

Biogeochemical cycling of dissolved organic C and nutrients

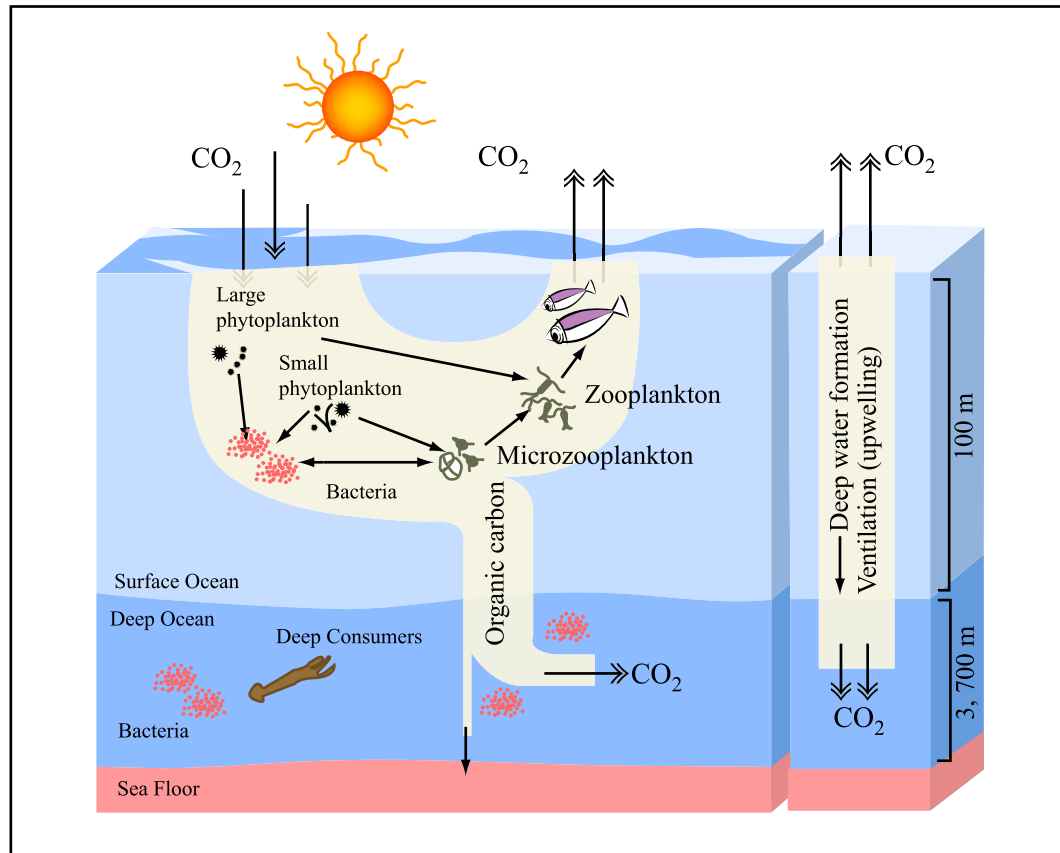
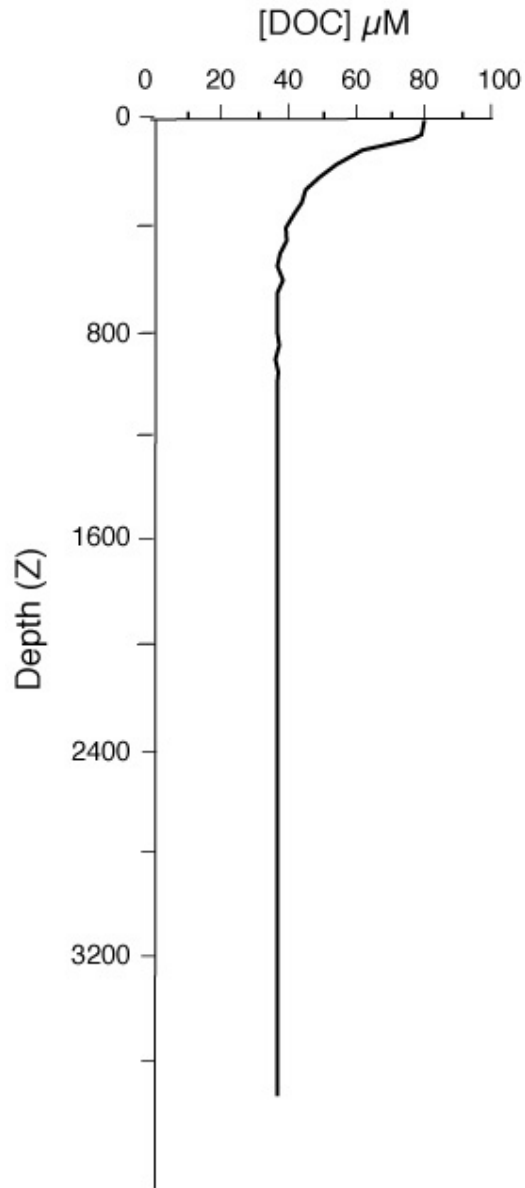


Figure by MIT OCW.



The profile of [DOC] With depth in the ocean

1. Measured by HTCO or wet chemical oxidation
2. Surface values are 60-80 μM C
deep sea values are 40 μM 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?

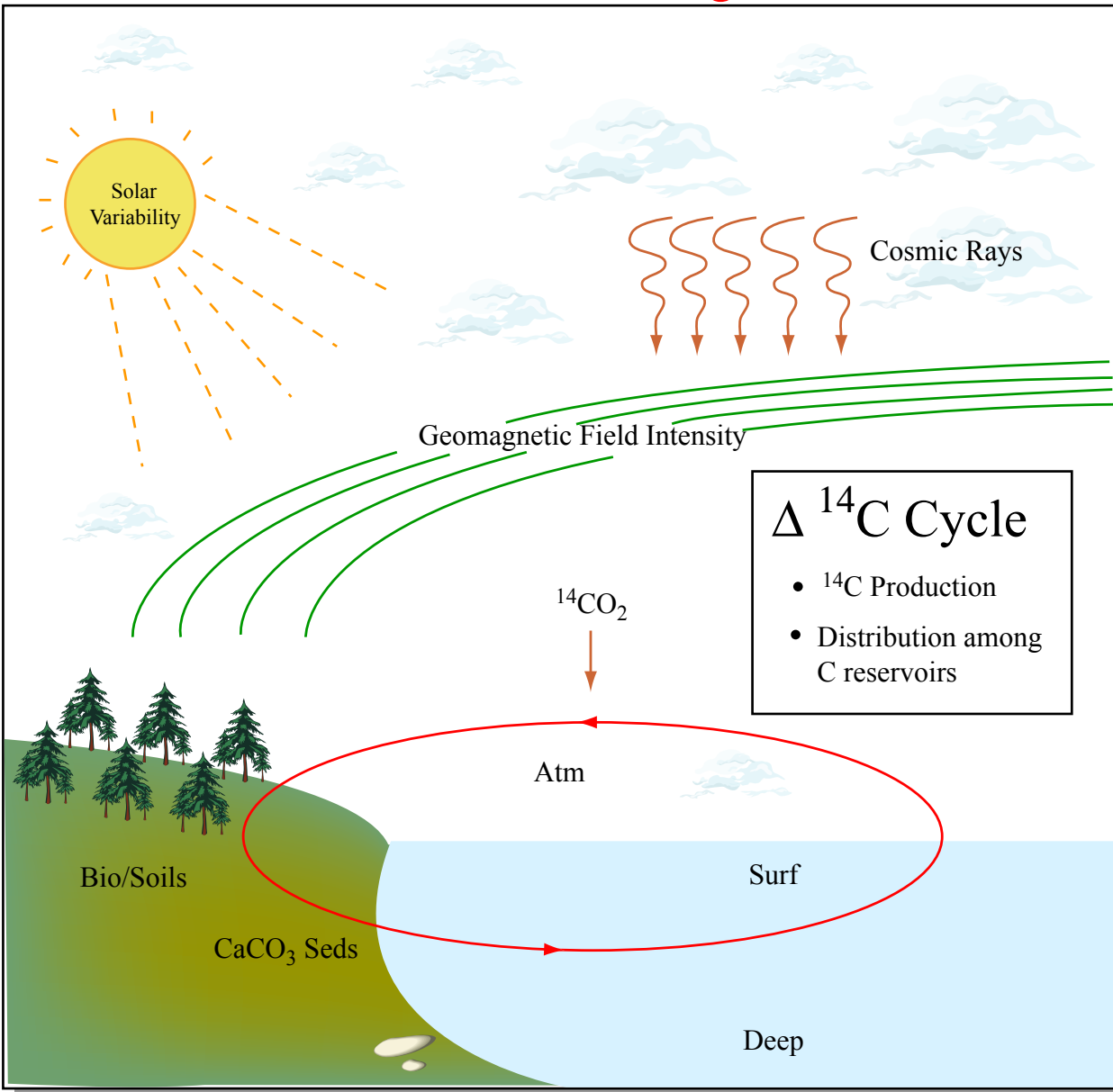
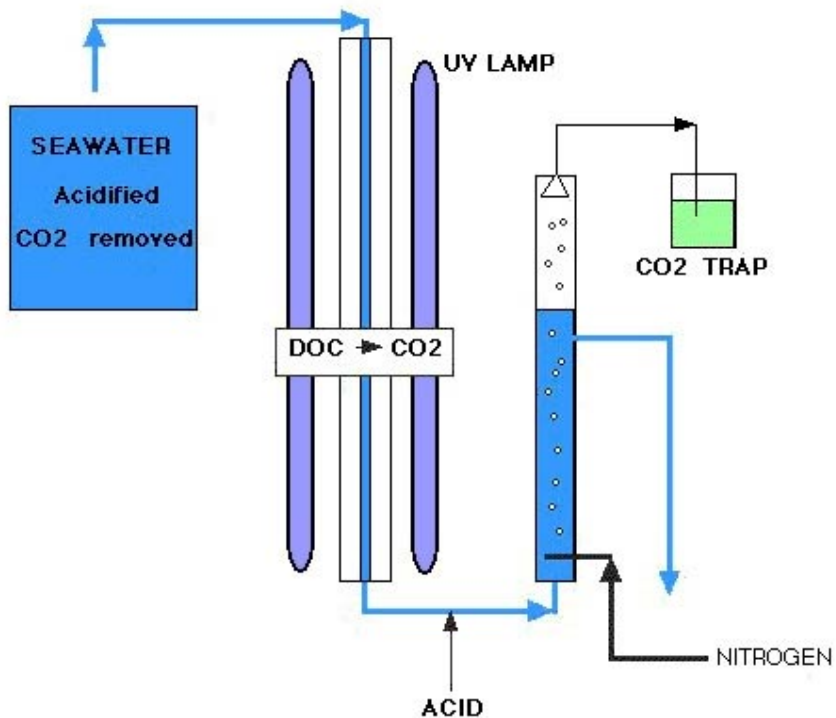


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Source Unknown.

Figure by MIT OCW.

□ Radiocarbon Age of Dissolved Organic Carbon



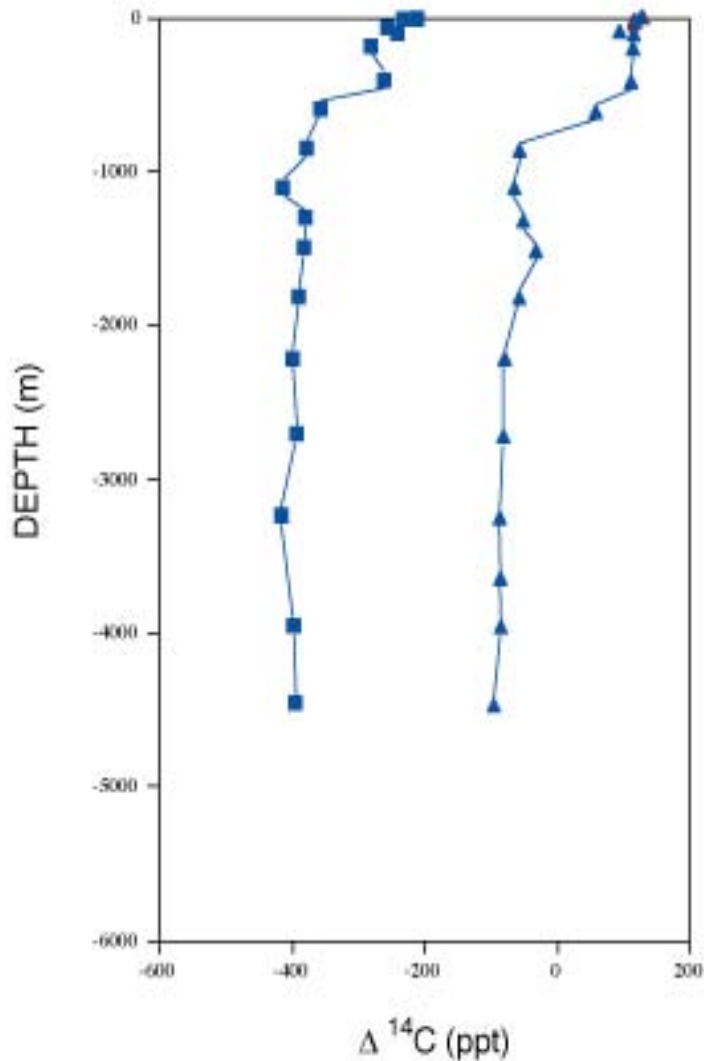
Pioneered by Pete Williams
At SIO.

Contamination is a
big problem!!!

Does UV get it all ?

Pre AMS 1g C (1m³)
Now about 1mg C (1L)

Radiocarbon in DOC and DIC



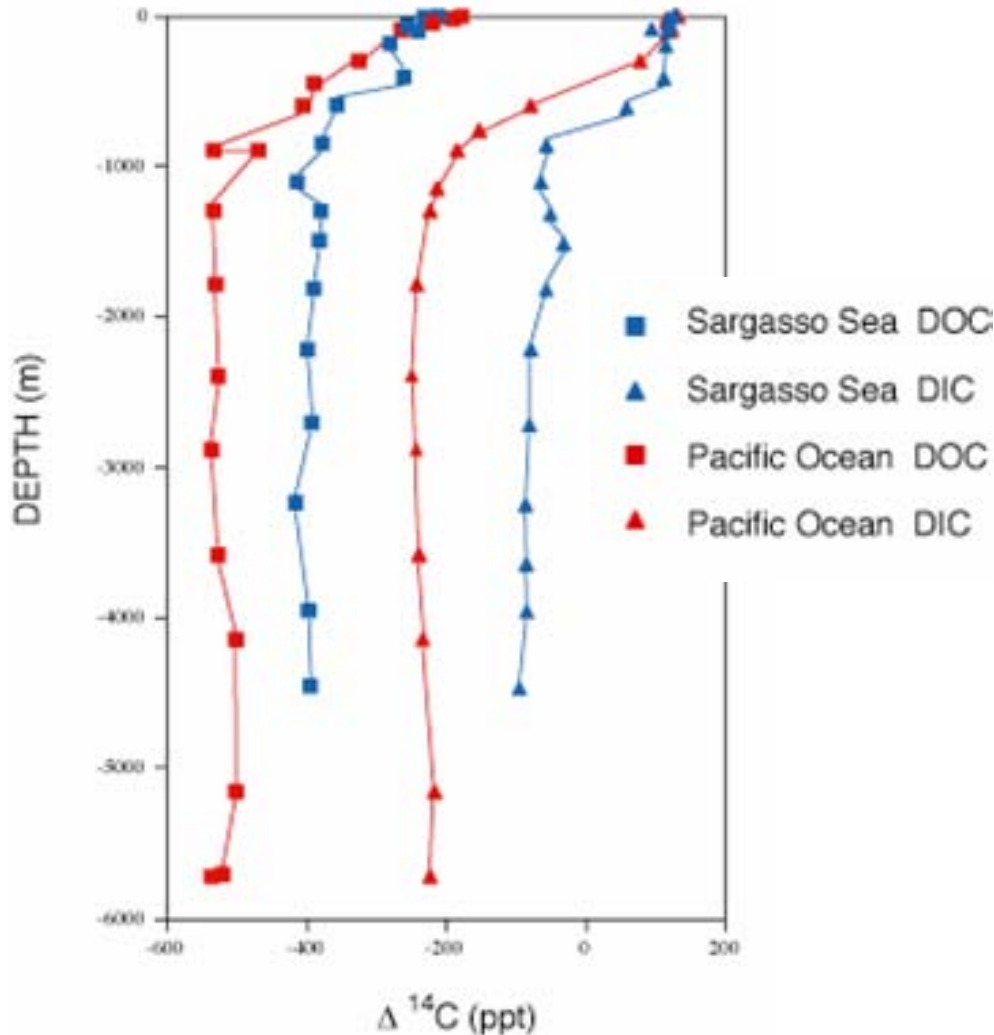
$\text{CO}_2 \rightarrow \text{DIC} \rightarrow \text{POC} \rightarrow \text{DOC}$

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



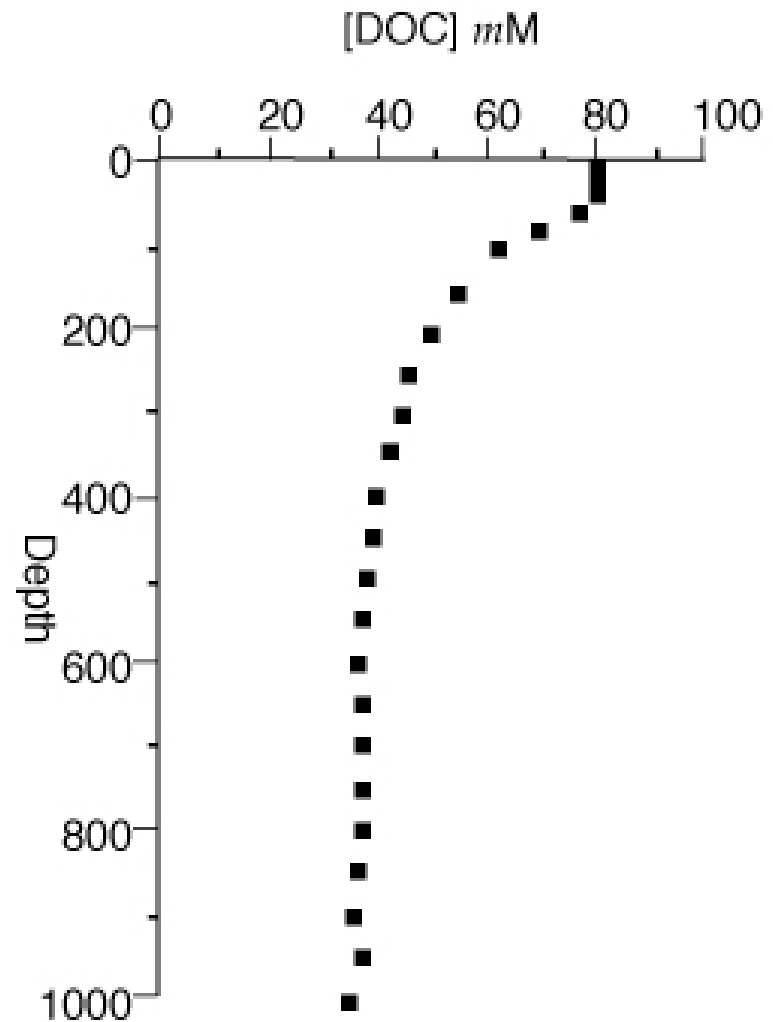
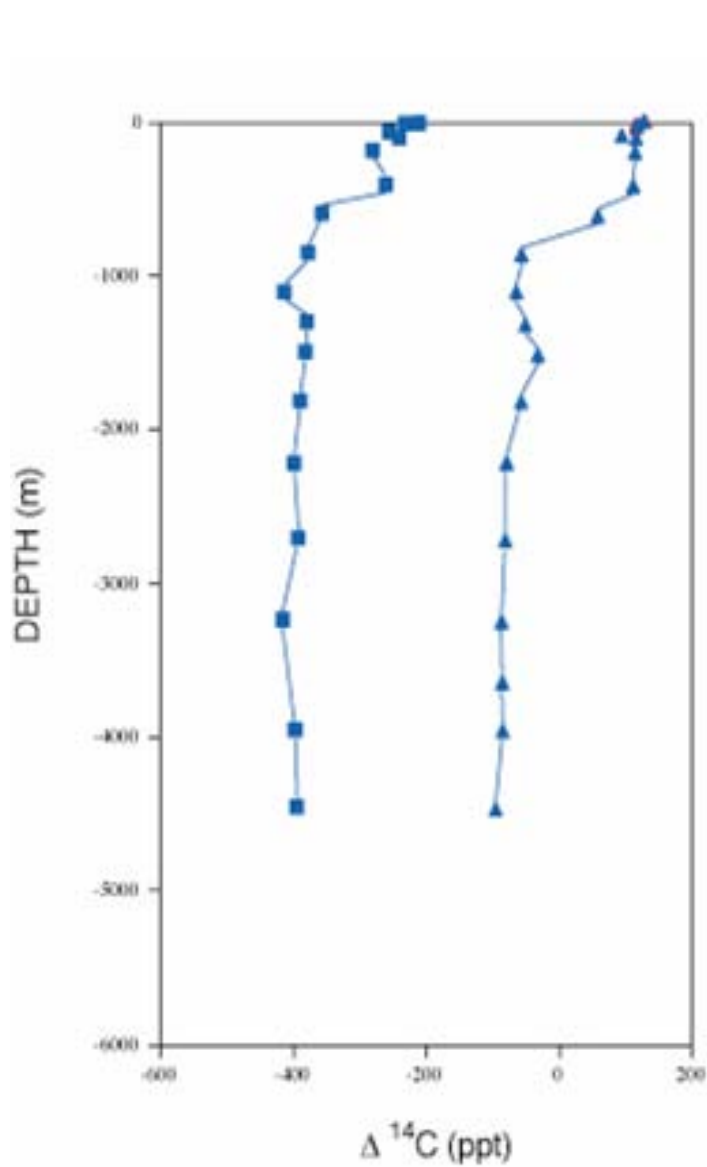
DIC ^{14}C has the same Value in the Atl and Pac

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

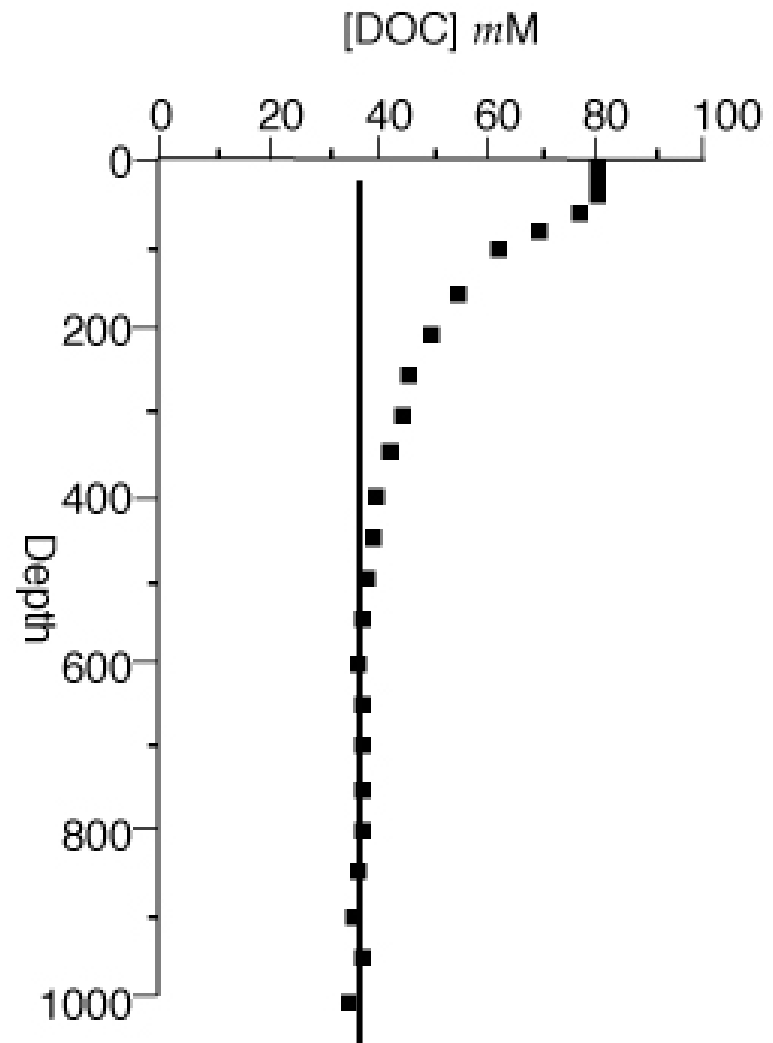
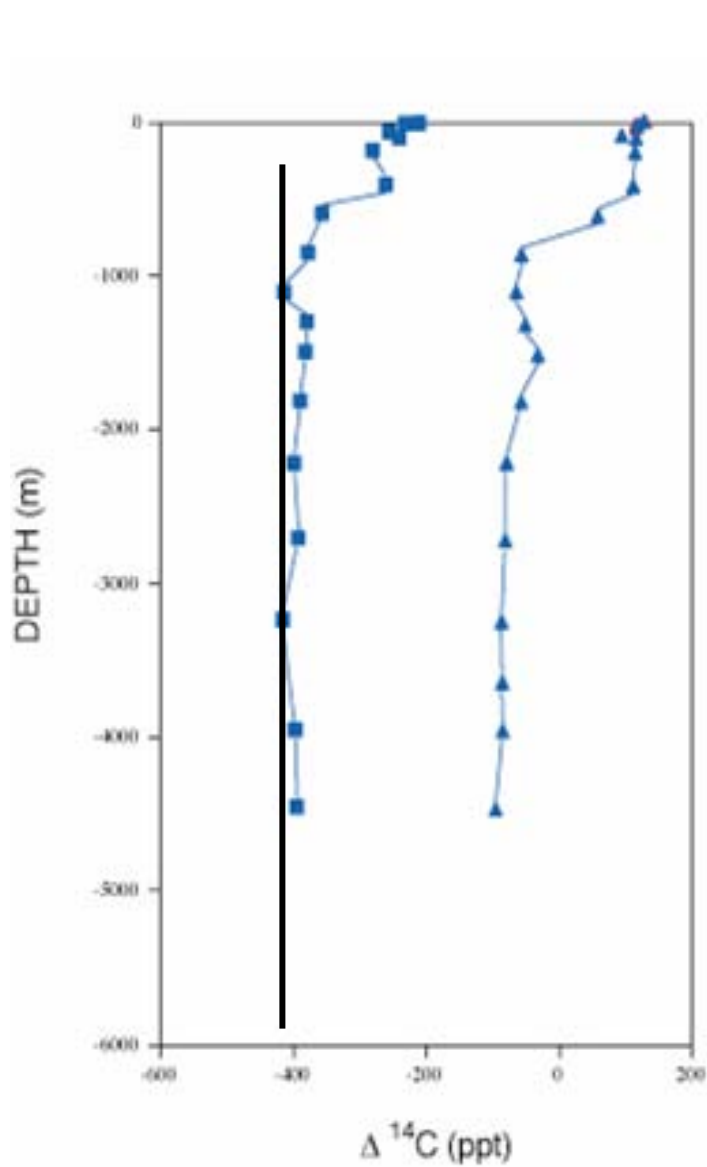
Deep ocean values are equal to a RC age of Several 1000's years

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

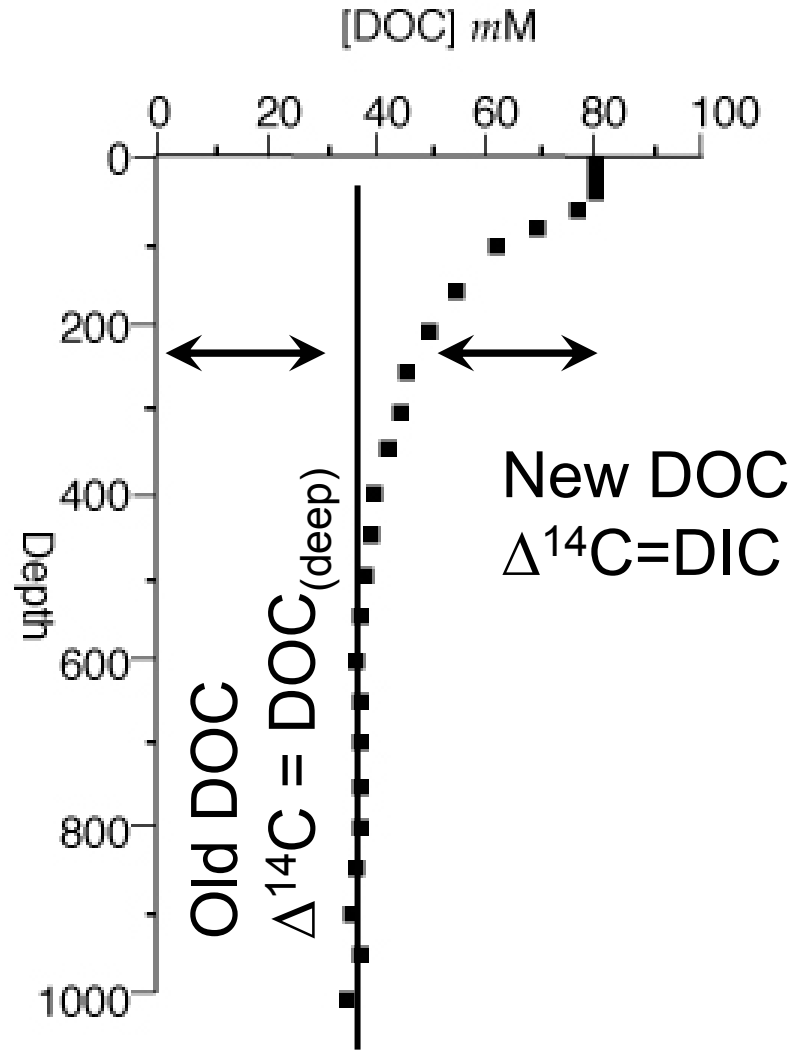
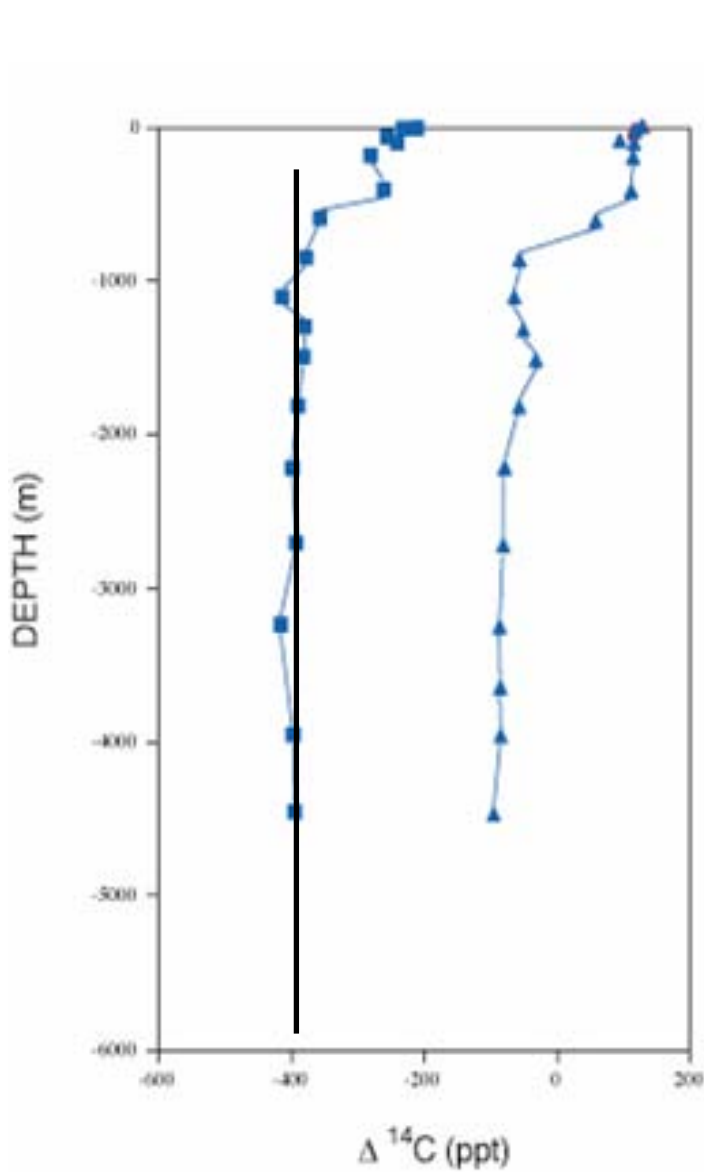
Why is DOC old in surface water?



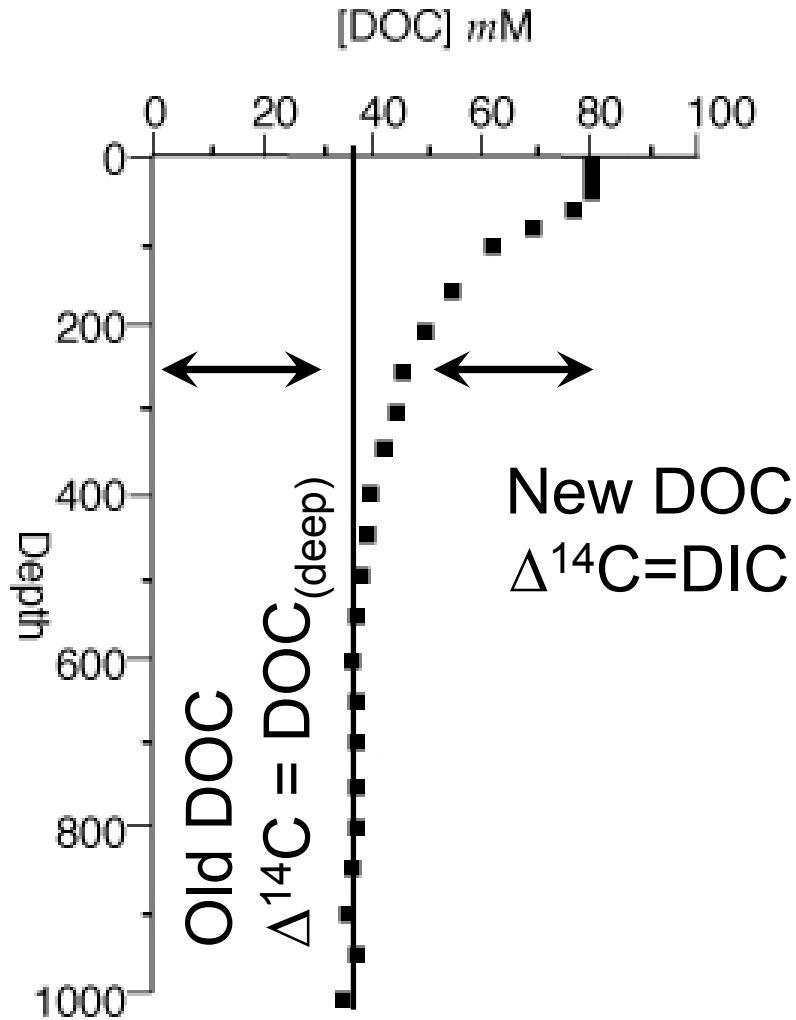
Why is DOC old in surface water?



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

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

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

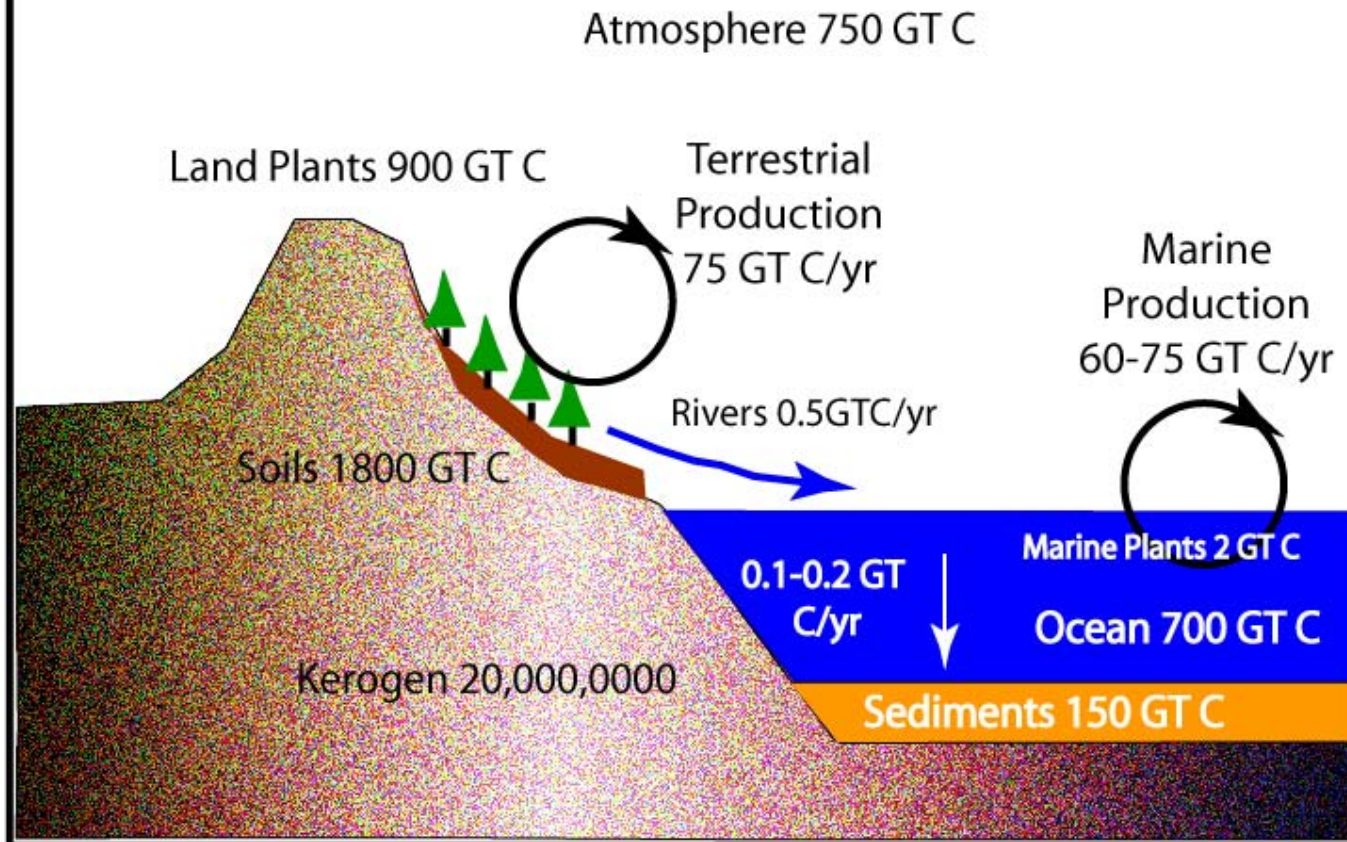
What flux of carbon is needed to maintain the marine DOC reservoir?

Global inventory/residence time = annual flux

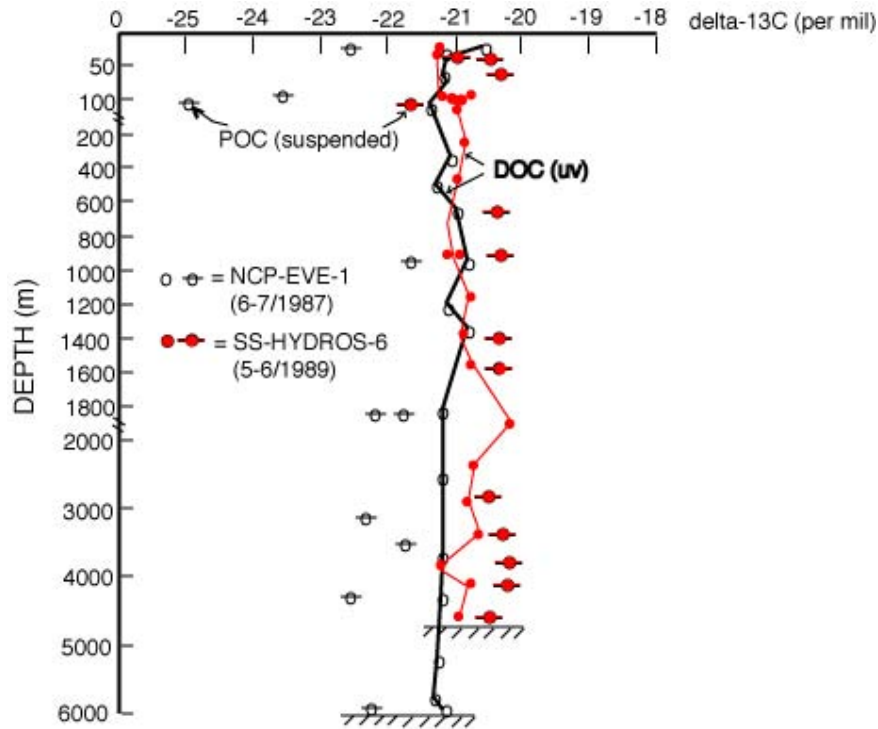
680 GT C/ 5000-6000 yr = 0.11-0.14 GT C/yr !!!

How does this compare with other C fluxes?

Major Carbon Reservoirs



What is the source of Marine DOC ?



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.

Stable C isotopes

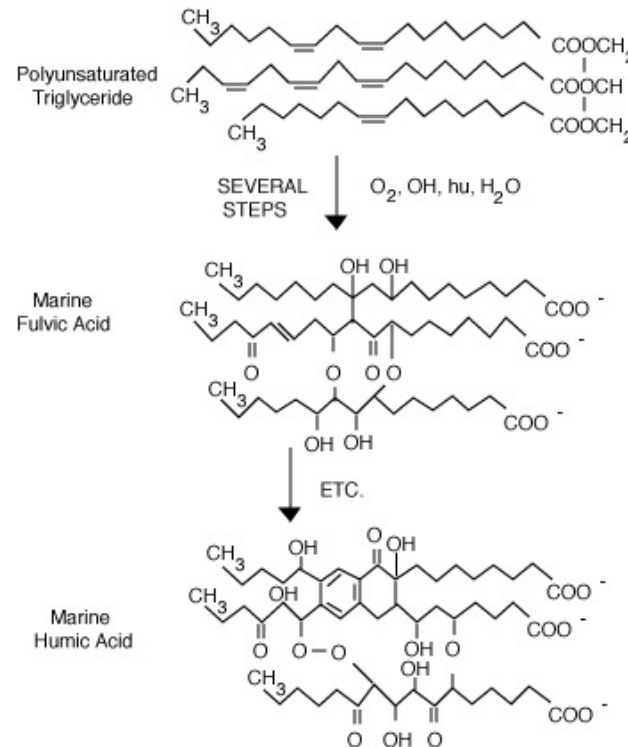
Marine C -21‰

Terrestrial C

C3 plants -27‰

C4 plants -15‰

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

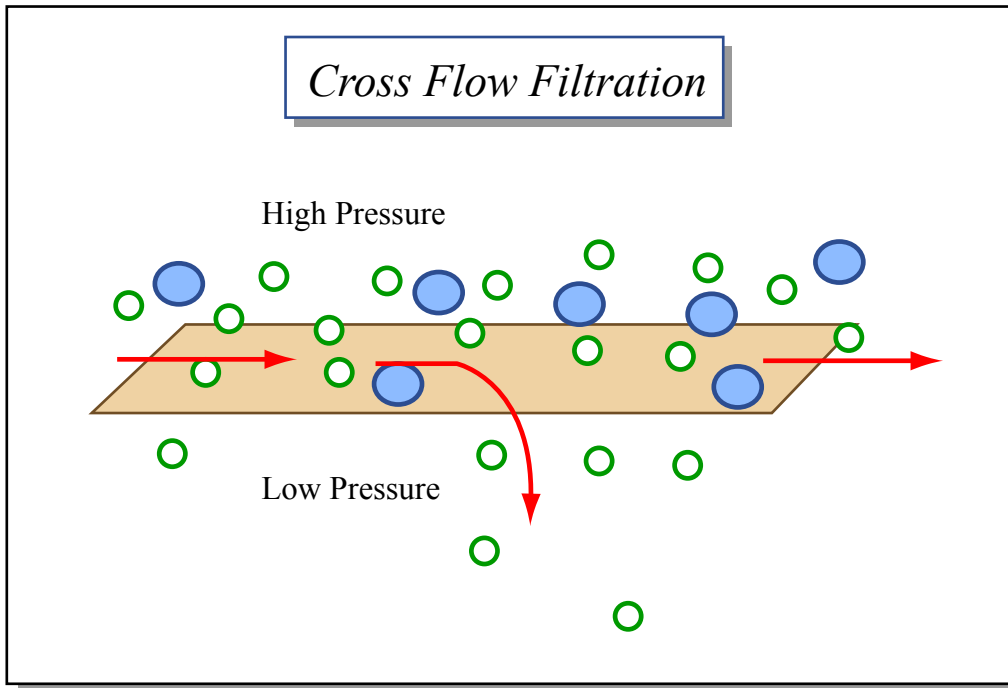


Figure by MIT OCW.

Separation based on size

1 nm pore @ 1 kD

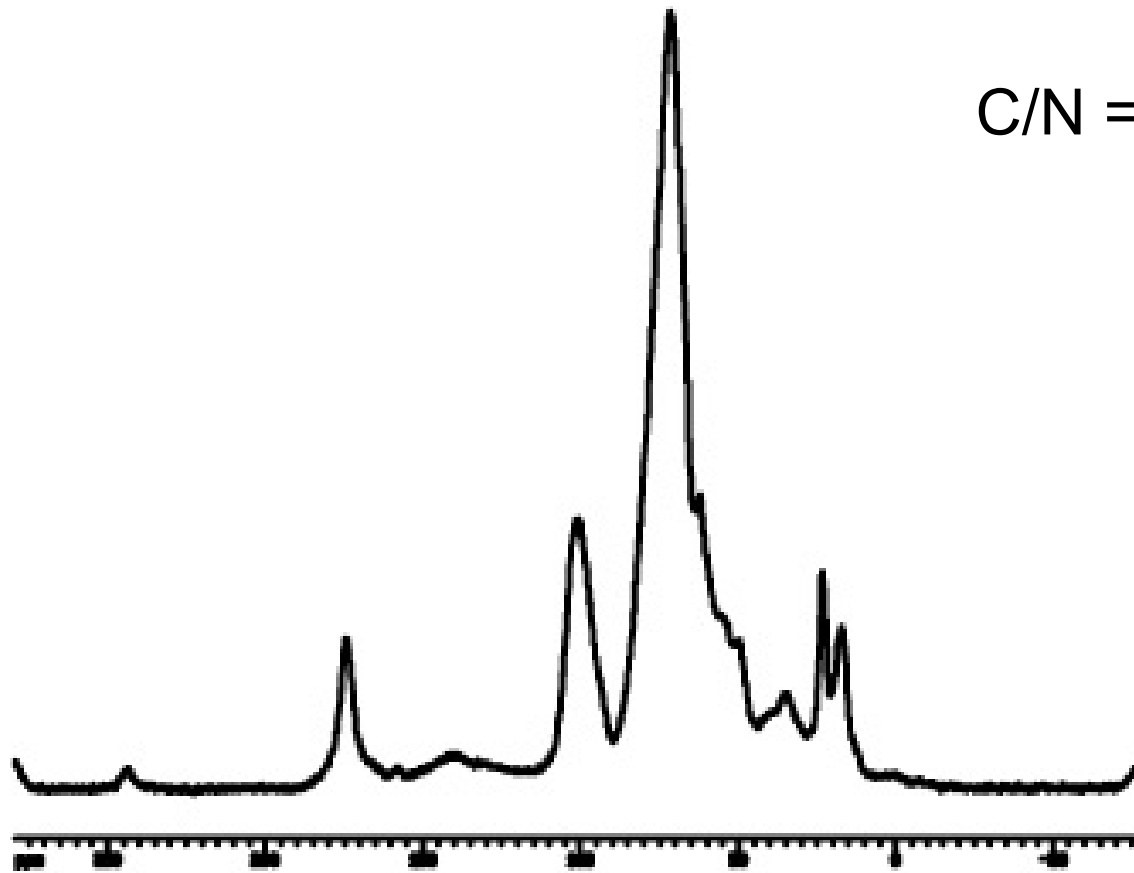
Selects for HMW fraction

about 30-35% TOC

Membrane effects what
Is collected

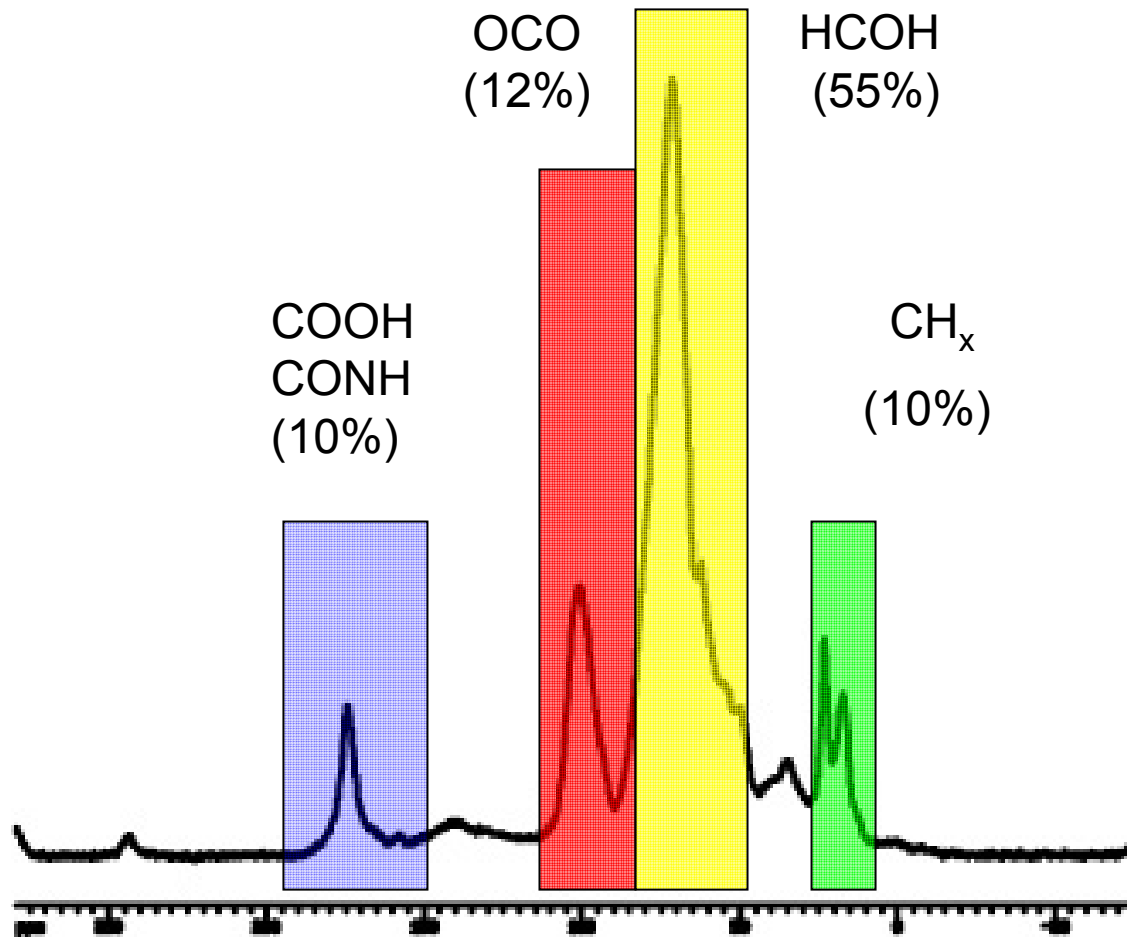
Some salts collected too!

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

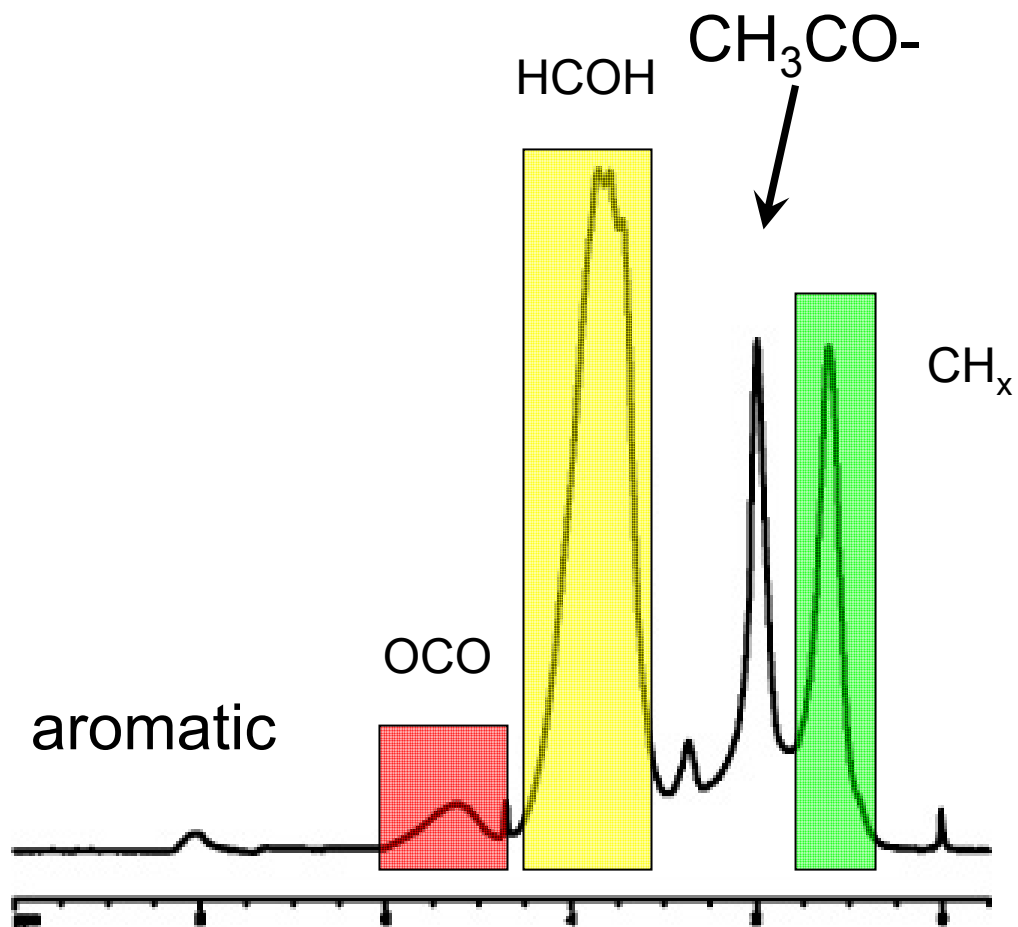


C/N = 15 ± 3

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



^1H NMR of high molecular weight DOC



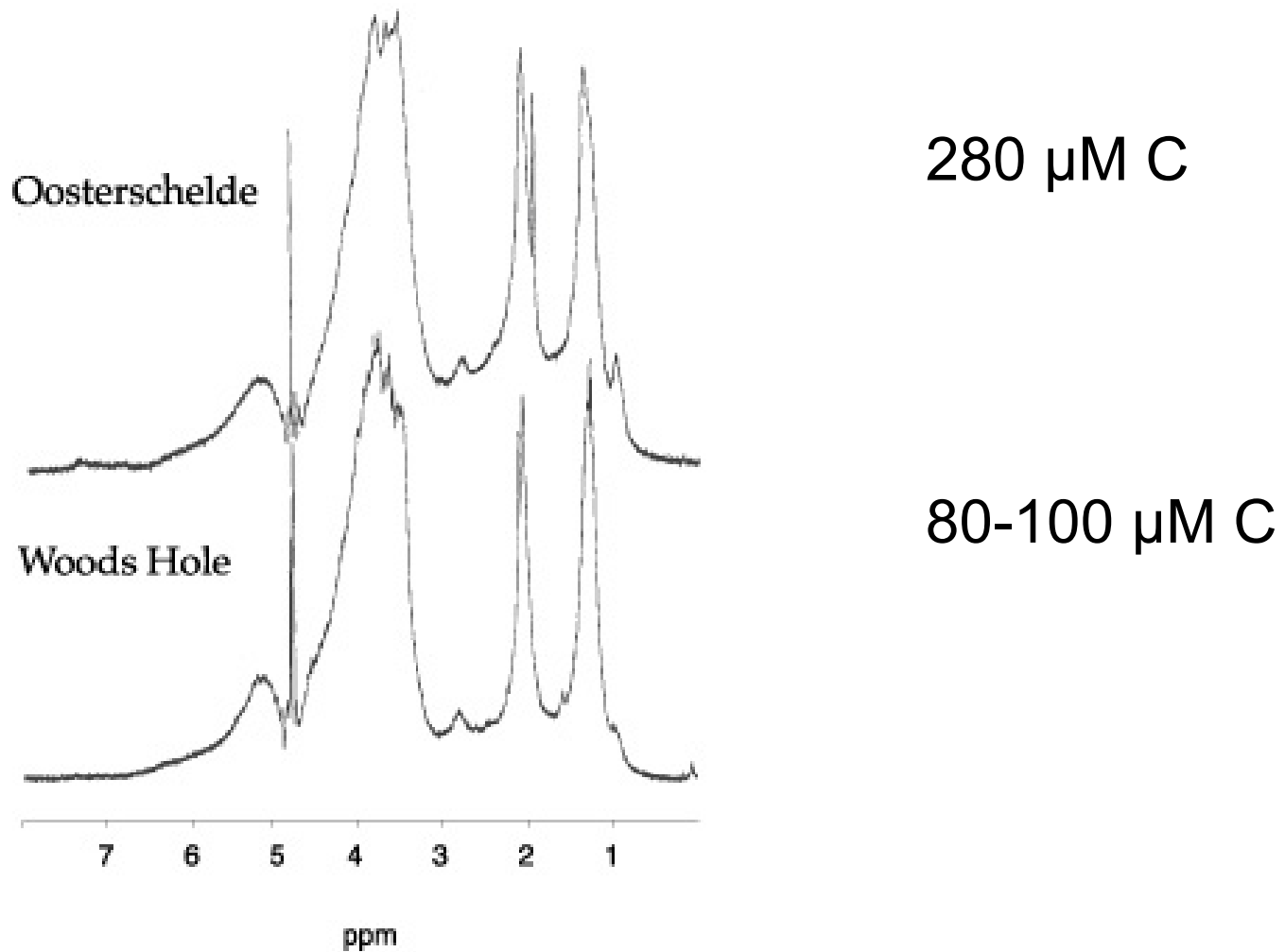
HMWDOC, what could it be?

From our knowledge of cell biochemicals...

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

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

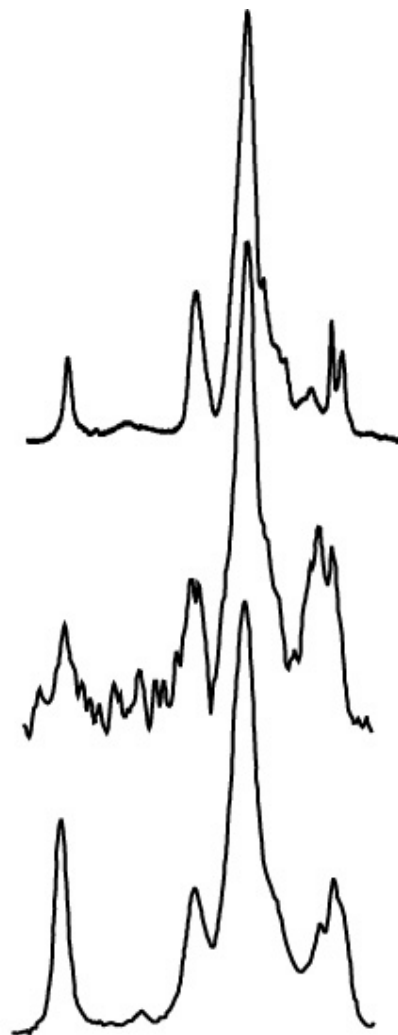
Chemical characterization of UDOM in seawater



Relative abundance of major biochemicals in HMWDOC

Sample	DOC	Carbon (relative %)		
		Carbohydrate	Acetate	Lipid
Atlantic Ocean				
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
Pacific Ocean				
Scripps Pier	ND	81	12	6
Peru coast	ND	81	13	6
Hawaii	ND	85	7	8
Average		80\pm4	10\pm2	9\pm4

HMWDOC in freshwater and marine environments



NPSG

Andrews Creek
RMNP 3400M

Great Salt Lake (UT)

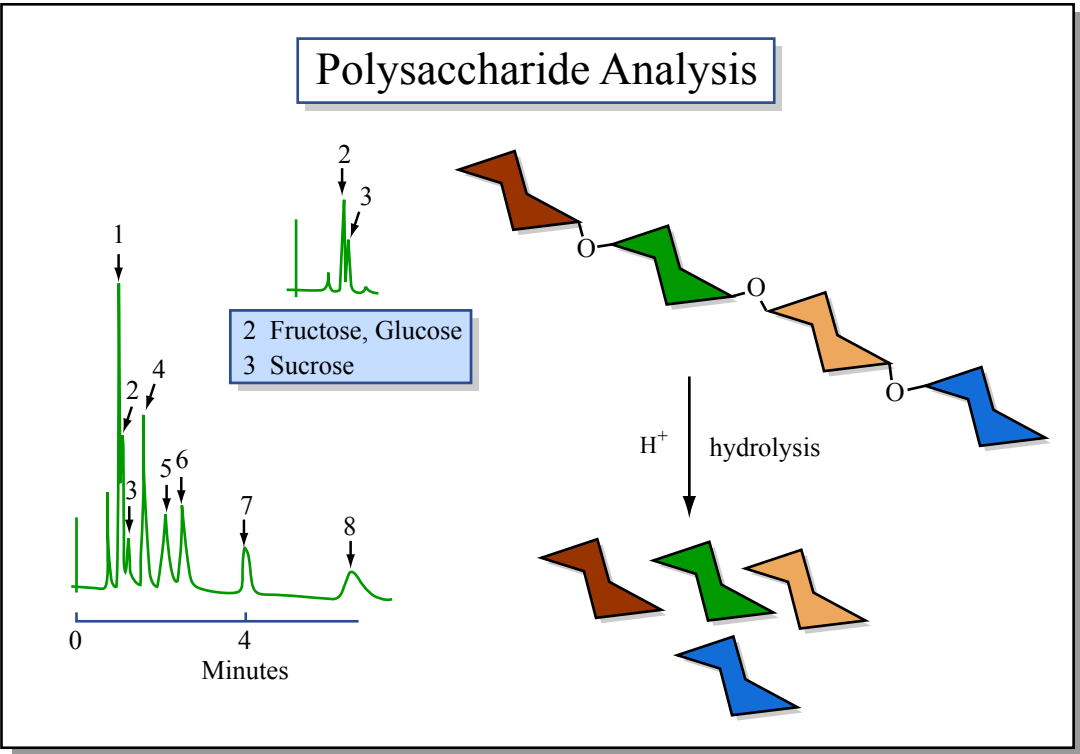
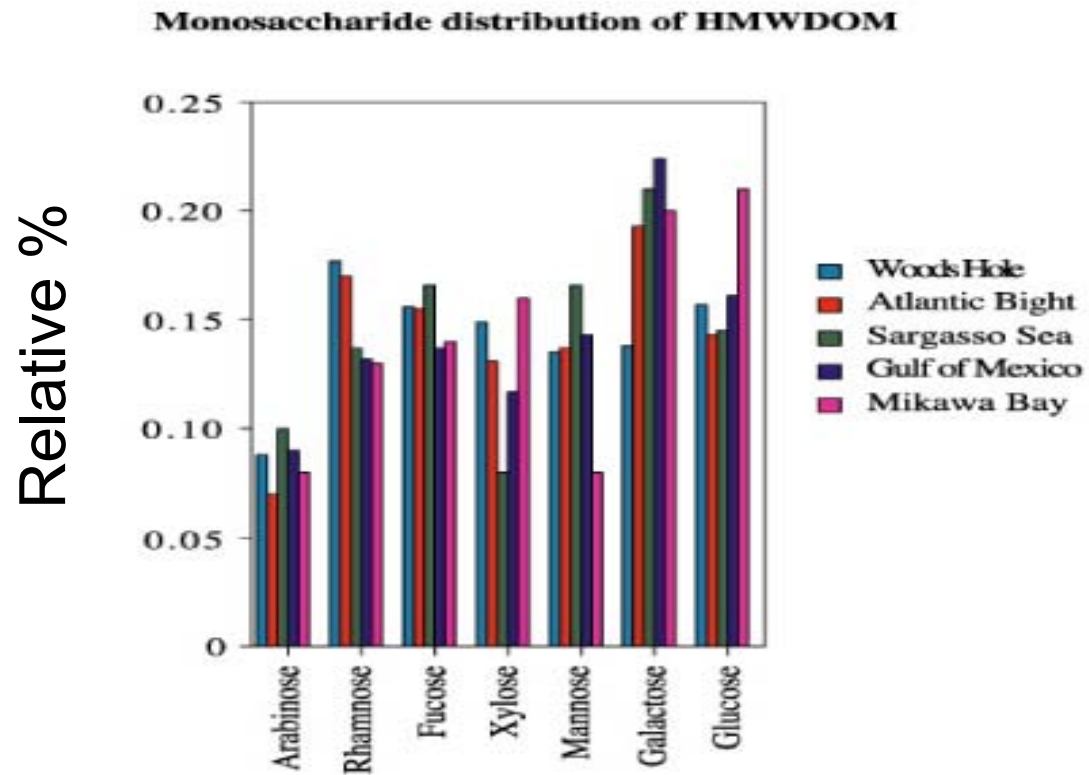


Figure by MIT OCW.

Relative abundance of sugars in HMWDOC



HMWDOC monosaccharides in rivers, lakes, and seawater

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Locations of sampling:

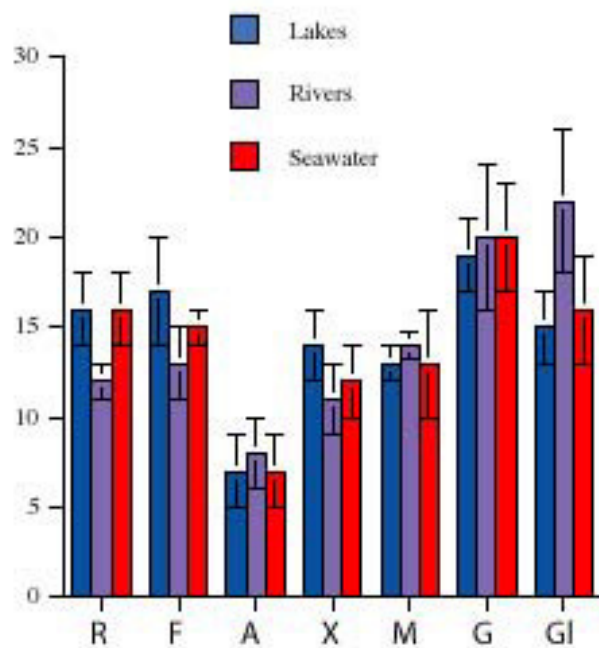
Eel River

Lake Superior

Nobska Pond

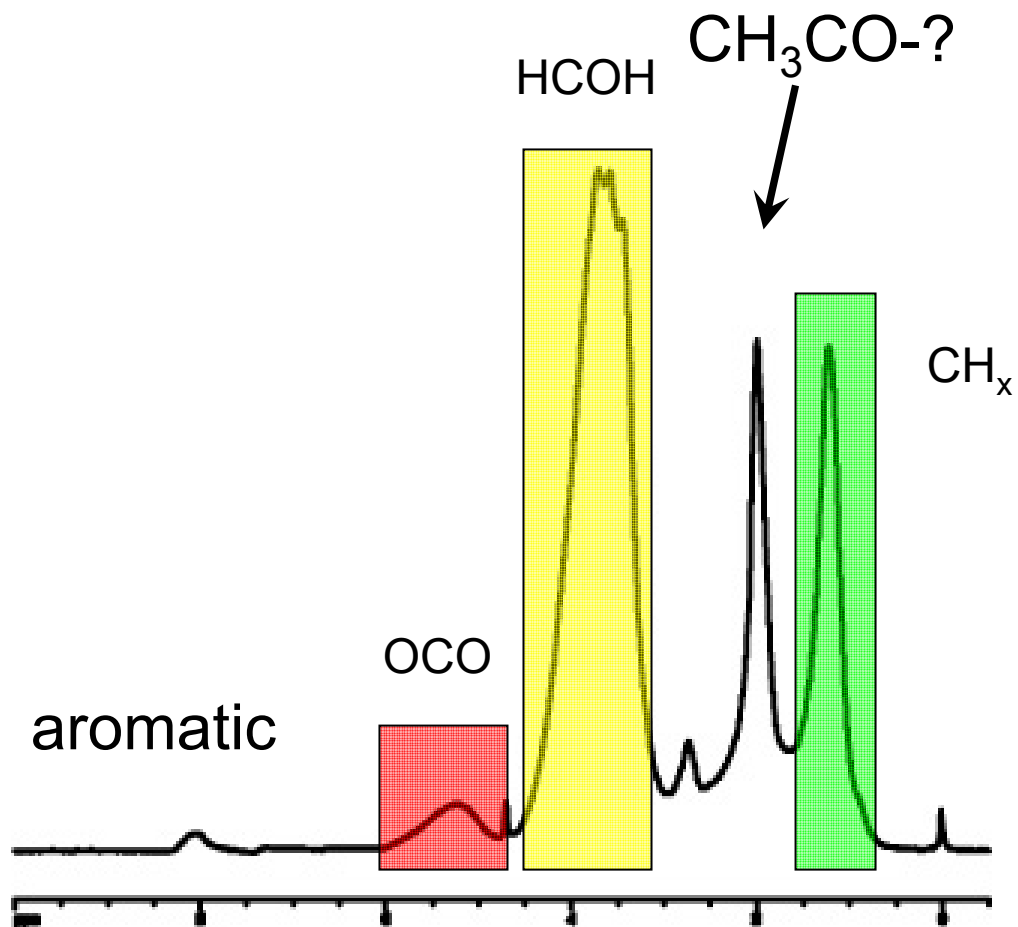
Delaware River

Mississippi River



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

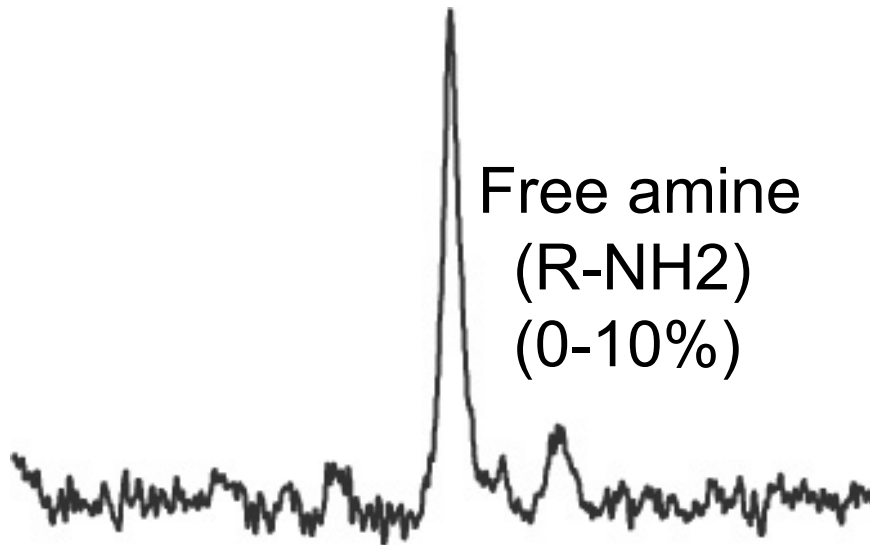
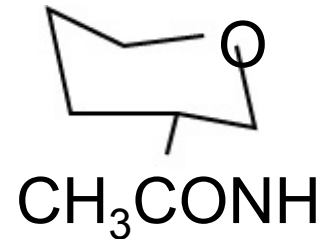
^1H NMR of high molecular weight DOC



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

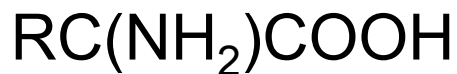
Amide (RCON)
(90-100%)

amino sugars

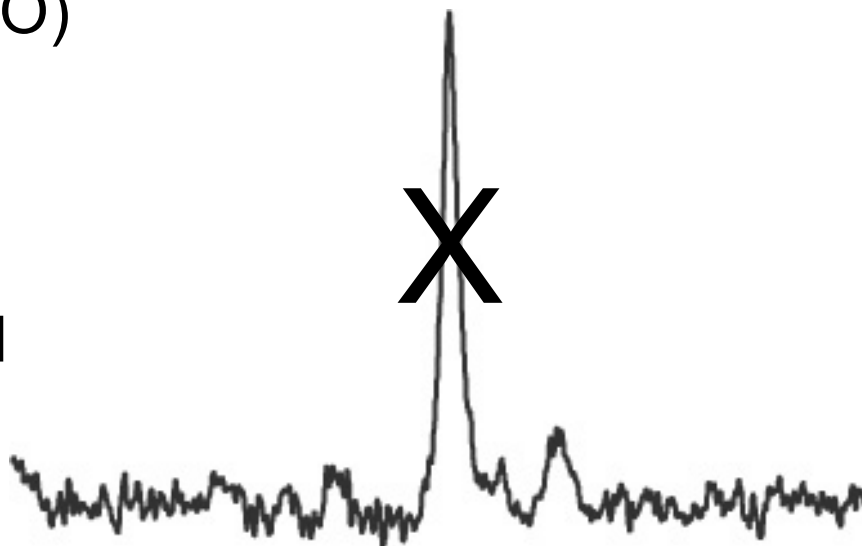


Is a large fraction of HMWDOC and HMWDON
from amino sugars or proteins?

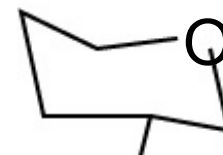
proteins



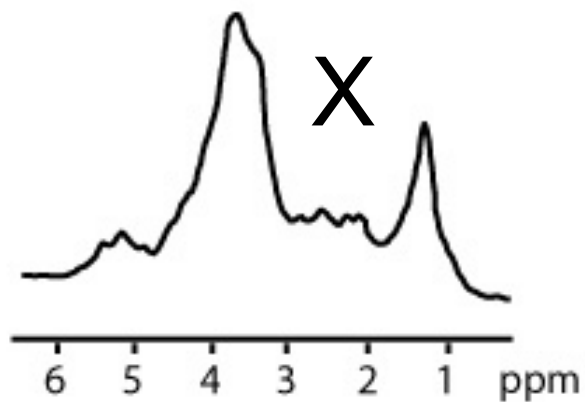
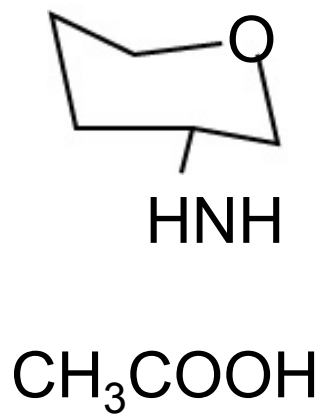
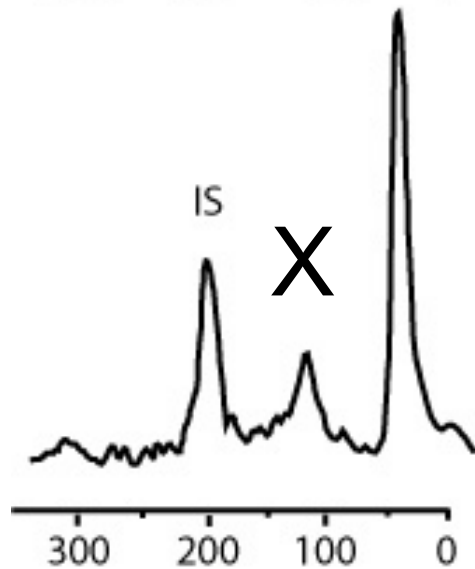
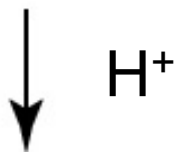
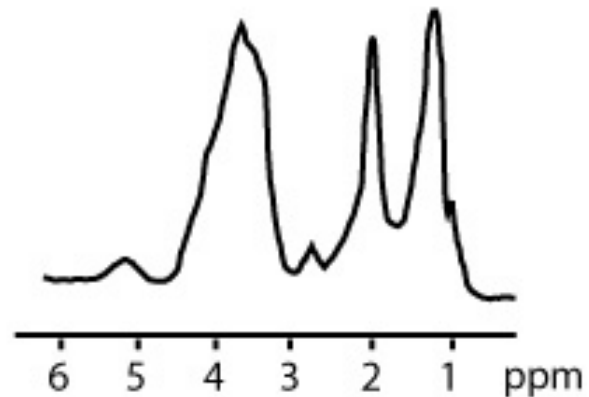
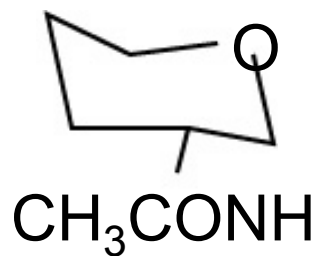
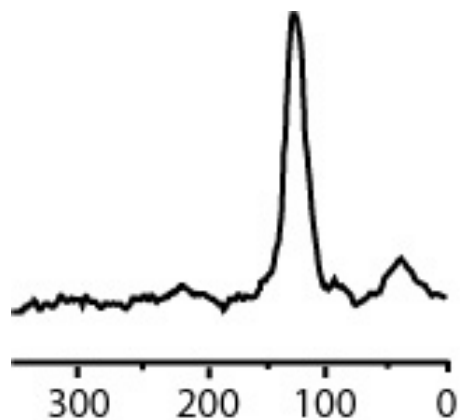
(amino acids)



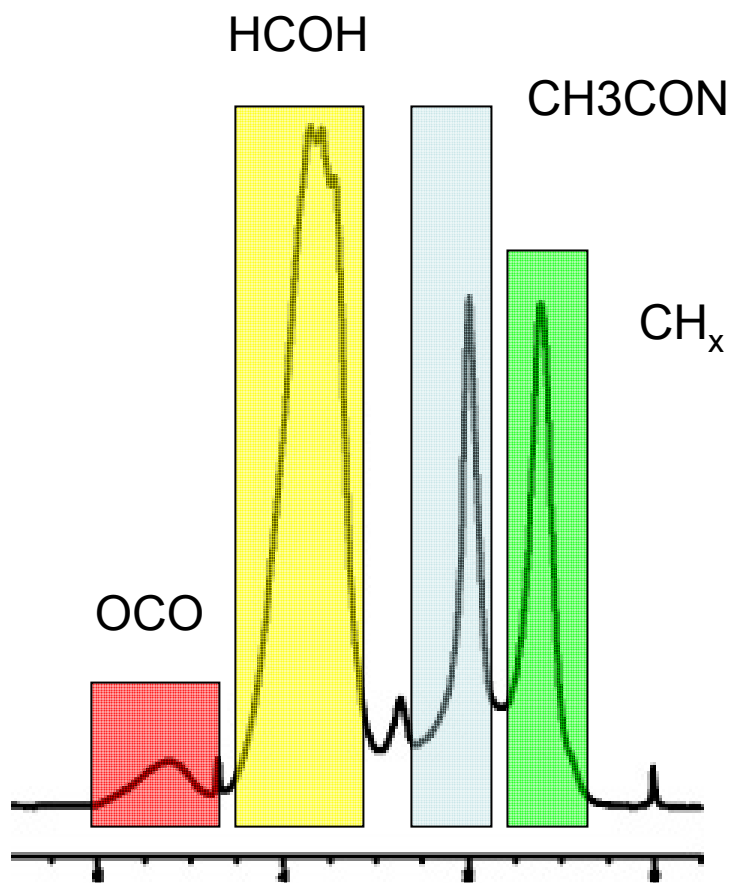
amino sugars



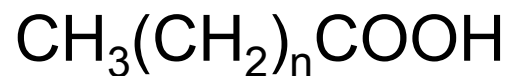
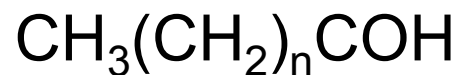
Is a large fraction of HMWDOC and HMWDON
from amino sugars?



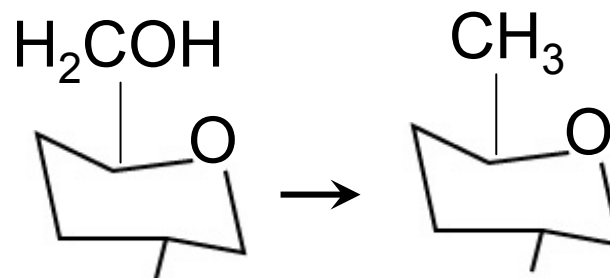
What is the 'lipid' in HMWDOC?



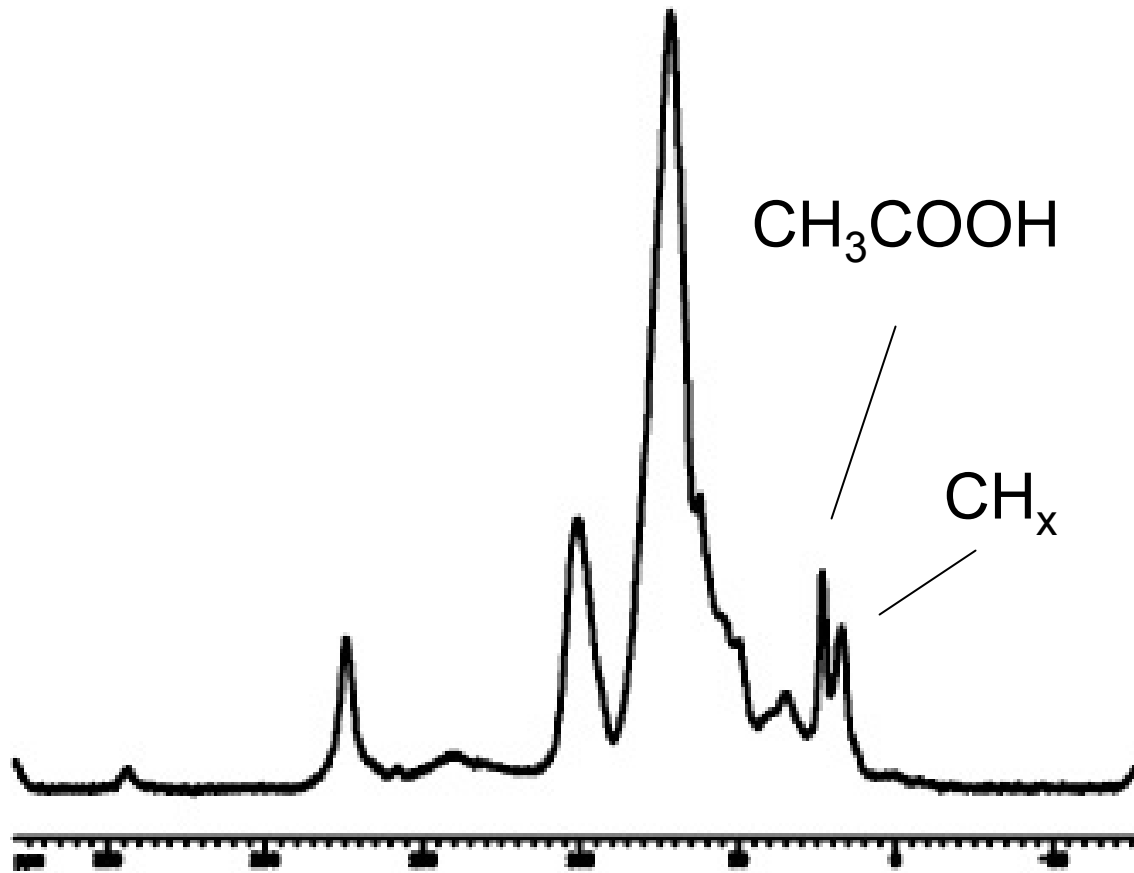
Lipid



Deoxy sugars

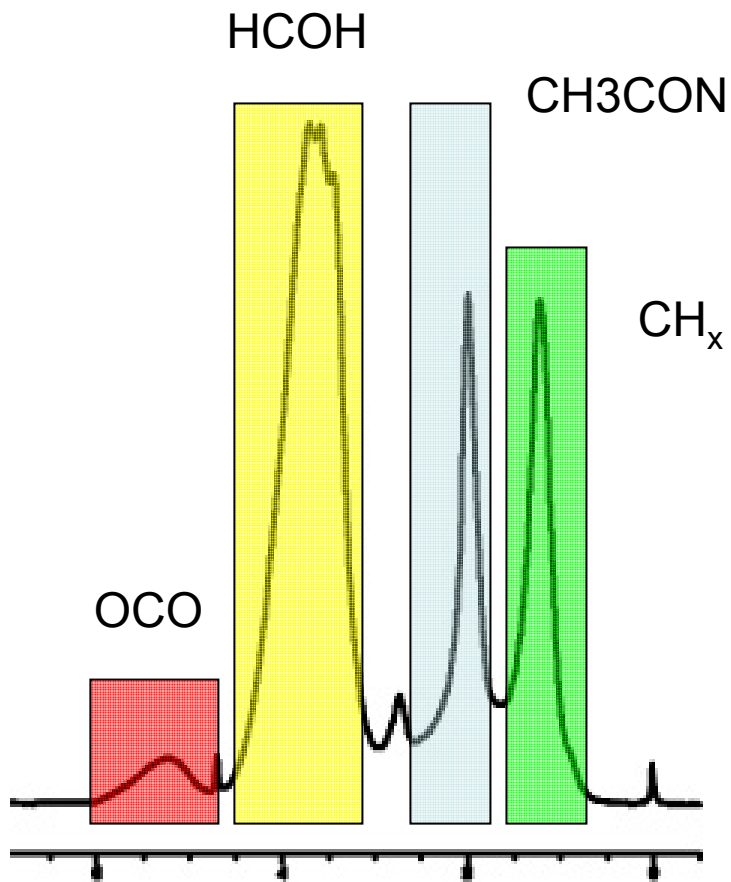


There are really “two” types of lipid in HMWDOC



The effect of periodate on HMWDOC

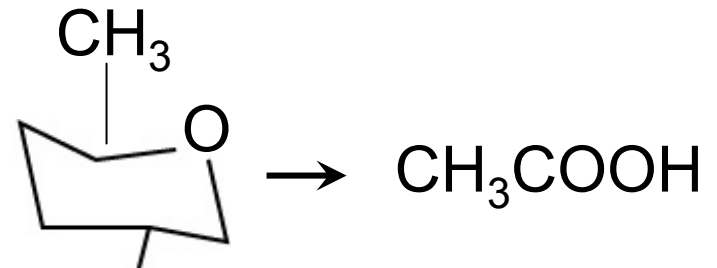
Is the lipid really lipid?



Lipid

$\text{RCOH} \rightarrow$ No Reaction

Deoxy sugars



Periodate oxidation of HMWDOC

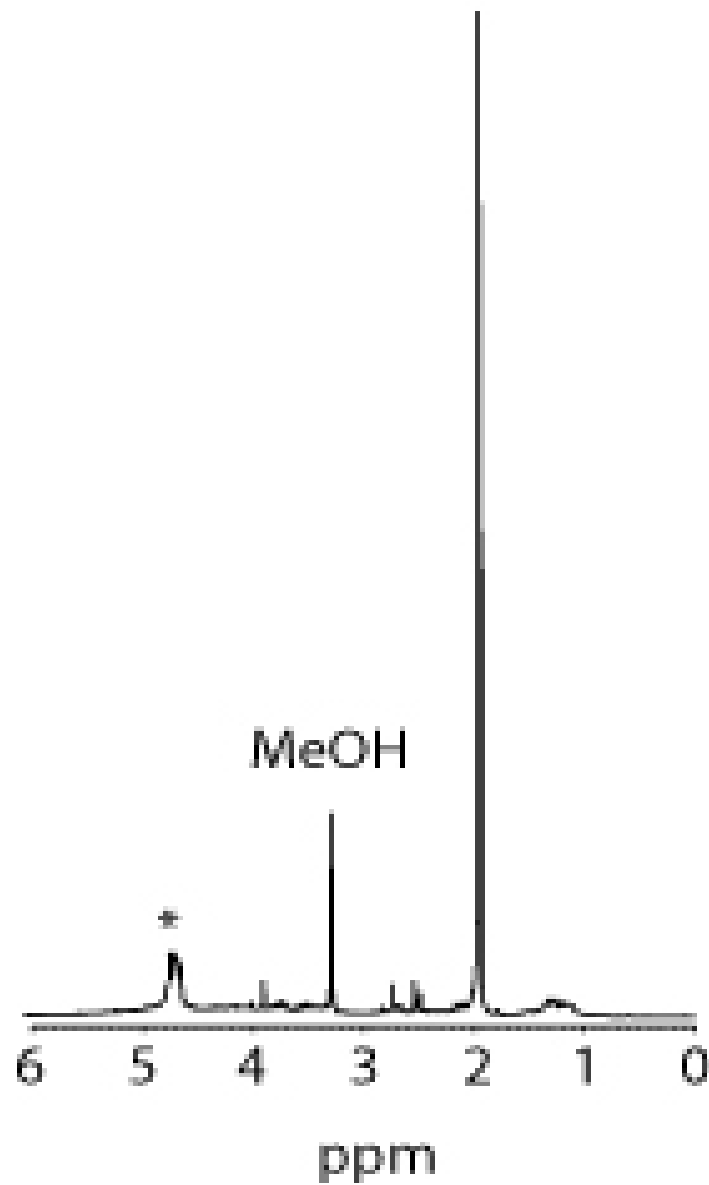
Acetic Acid



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.