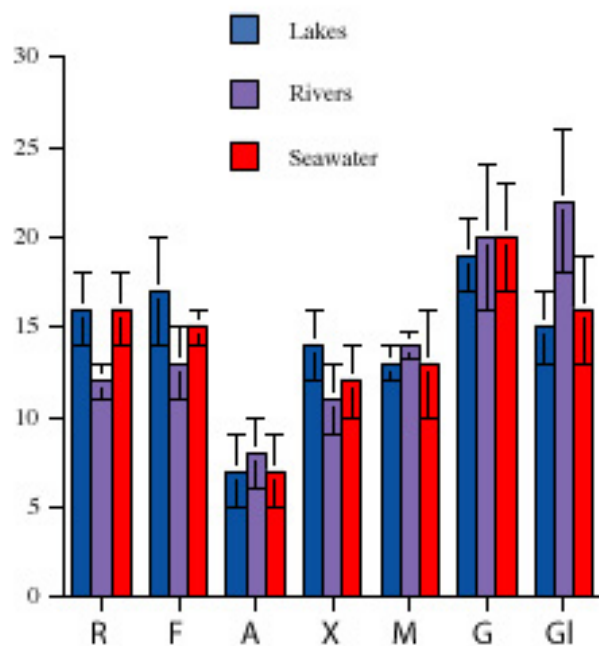
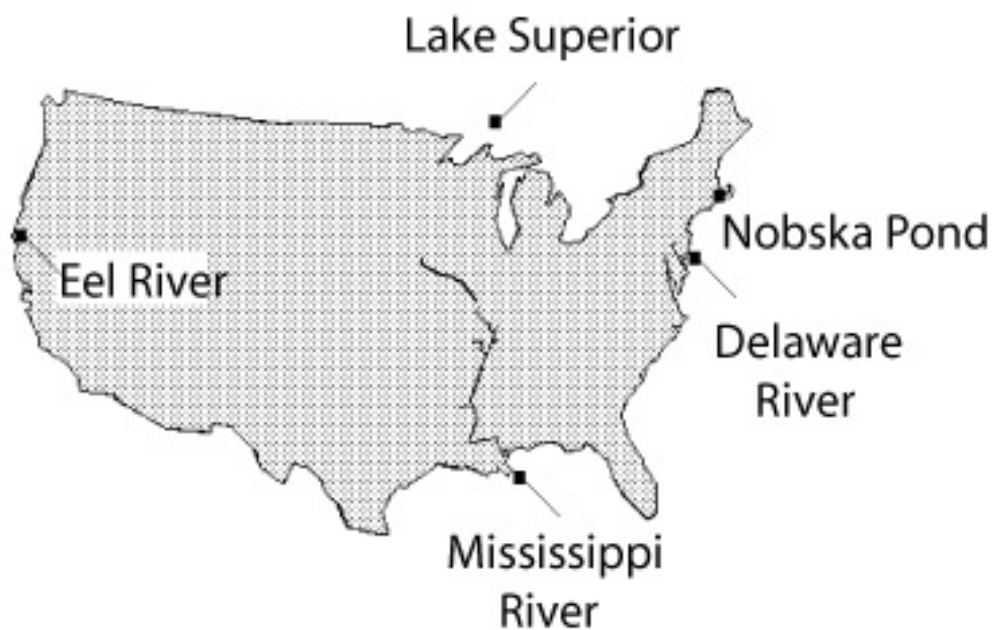


# Relative abundance of sugars in HMWDOC



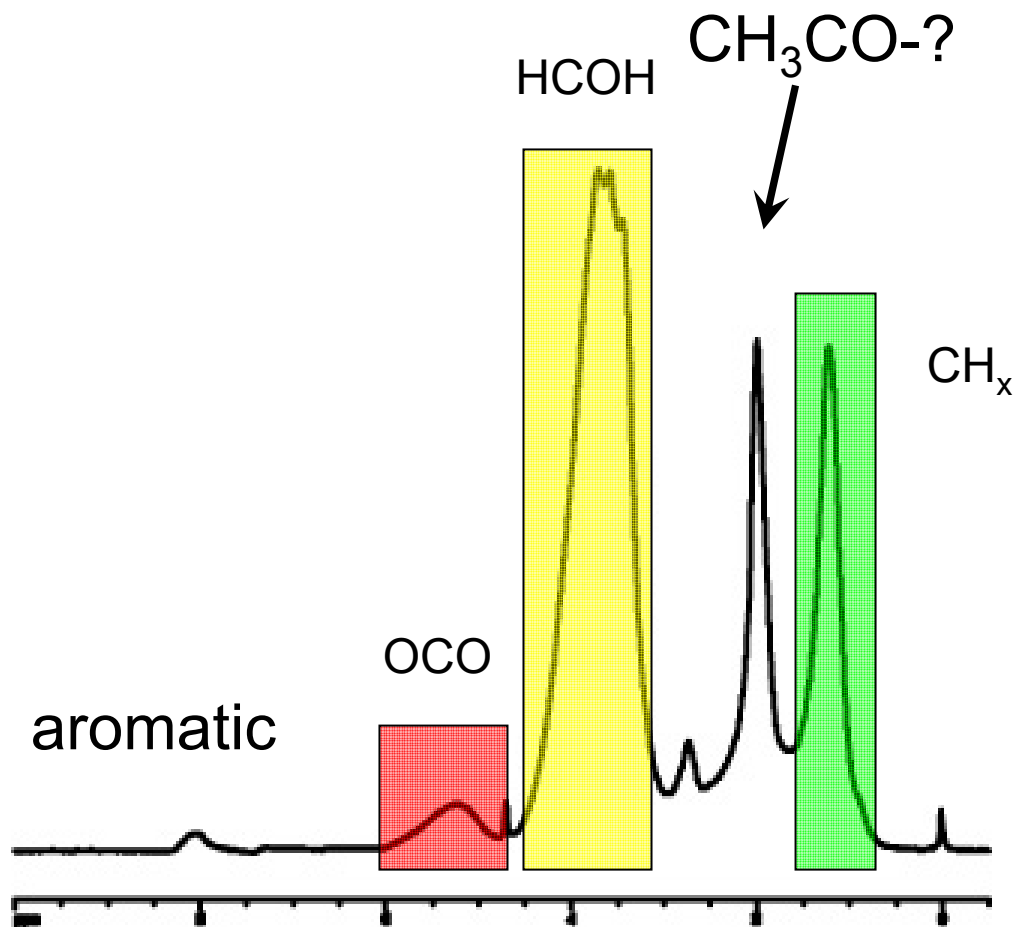


# HMWDOC monosaccharides in rivers, lakes, and seawater



BUT.....yields of sugars are only 5-15% HMWDOC

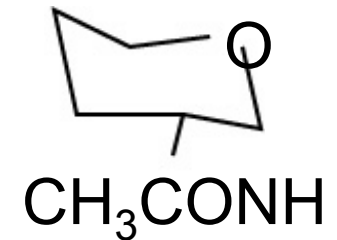
# $^1\text{H}$ NMR of high molecular weight DOC



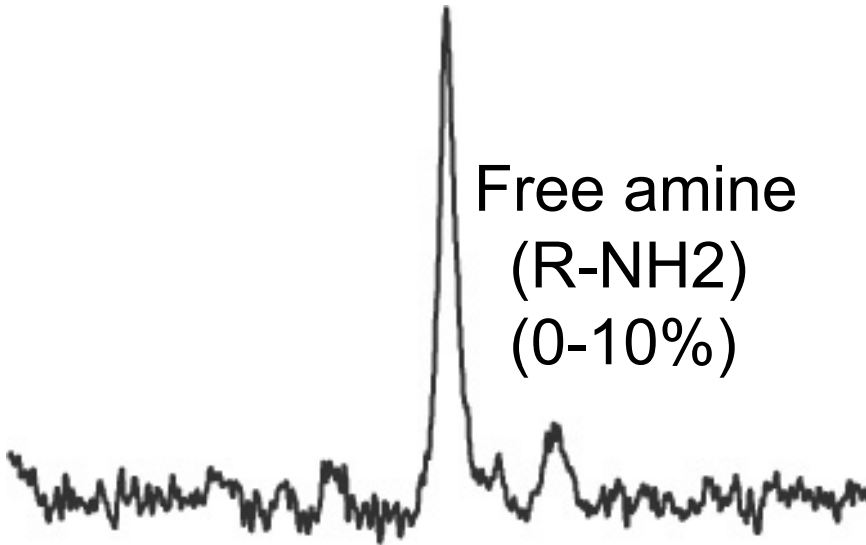
$^{15}\text{N}$ -NMR of HMWDOC. Is HMWDON from proteins or from amino sugars?

Amide (RCON)  
(90-100%)

amino sugars

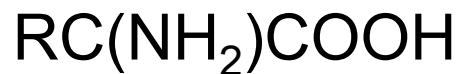


Free amine  
(R-NH<sub>2</sub>)  
(0-10%)

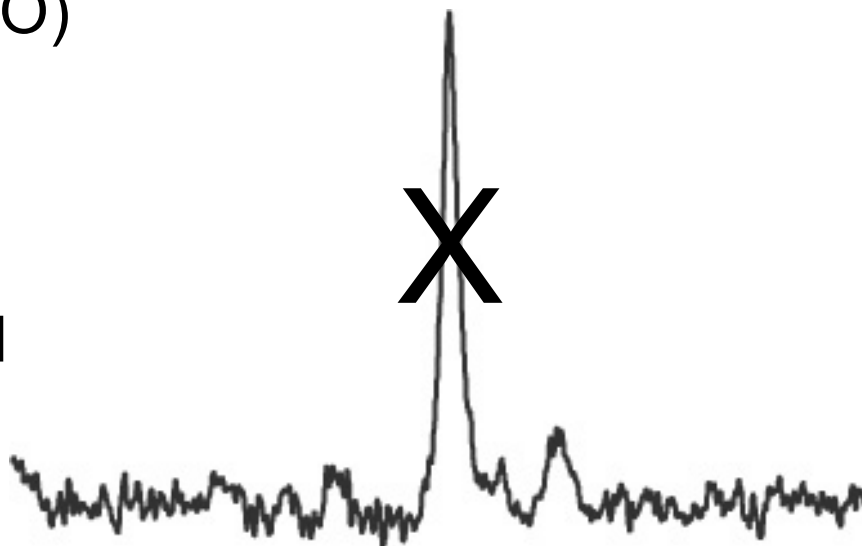


Is a large fraction of HMWDOC and HMWDON  
from amino sugars or proteins?

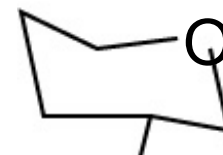
proteins



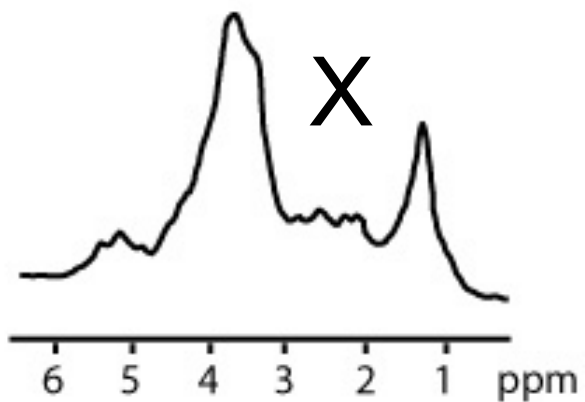
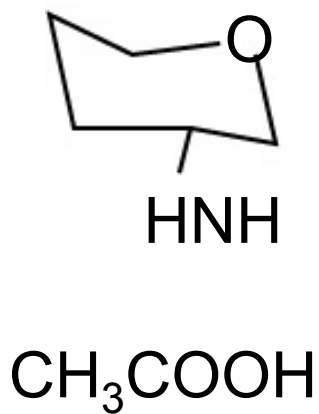
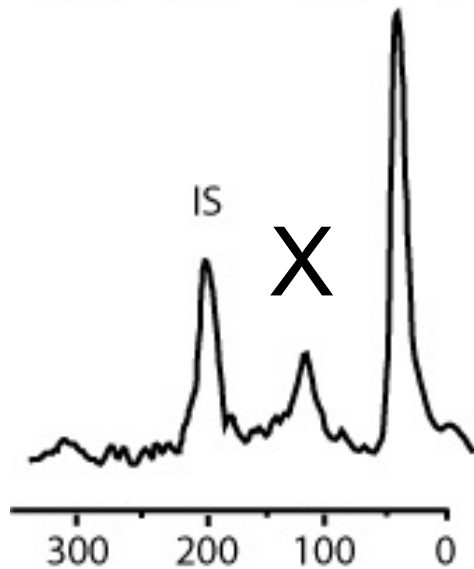
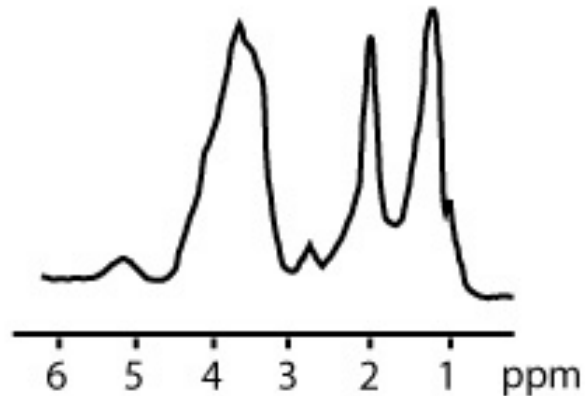
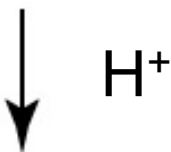
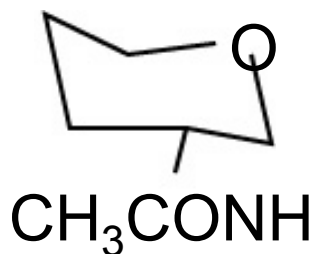
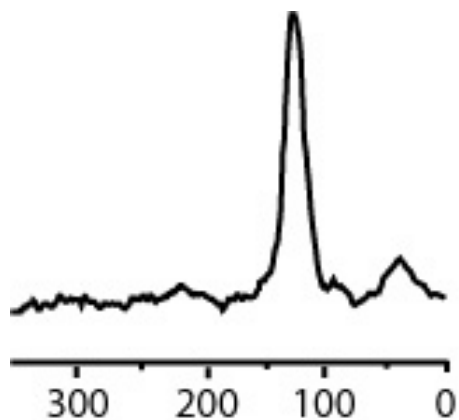
(amino acids)



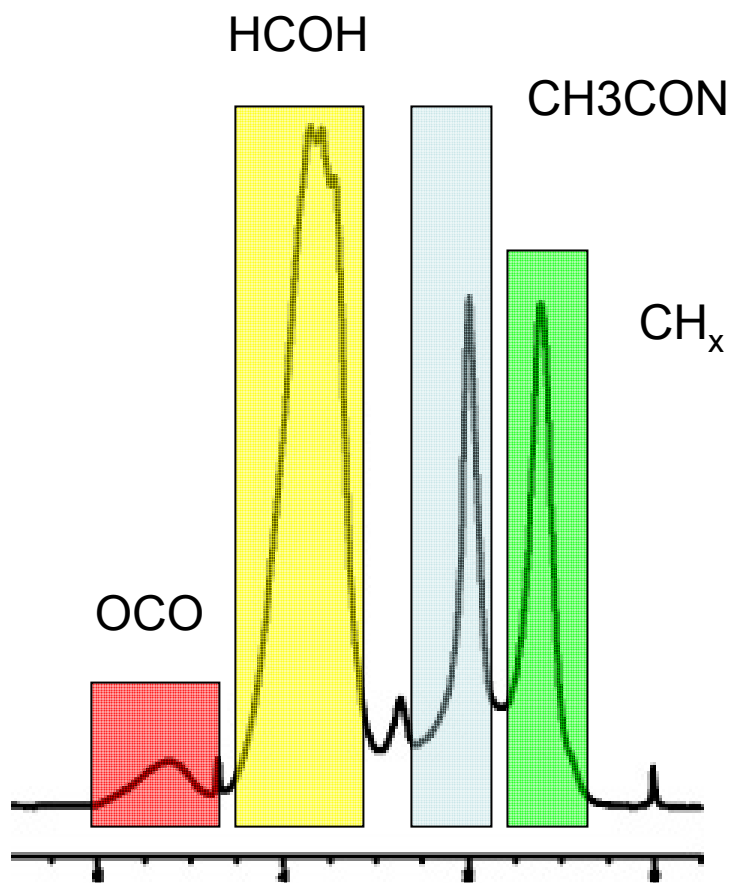
amino sugars



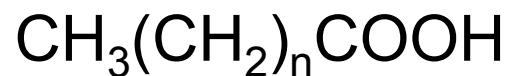
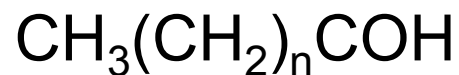
Is a large fraction of HMWDOC and HMWDON  
from amino sugars?



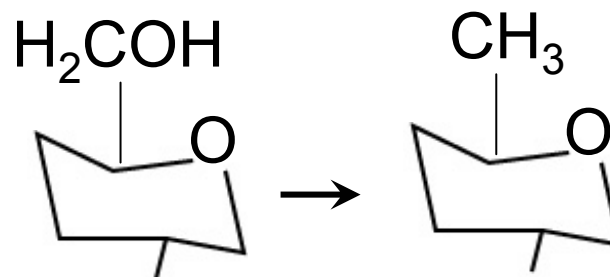
What is the 'lipid' in HMWDOC?



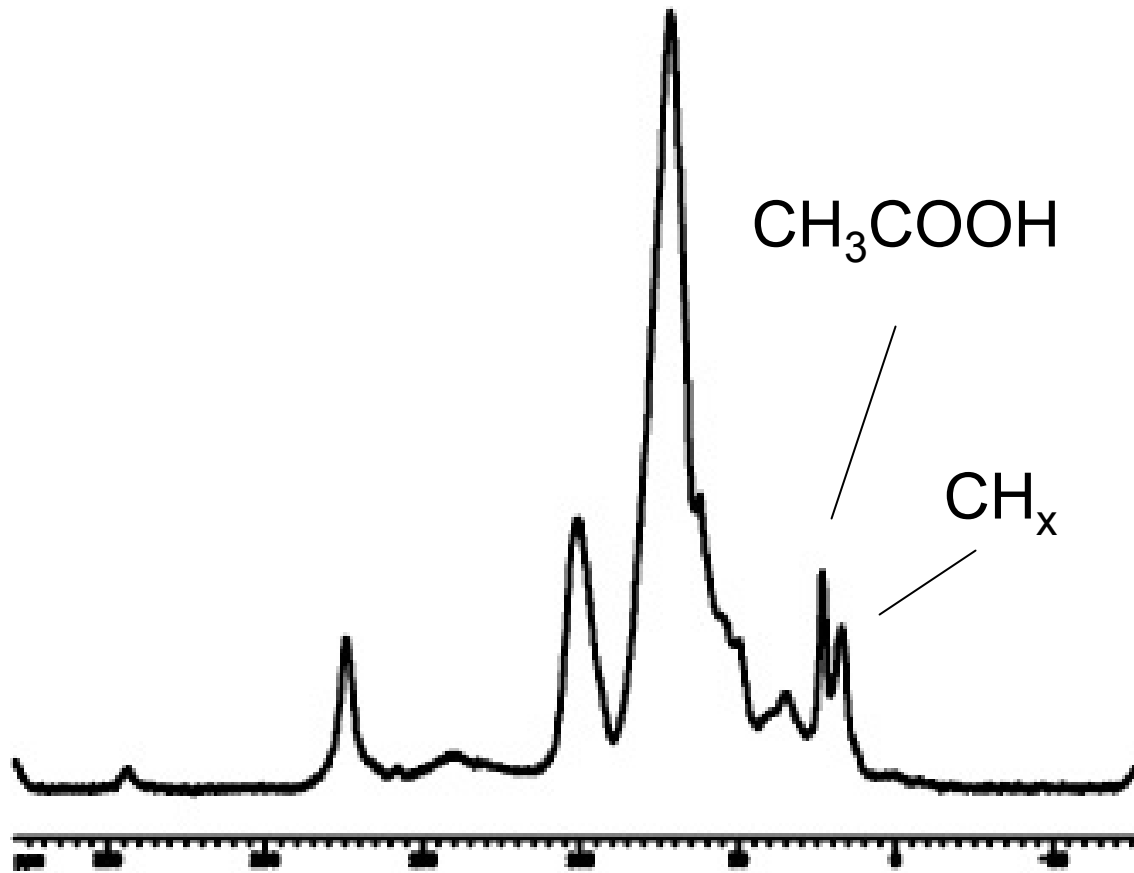
Lipid



Deoxy sugars

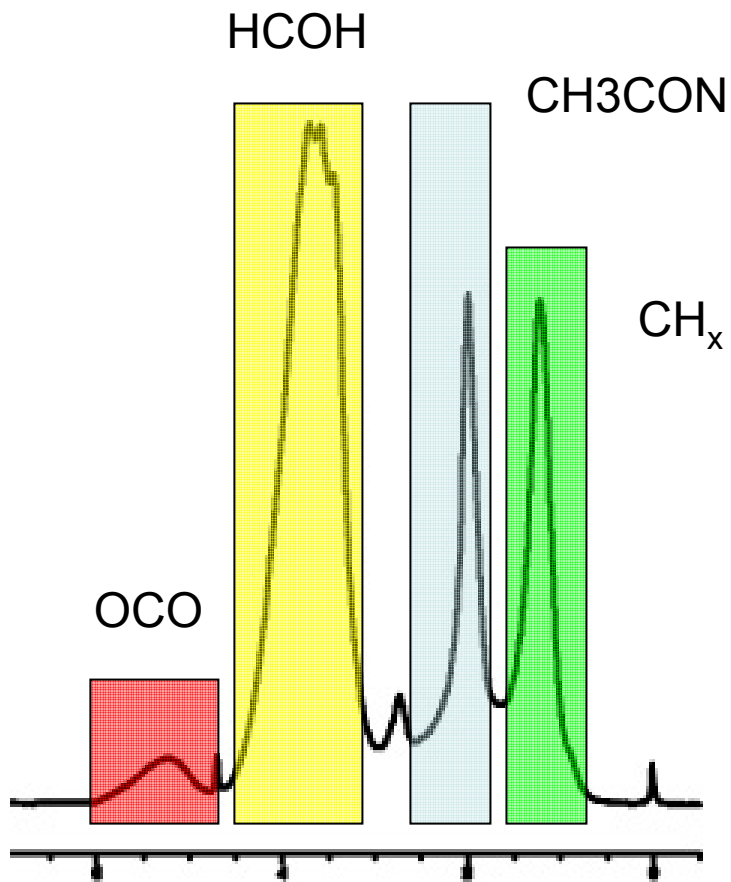


There are really “two” types of lipid in HMWDOC



# The effect of periodate on HMWDOC

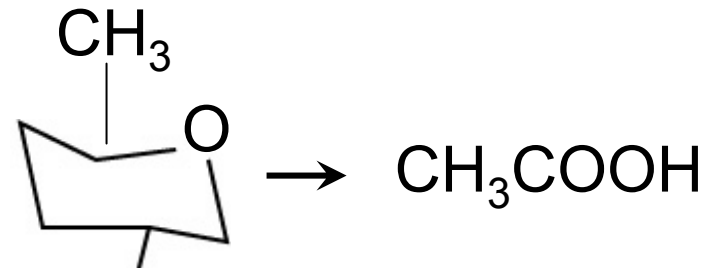
## Is the lipid really lipid?



Lipid

$\text{RCOH} \rightarrow$  No Reaction

Deoxy sugars





Periodate oxidation of HMWDOC

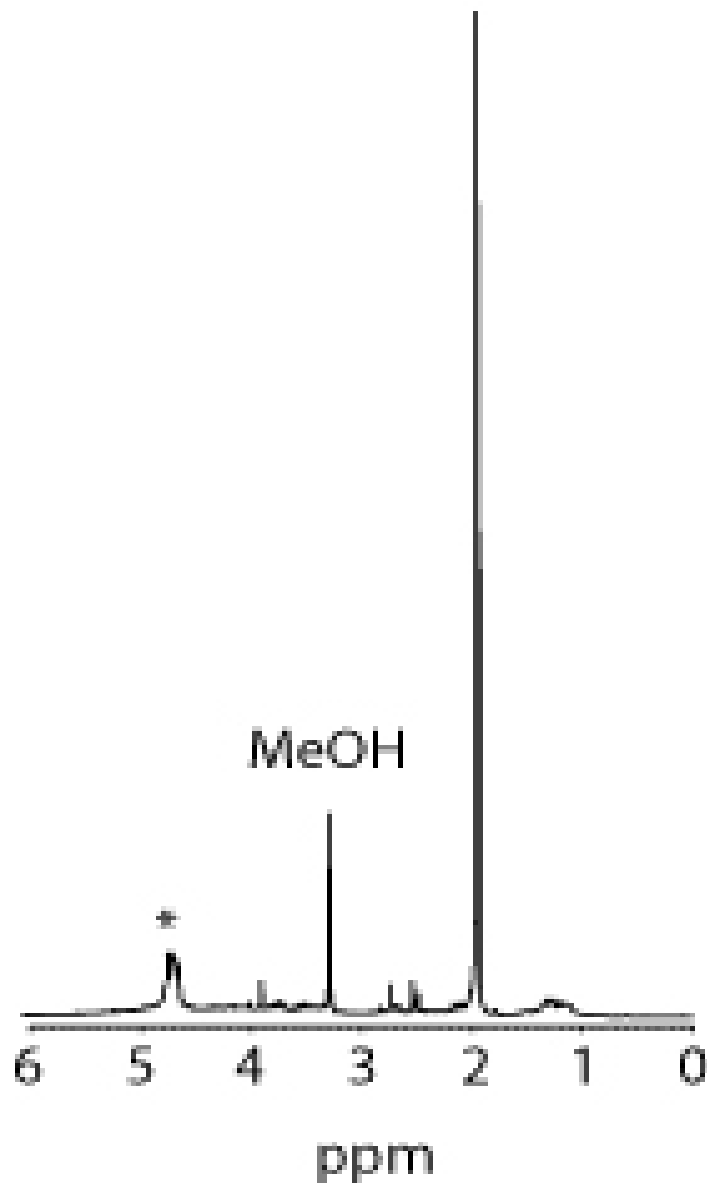
Acetic Acid



$\text{NaIO}_4$



$\Delta 80^\circ\text{C}$



## HMWDOC composition summary

Direct chemical analyses show that HMWDOC is 50-70% carbohydrate, 5-6% acetamide, and 5-6% "lipid"

Chemical hydrolyses techniques show HMWDOC to be 15% carbohydrate, 3-5% protein, and <1% lipid

Indirect chemical analyses show that an additional 25% is amino sugars, and 25% is deoxysugars. However, There is no direct confirmation of this.

A good portion of >25% remains uncharacterized. Much more at the molecular level.

