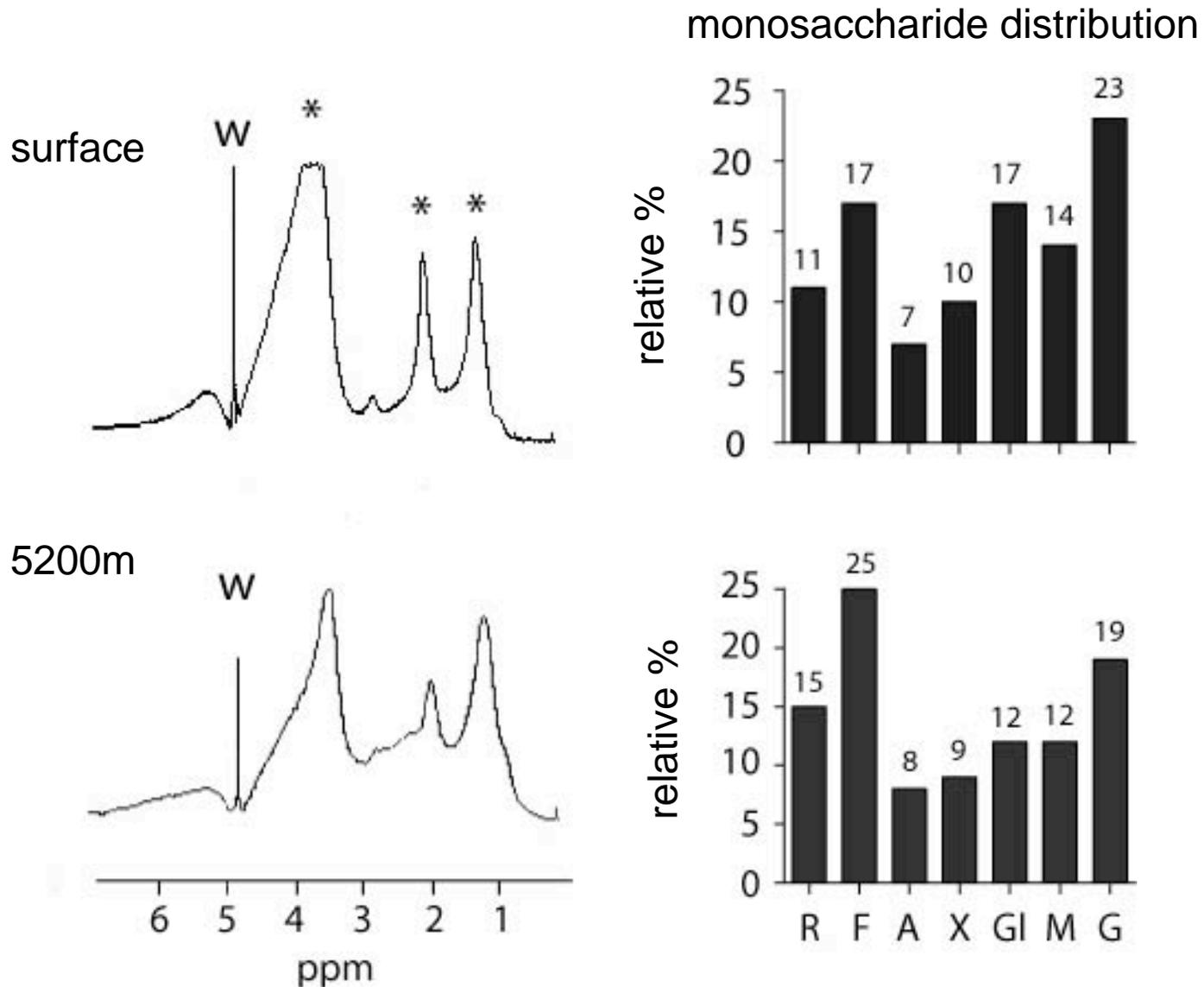


Deep sea gradients in [DOC]

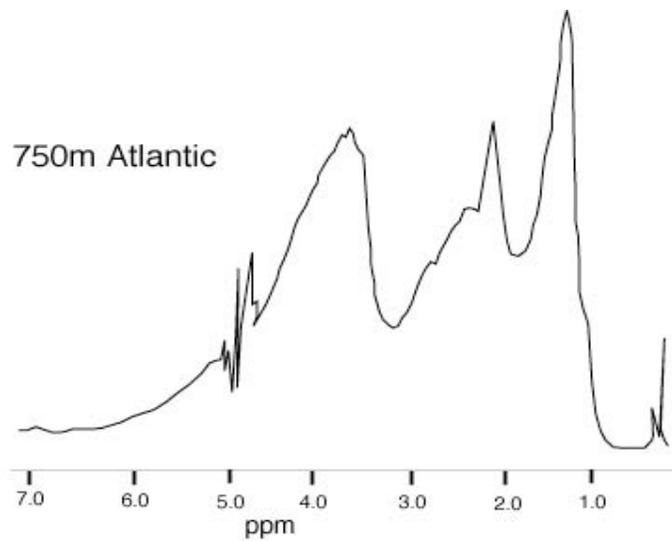
Figures removed due to copyright restrictions. Figures from Hansell, D., C. Carlson.
Deep-ocean gradients in the concentration of dissolved organic carbon. *Nature* 395, 1998

NMR and carbohydrate analyses of deep sea HMWDOC

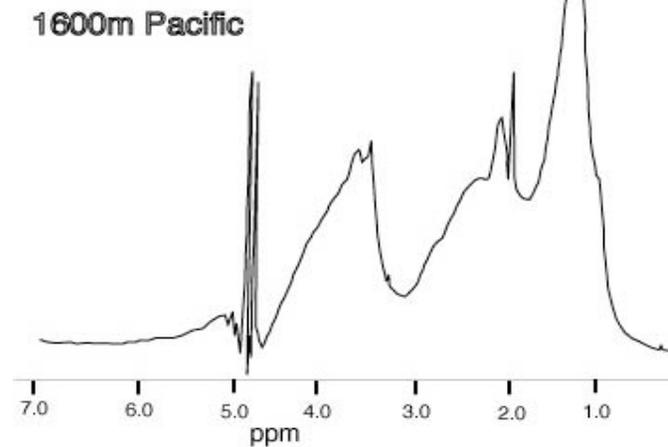


NMR and carbohydrate analyses of deep sea HMWDOC

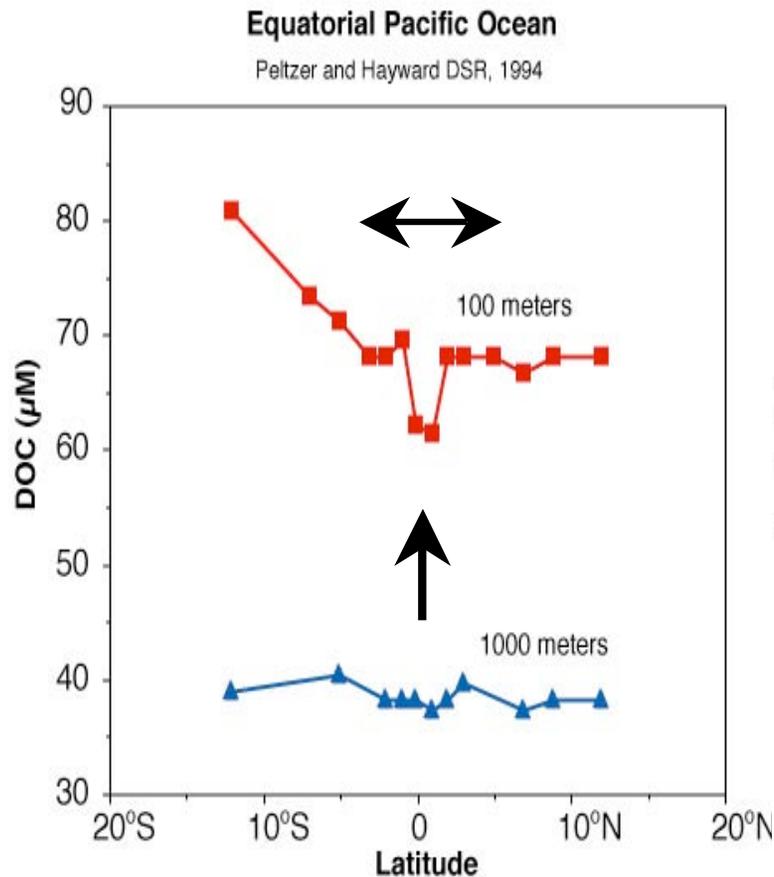
^{13}C - and ^1H NMR of HMWDOC from deep samples in the Atlantic and Pacific Oceans appear to be very similar, suggesting similar composition throughout the deep ocean



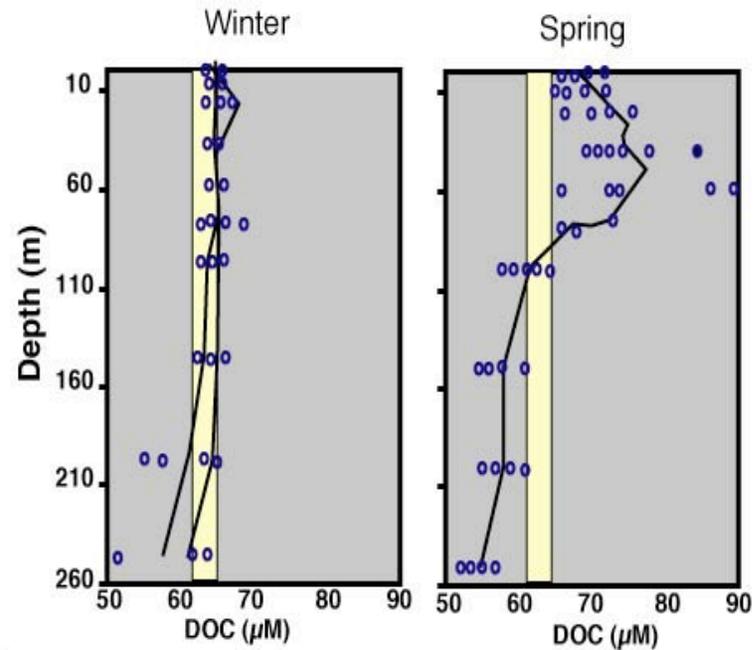
^



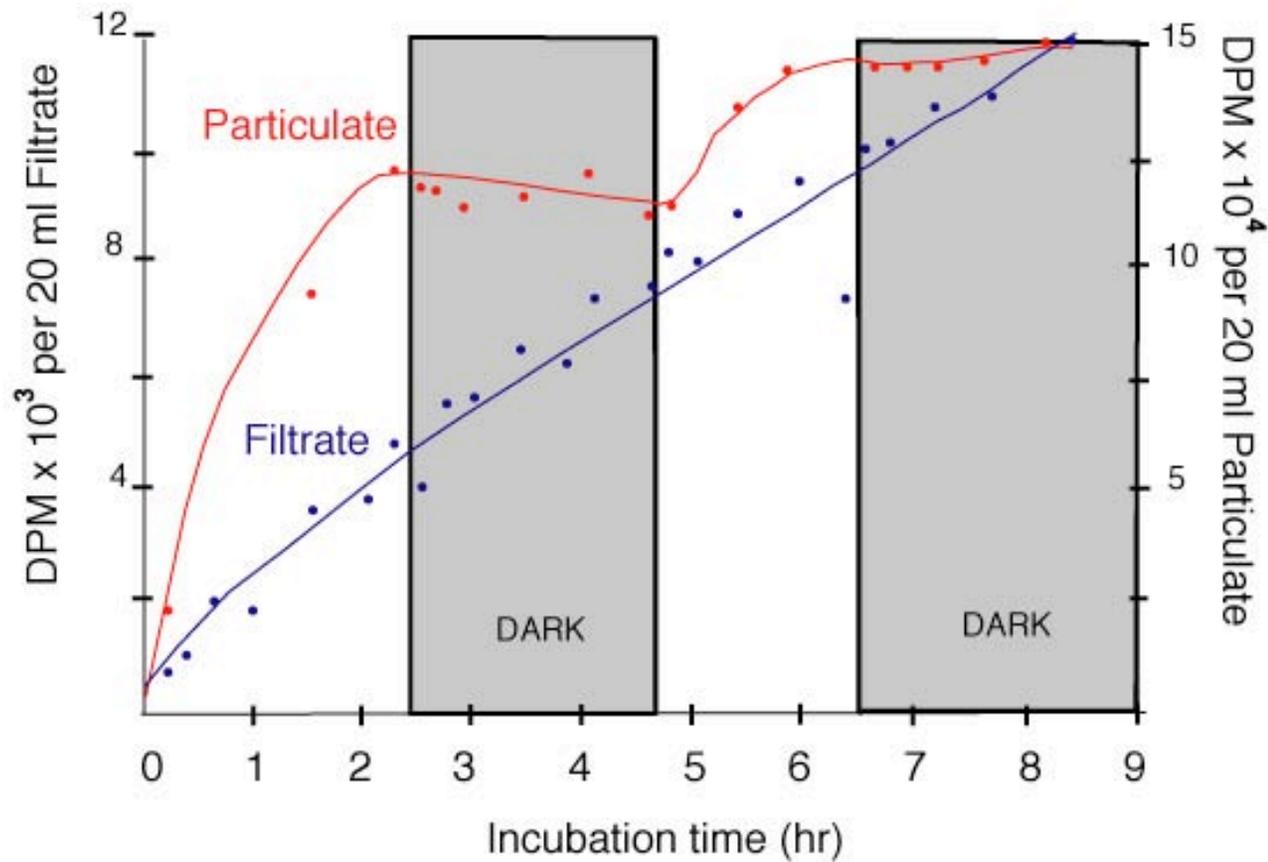
[DOC] can vary in space and time in the ocean due to changes in DOC production



Seasonal production of DOC at the Bermuda Atlantic Time Series (BATS) site.



Production of DOC by phytoplankton in laboratory culture



Mague et al, 197X

Photosynthesis and excretion of photosynthetic products during logarithmic growth of axenic algal cultures

Dunaliella tertiolecta

Hours	90	114	138	152
POM	9600	38600	103000	280000
DOM	373	1360	4140	11400
DOM(% total)	3.7	3.4	3.8	3.9

Skeletonema costatum

Hours	90	114	138	152
POM	9190	46400	116000	484000
DOM	457	1230	6700	28200
DOM (% total)	4.7	2.6	5.5	5.5

Monochrysis lutheri

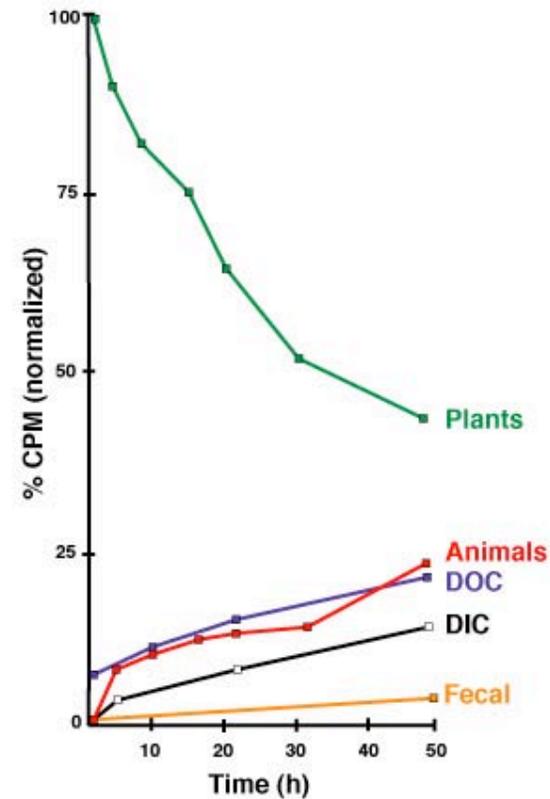
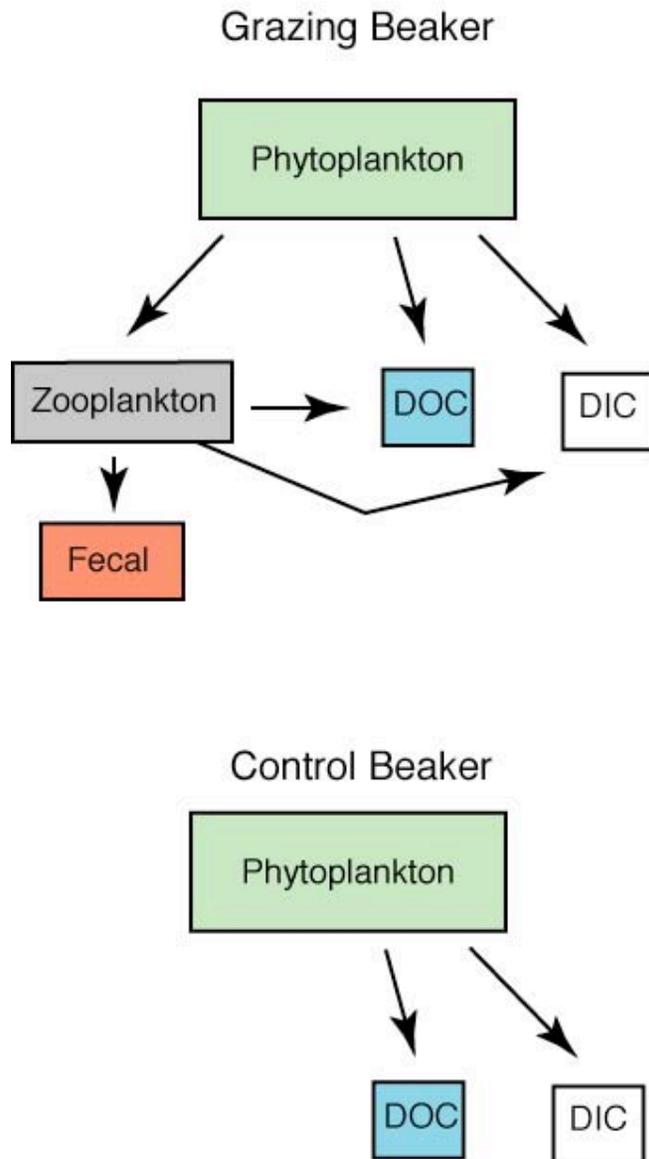
Hours	59	71	83	108	120	163
cells/ml	6530	11700	20200	57000	90500	576000
POM	3680	7070	12800	43200	68000	353000
DOM	86	134	320	1110	1710	10000
DOM (% total)	2.3	1.9	2.4	2.5	2.5	2.8

Rate of CO₂ fixation and excretion of photosynthetic products

Incubation time	depth	Total CO ₂ fixation (μg C/l day)	Excretion (μg C/l day)	%Excretion
6/9				
07:45-12:30	0	5.7	<0.04	<1
	10	5.4	<0.04	<1
	50	7.0	<0.04	<1
13:15-17:55	0	6.7	0.11	1.6
	10	6.1	0.13	2.1
	50	12.7	1.30	10
6/11				
15:00-19:45	0	3.3	0.55	17
	10	2.2	0.50	23
	50	2.3	0.37	16
6/12				
08:00-13:00	0	4.1	0.42	10
	10	3.1	0.09	3
	50	6.9	0.41	6
7/23				
08:15-15:15	0	3.1	0.25	8
	10	2.2	0.20	9
	50	3.4	0.22	7
14:10-19:10	0	1.7	0.04	2
	10	2.5	0.06	3
	50	3.5	0.14	4
7/24				
09:00-13:30	0	2.5	0.10	4
	10	3.0	0.36	12
	50	2.6	0.17	7
		4.3	0.26	7

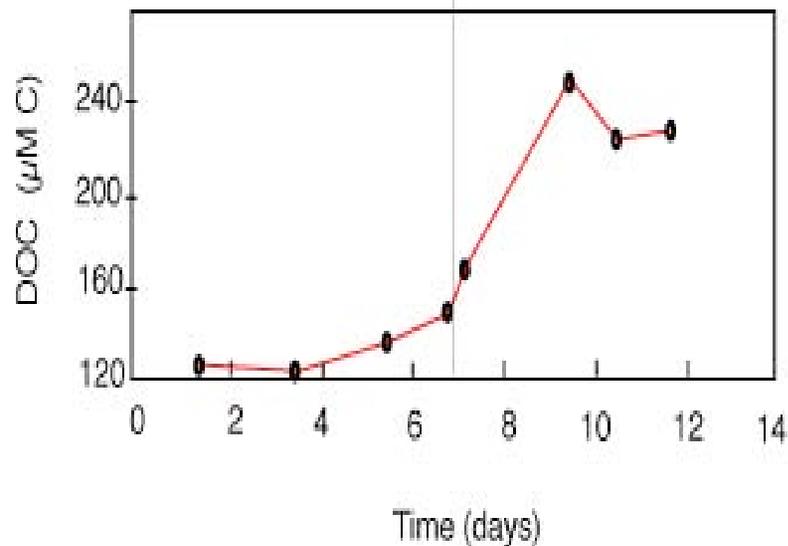
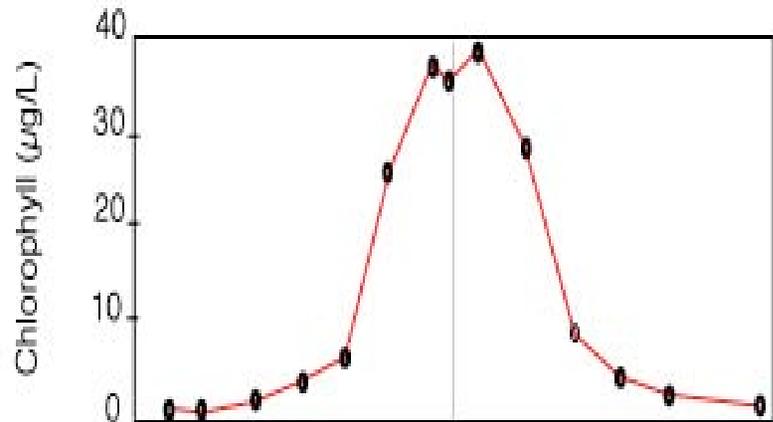
Production of DOC during grazing by macrozooplankton

Production of DOC in laboratory culture grazing experiments



¹⁴C activity with time for *Calanus pacificus* feeding on labeled *Thalassiosira fluviatilis*.

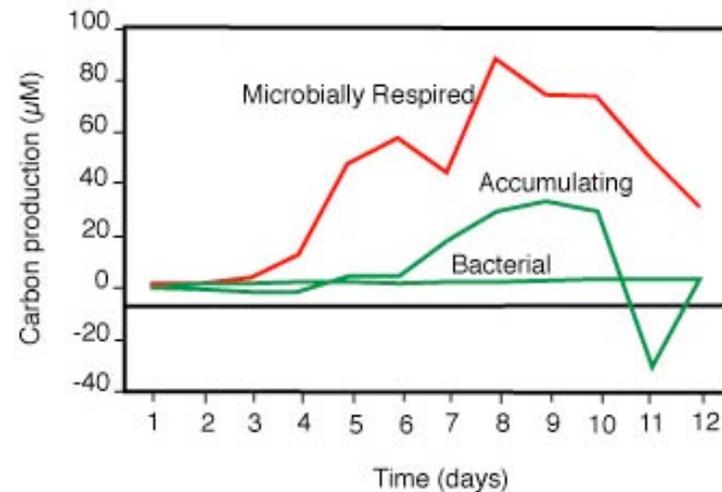
DOC dynamics in a simulated algal bloom



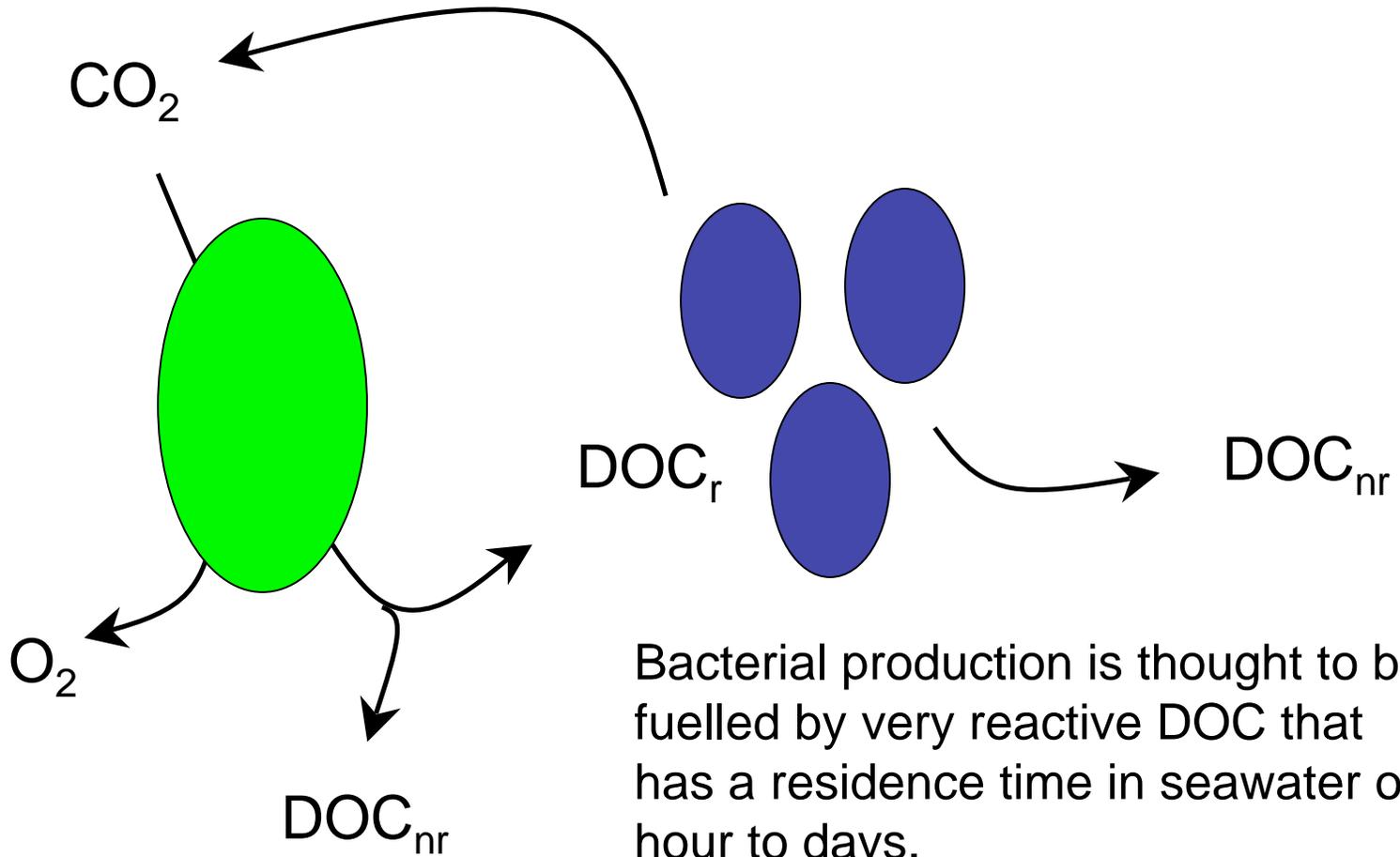
Most DOC accumulation occurs after nutrients are exhausted (bloom crashes)

During early log phase growth DOC is being respired by bacteria

Two pools of DOC, reactive and non-reactive (timescale of exp!). Are they being produced by two different classes of microbes?

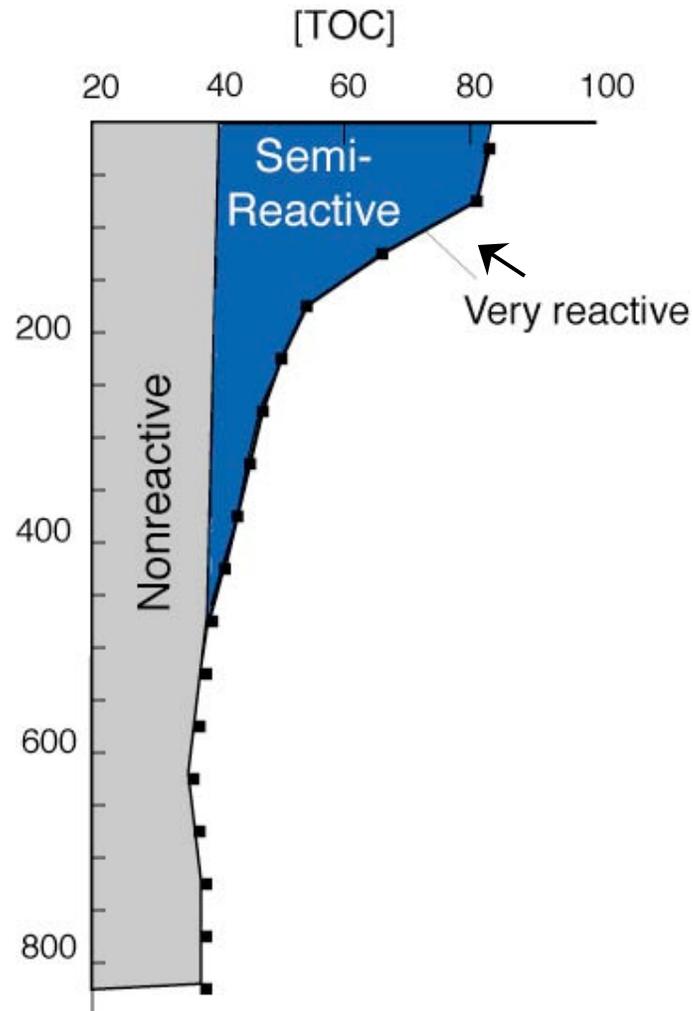


Production of reactive and non reactive DOC by phytoplankton and bacteria



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

DOC cycling and bacterial production in the ocean



DOC is the presumed substrate that supports bacterial metabolism in seawater.

There are three “types” of DOC that Occur in seawater:

Very reactive DOC- supports bacterial Production

Reactive DOC that is produced and Accumulates in surface seawater. Lost During convective mixing.

Non reactive DOC (most DOC)

Bacterial production and Bacterial Carbon demand

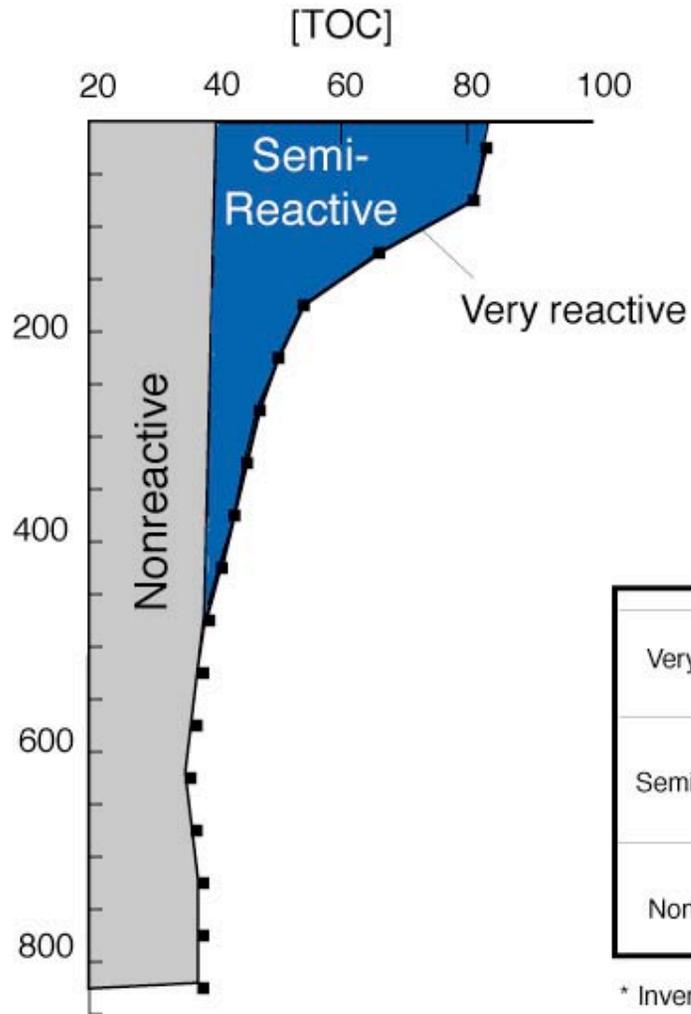
Bacteria are believed to be the principal sink for DOC in seawater. DOC fuels free-living bacterial production (BP) of biomass. It is assumed that bacteria can out compete phytoplankton for nutrients, and that bacteria are substrate (C) limited.

Bacterial production is most often measured by changes in cell #s in a sample over time, or the uptake of ^3H -leucine to measure protein synthesis or ^3H -thymidine to measure nucleic acid synthesis.

Current estimates of global bacterial production have a wide range of values, but a mean of about 15% PP.

Bacterial production is the product of bacterial carbon demand (BCD) and efficiency. Estimates of bacterial efficiency also vary from About 10-50%. Therefore BCD may be 30-50% of PP.

Is there enough production of DOC to support BCD?



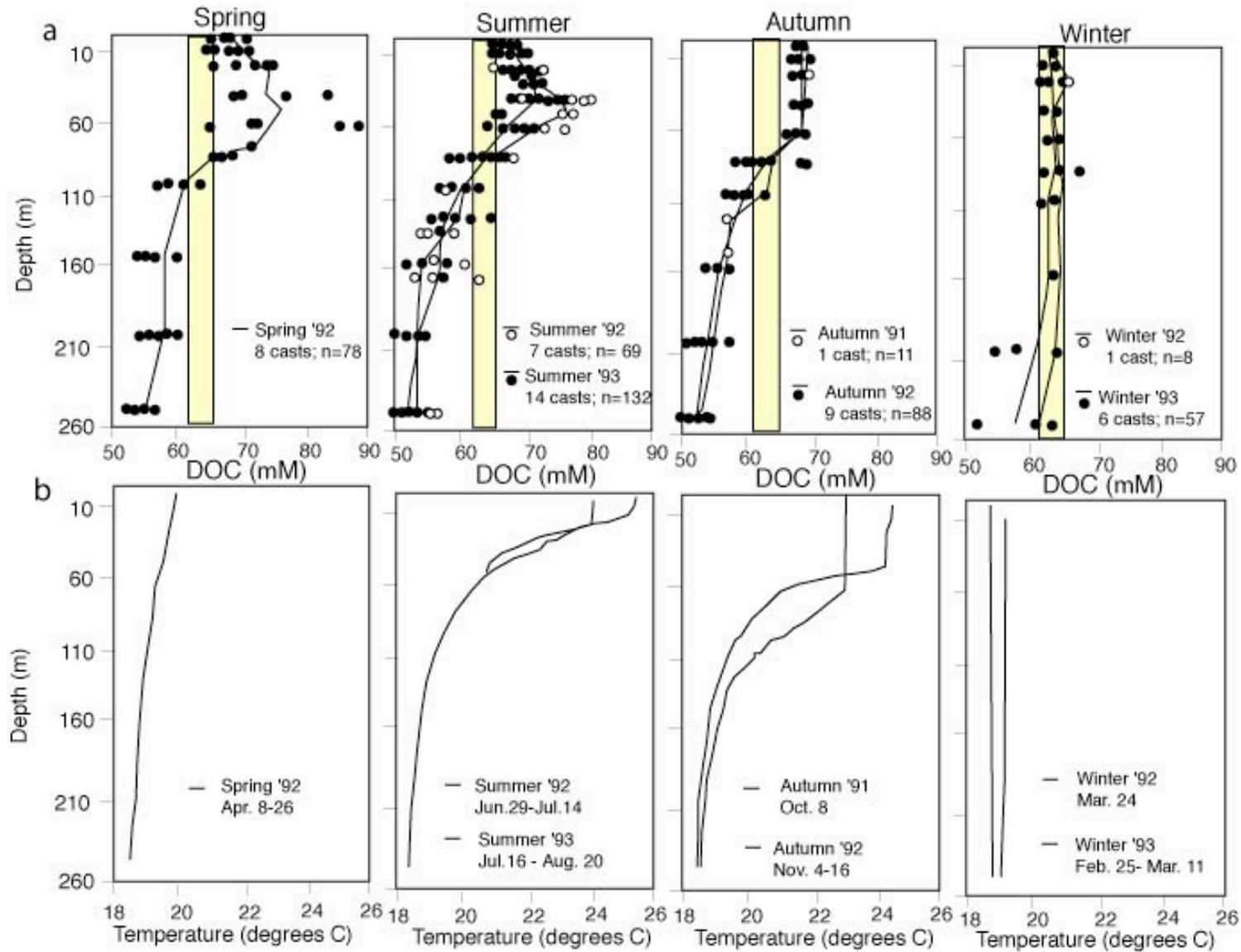
Annual primary prod @ 70GT C yr⁻¹

Estimates of DOC production and how this C is partitioned vary widely:

	TOC	T(yr)	Flux (yr ⁻¹)
Very reactive	0.1-1	0.01	10-100
Semi-reactive	30-50	?	?
Non reactive	650	5000	0.1

* Inventory in GT

Annual cycle of DOC production at BATS*



*Bermuda Atlantic Time Series, a JGOFS LTEM site

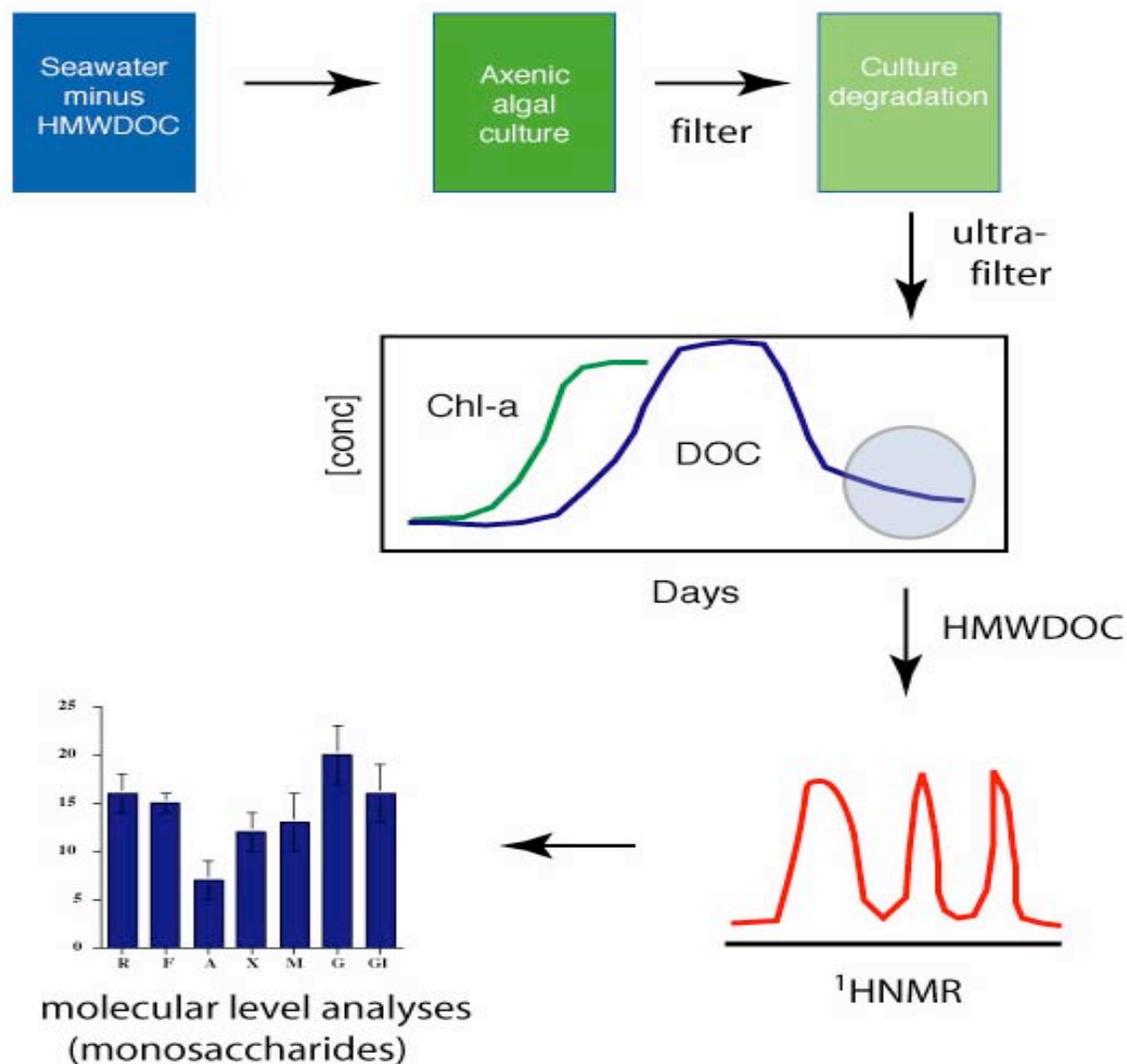
**Estimates of Net DOC Production Based on Regional Estimates of New Production
for Component Regions of the World's Oceans**

Region	New Production, Pg C yr ⁻¹	Δ DOC:NP	Net DOC Production, Pg C yr ⁻¹
Tropical open ocean			
- Upwelling	1.5 (21)	0.2	0.3 (24.6)
- Turbulent mixing	0.7 (9.5)	0.1	0.07 (5.7)
Southern Ocean	1.1 (15.5)	0.12	0.13 (10.8)
Subarctic gyres	0.3 (4)	0.15	0.04 (3.7)
Coastal upwelling	0.8 (11)	0.2	0.16 (13.1)
Monsoonal	0.4 (5.5)	0.2	0.08 (6.6)
Subtropical gyre	0.5 (7)	0.1	0.05 (4.1)
Continental margins			
- Western boundary currents	0.7 (9.5)	0.2	0.14 (11.5)
- Estuarine influenced shelves	1.2 (17)	0.2	0.24 (19.7)
Total	7.2		1.2

The ratios of net DOC production to new production (Δ DOC:NP) have been taken from the analyses presented in this paper, and from assumptions listed in the text. Values in parentheses represent percentages of the global estimate.

Production of “semi”-reactive DOC by phytoplankton in culture

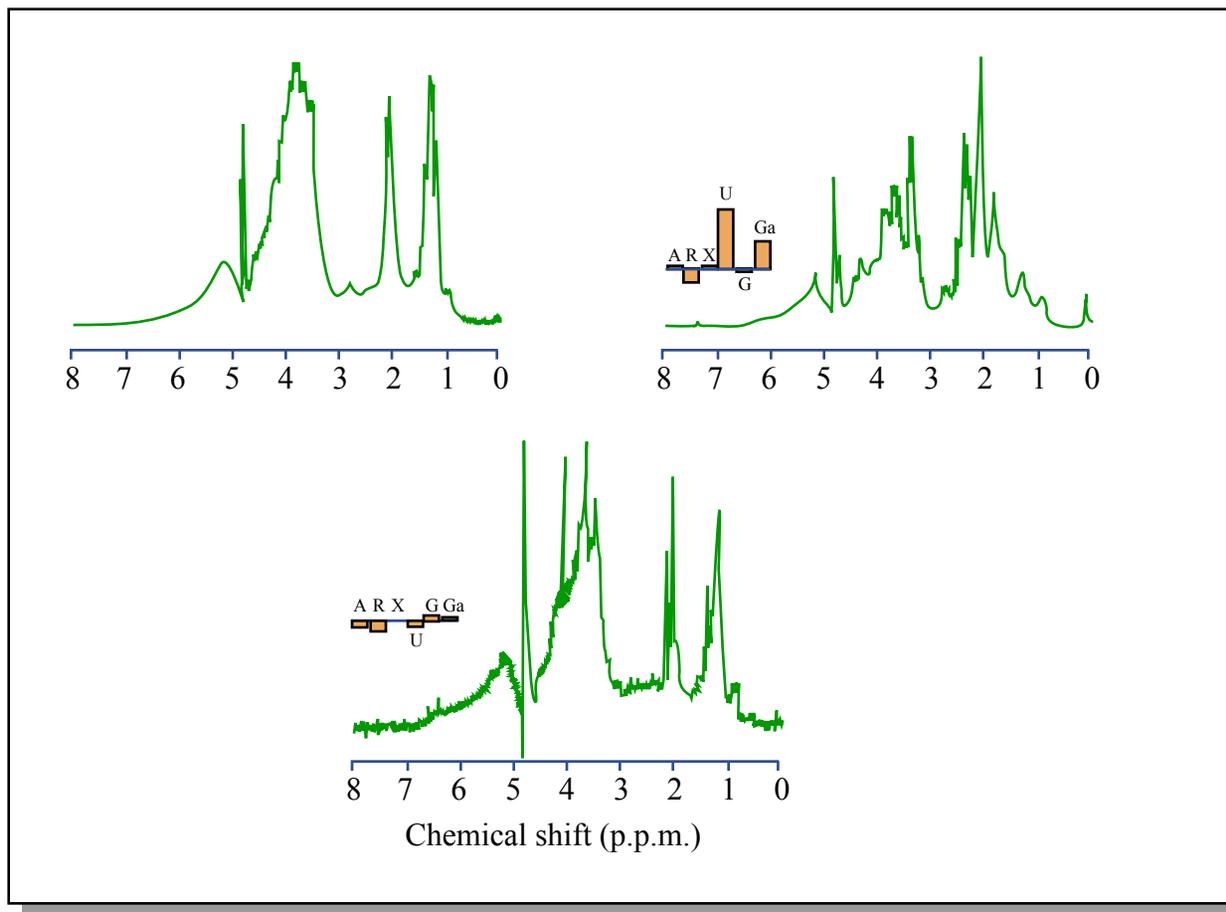
Is the composition of accumulating DOC similar to DOC in seawater?



Do phytoplankton produce semi-reactive DOC?

In culture, phytoplankton release a large amount of DOC. The composition of this DOC does not look like DOC in seawater however (left). After bacterial degradation, labile DOC is removed leaving the semi-labile material behind.

^1H NMR of seawater



After filtration

Figure by MIT OCW.

After 37 day of degradation

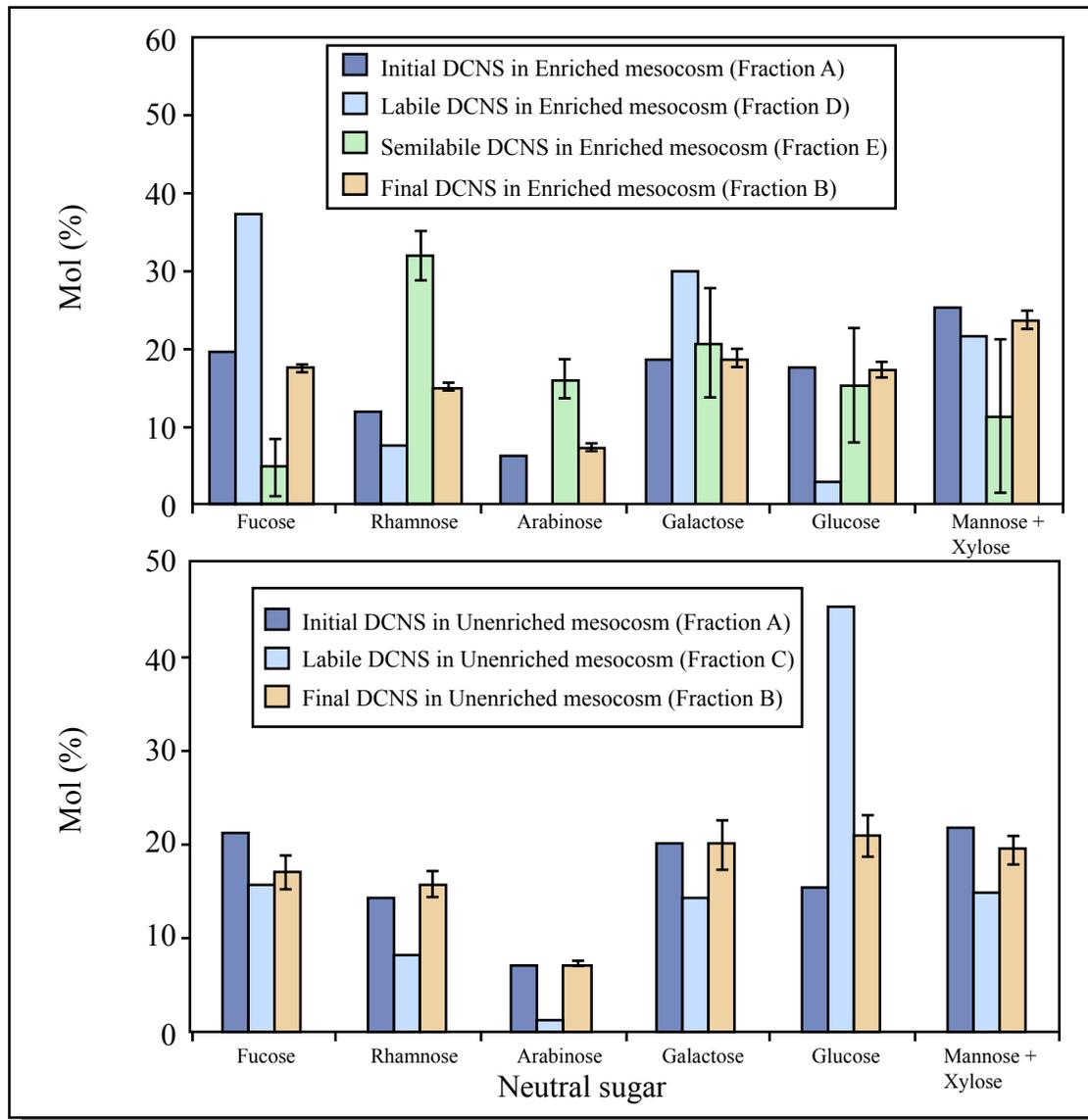
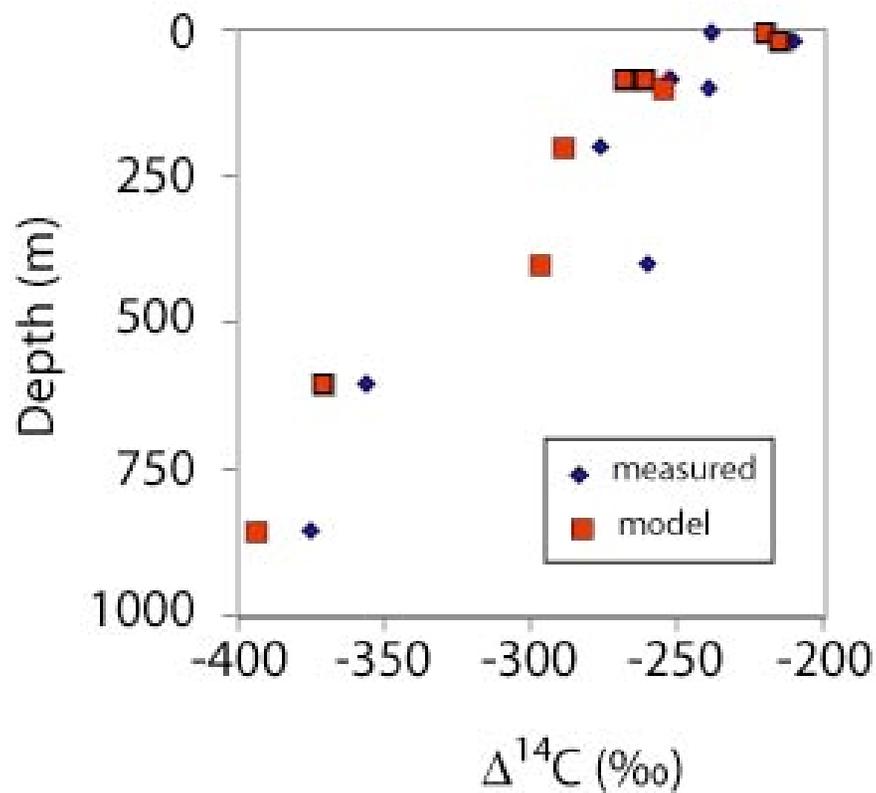
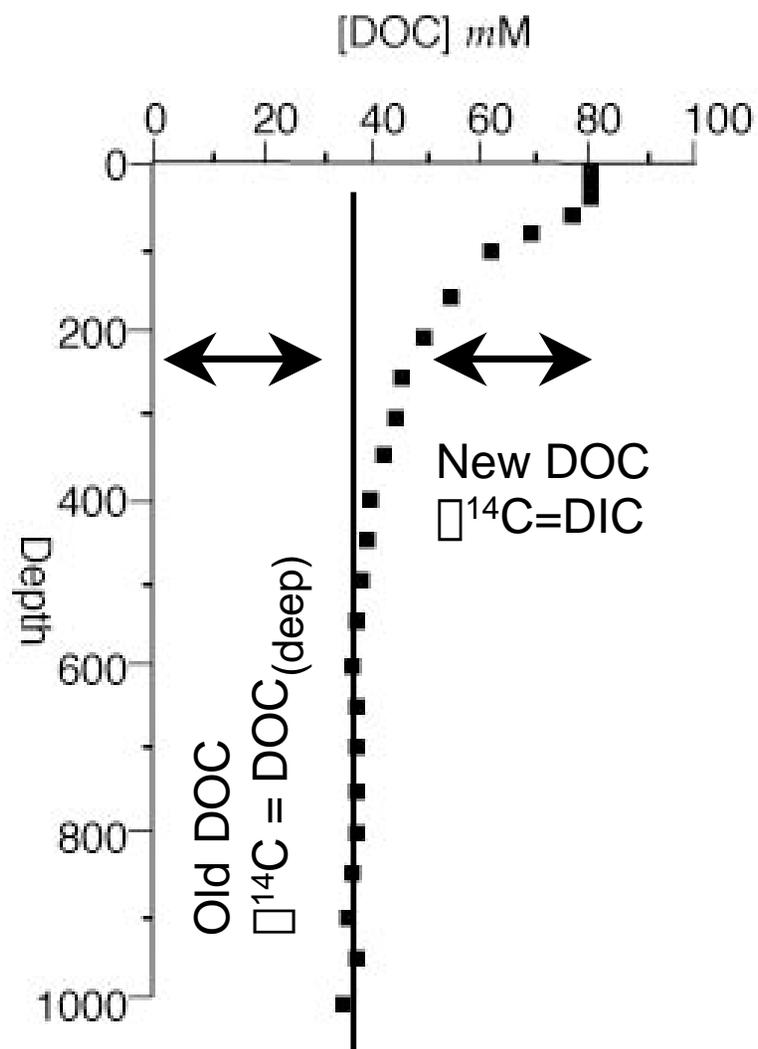


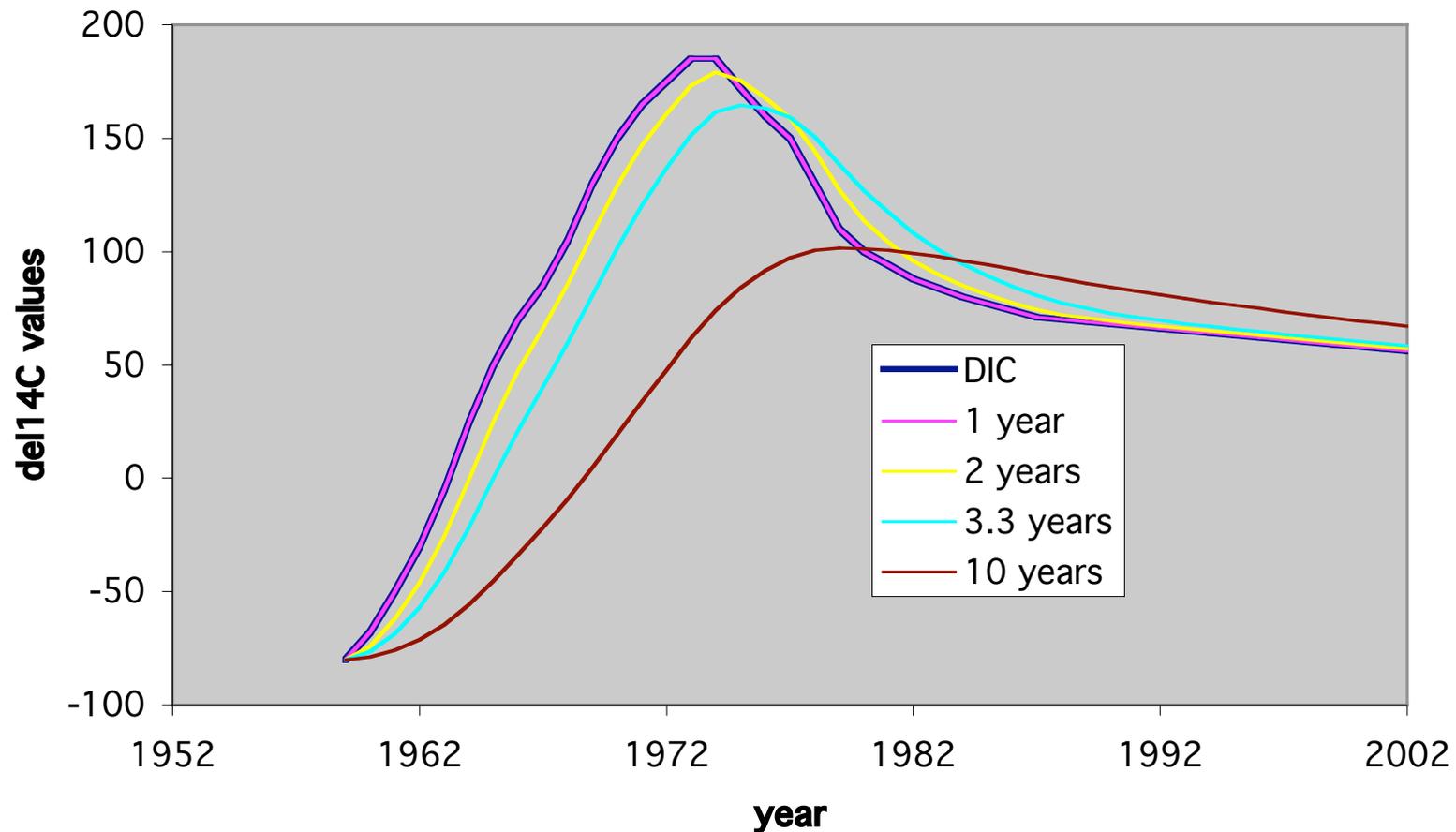
Figure by MIT OCW.

Radiocarbon model of DOC cycling



Changes in the semi-reactive DOC-14C value with residence time

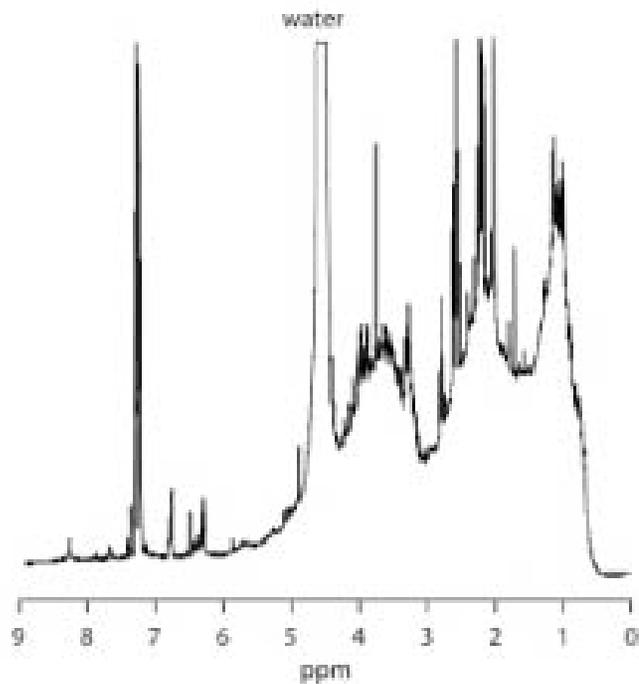
As the difference between DOC(sr) and DIC residence time increases the difference in RC age will increase as well due to non-steady state conditions in upper ocean 14C.



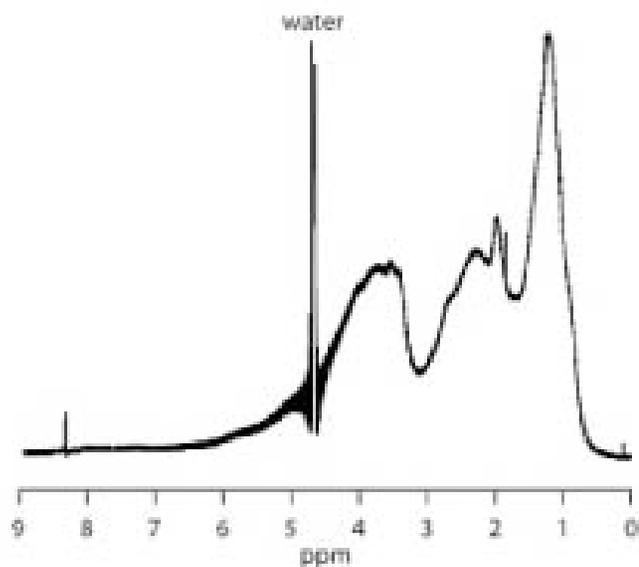
Radiocarbon analyses of HMWDOC carbohydrates

Sample	Hawaii	NPSG
DIC	72 \pm 7‰(n=4)	89 \pm 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	56 \pm 6‰	89 \pm 13‰

Purification of a modern carbohydrate fraction from HMWDOC also isolates an older “humic” like fraction for chemical and isotopic analyses.



The “humic” fraction isolated from surface seawater. $\delta^{14}\text{C} = -416\text{‰}$



HMWDOC from the deep sea
 $\delta^{14}\text{C} = -380$ to -440‰

How is nonreactive DOC removed from the ocean?

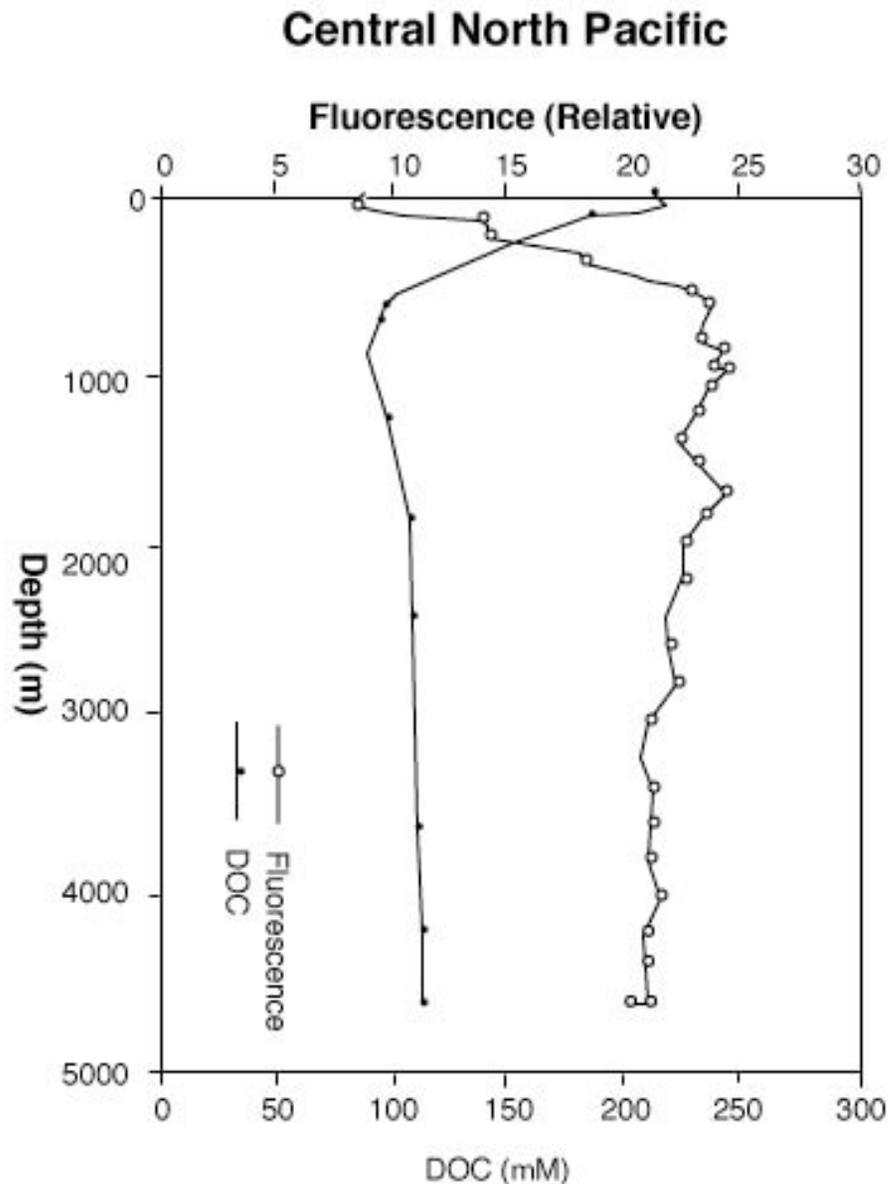


Photo-oxidation of CDOM

Generally noted that DOC in surface waters is not colored

However, deep sea DOC is colored and has fluorescence

Does sunlight bleach DOC in surface water?

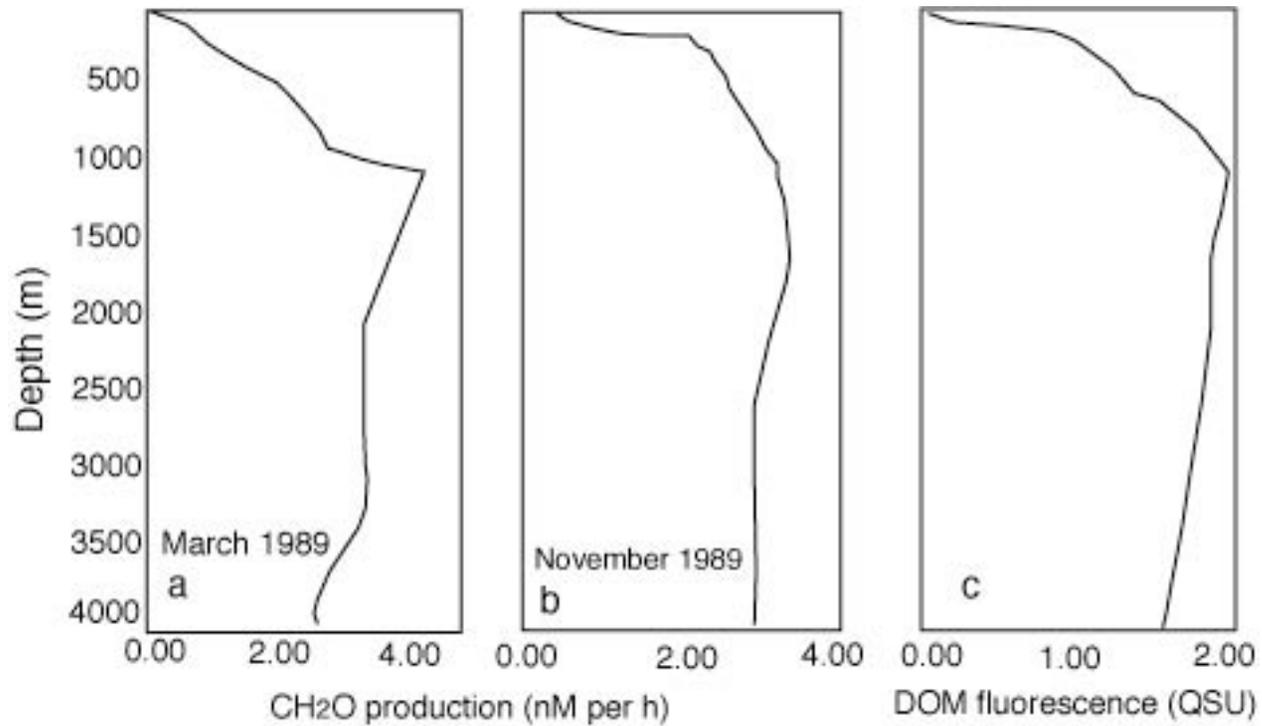
Is this the mechanism by which non-reactive DOC is removed from the ocean?

Ultrafiltration of 4000m NPSG water



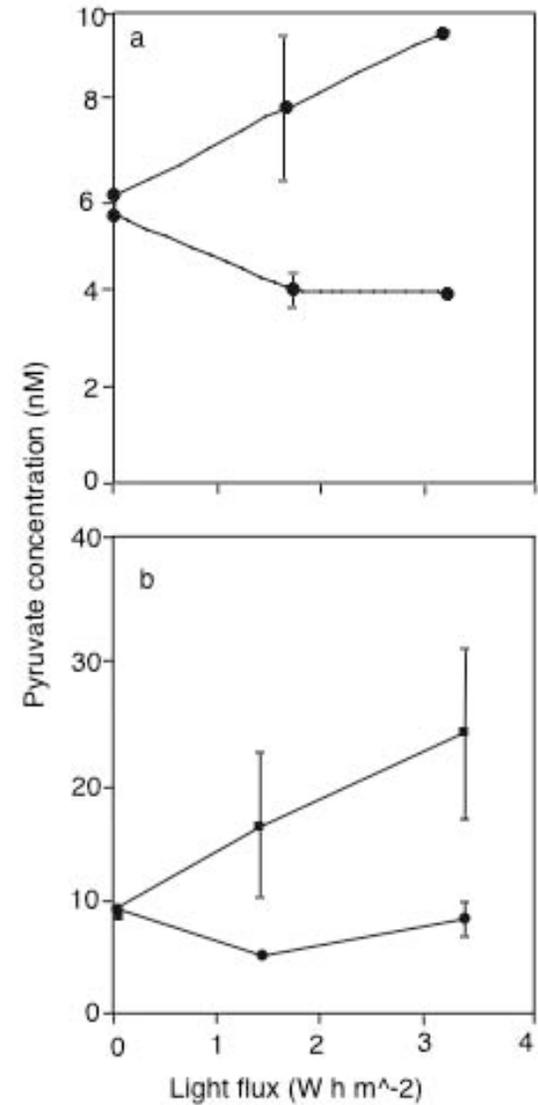
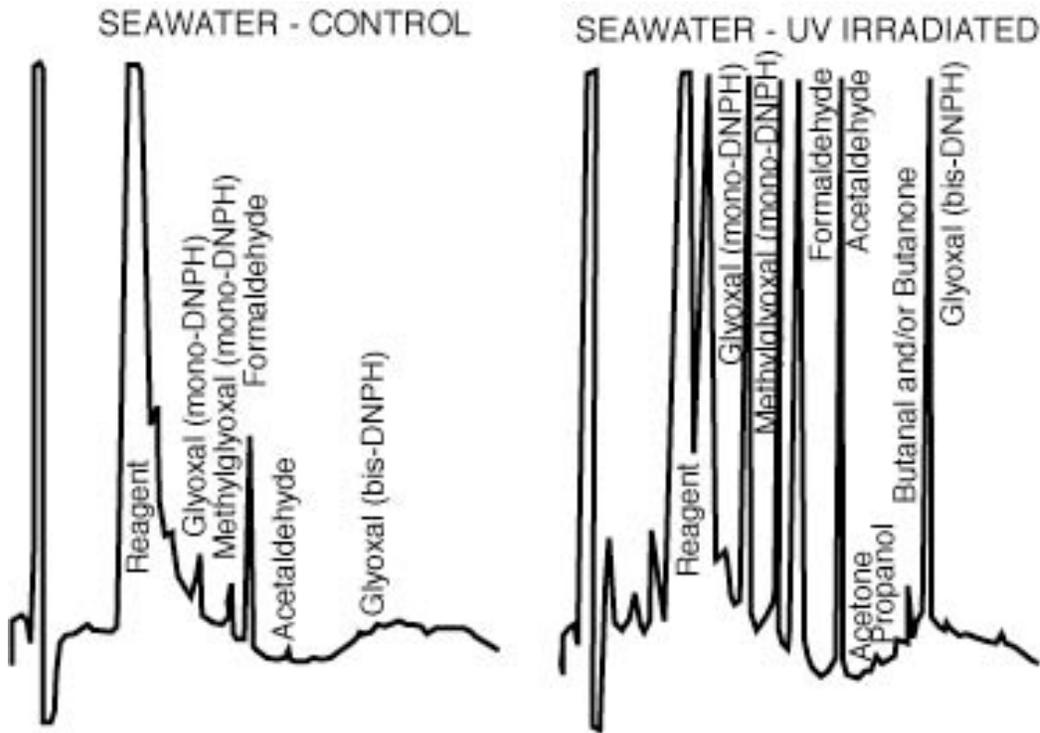
Production of LMW highly oxidized DOC with depth in the ocean

DOC + hv ---->> LMW photo-oxidation products



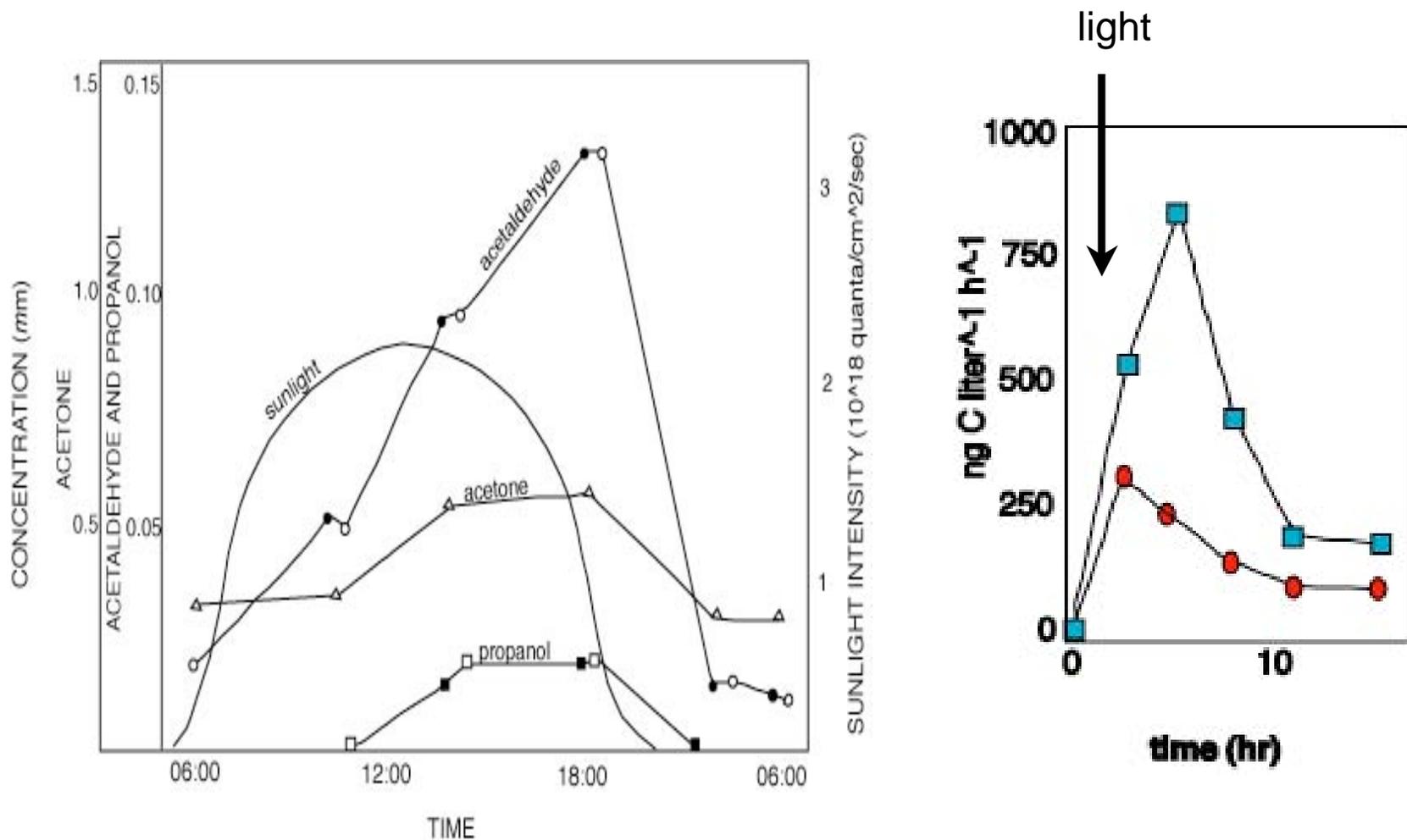
DOC + $H\nu$ \rightarrow LMW carbonyls (C=O)

C=O + Uvtag \rightarrow HPLC



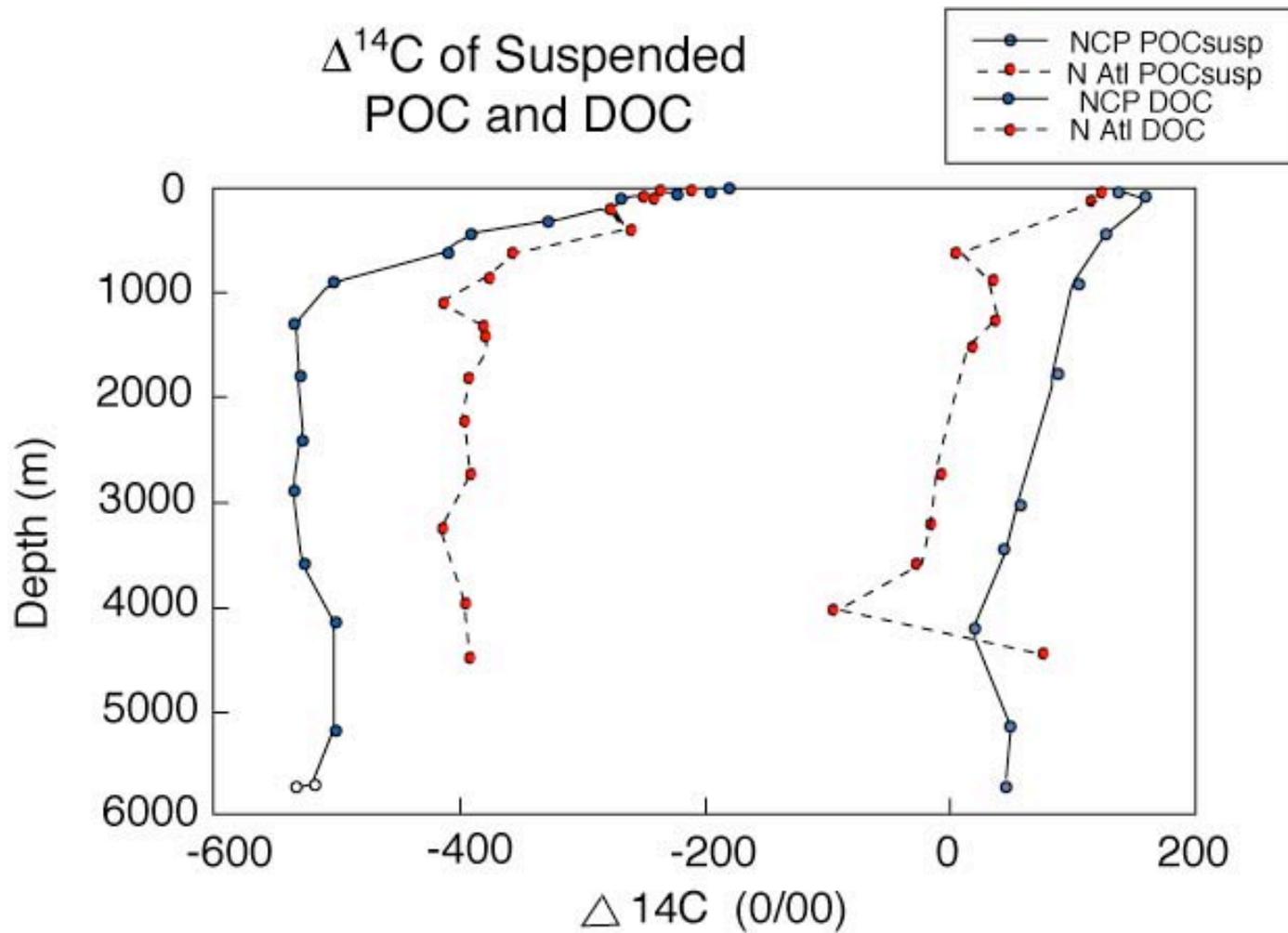
Not produced in dark controls, but are produced in sterile controls

Highly oxidized LMW compounds are produced every Day in seawater by photo-oxidation. They serve as a substrate For bacteria and therefore a sink for non-reactive DOC



Removal of DOC by adsorption onto POC

Why does suspended POC age so much with depth?



Summary

Isotopic evidence suggests that the large inventory of DOC_i in seawater is synthesized in-situ by phytoplankton or bacteria

In culture, phytoplankton release about 10% of total PP as DOC. Most of this DOC is considered to be very reactive and is metabolized by bacteria in a few days, but some persists

Global estimates of bacterial carbon demand require a large Fraction of PP is funneled through DOC to bacteria (> 10%)

The reservoir of DOC that accumulates in the upper ocean is Not thought to fuel BP by some, but RC data suggests otherwise

Non reactive DOC is removed by photo-oxidation, and perhaps By adsorption onto sinking particles