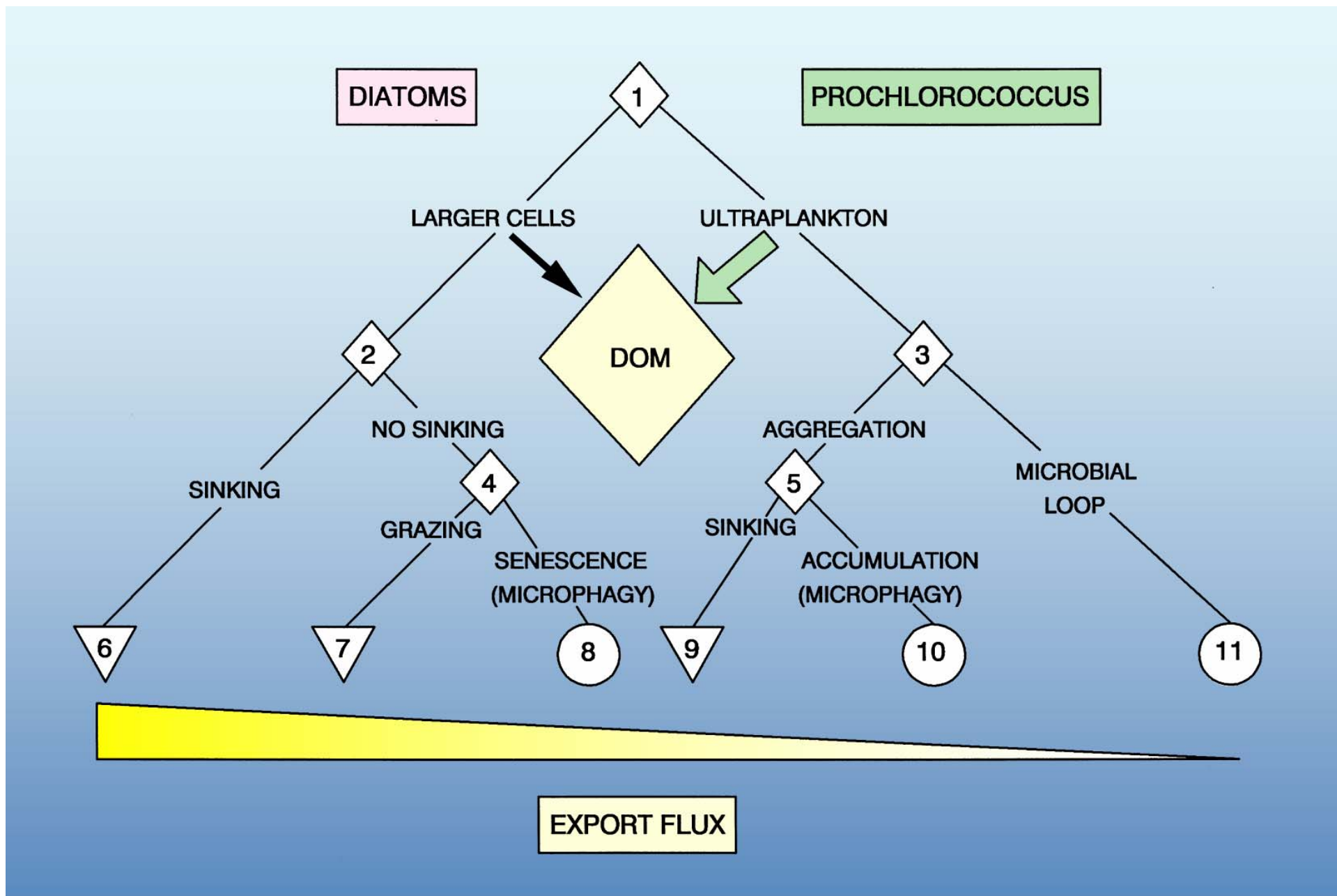
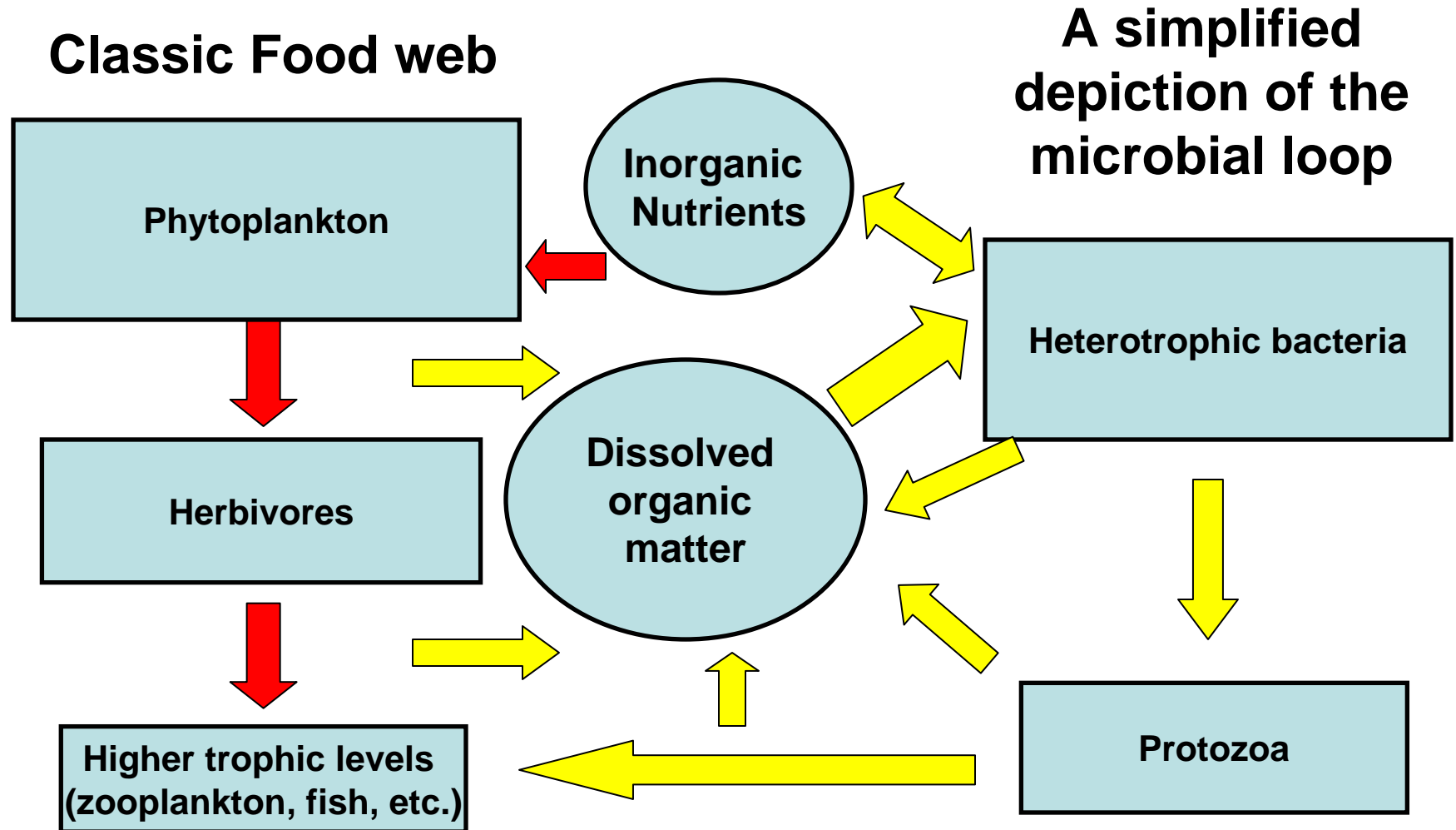


- Where does primary production go?
 - Export
 - Bacteria
 - Grazing
 - Dissolved organic matter



The Microbial Loop

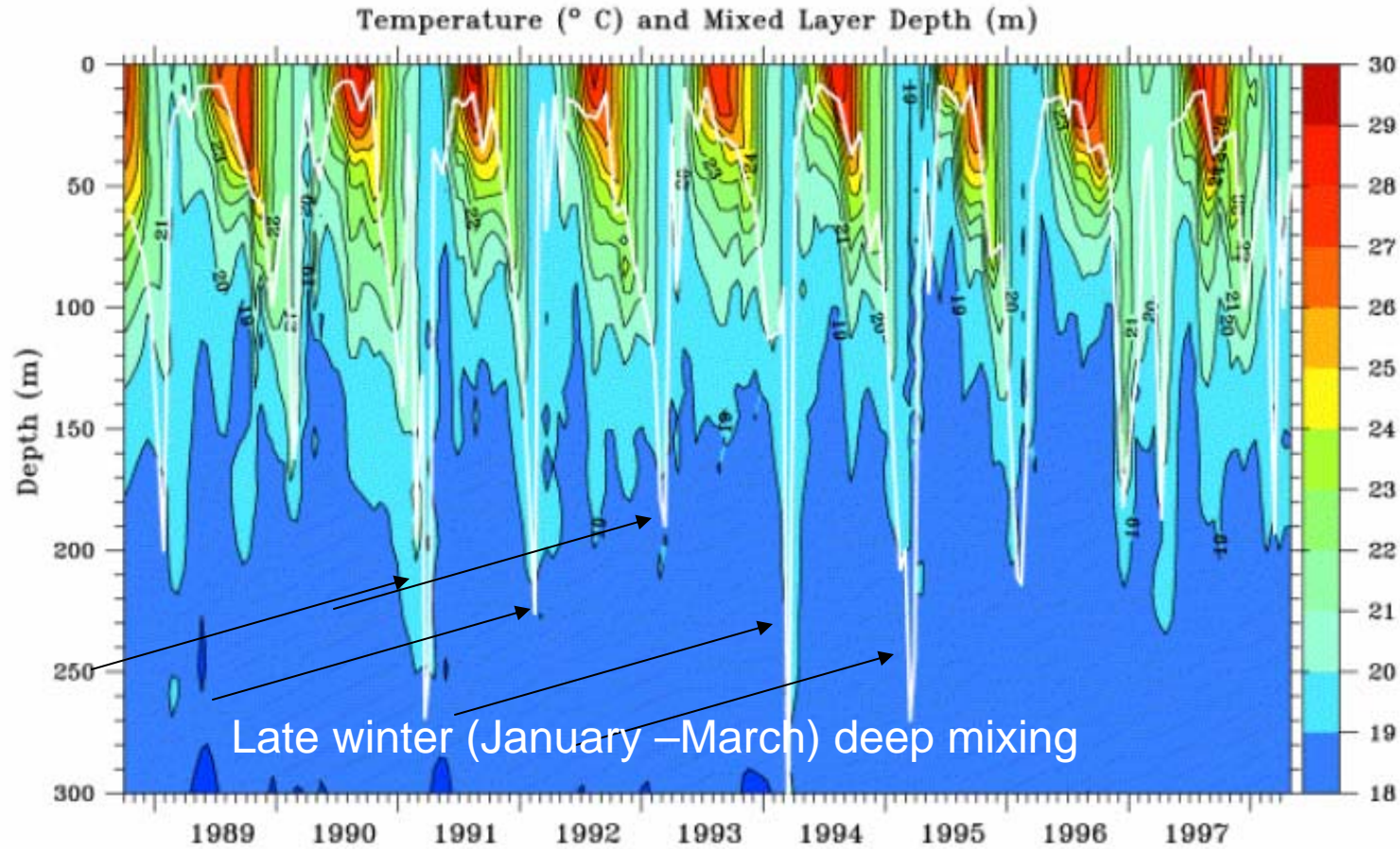


What other components of the biological pump are important?

- The majority of organic material in the ocean is in the dissolved phase (operationally defined as $<0.7 \mu\text{m}$ or $0.2 \mu\text{m}$)

Why dissolved organics matter

- Dissolved organic matter constitutes the largest global reservoir of fixed carbon $\sim 700 \times 10^{15}$ g C.
- Oxidation of even 1% of the seawater DOC pool in a 1 year period would exceed annual anthropogenic CO₂ emissions.
- DOC can also serve as an important component of new production.



Seasonal variations in mixing and temperature in the Sargasso Sea-note winter time deepening of the mixed layer coincides with seasonal cooling.

Upper ocean total organic carbon at BATS

Remember DOC = ~98% of the TOC.

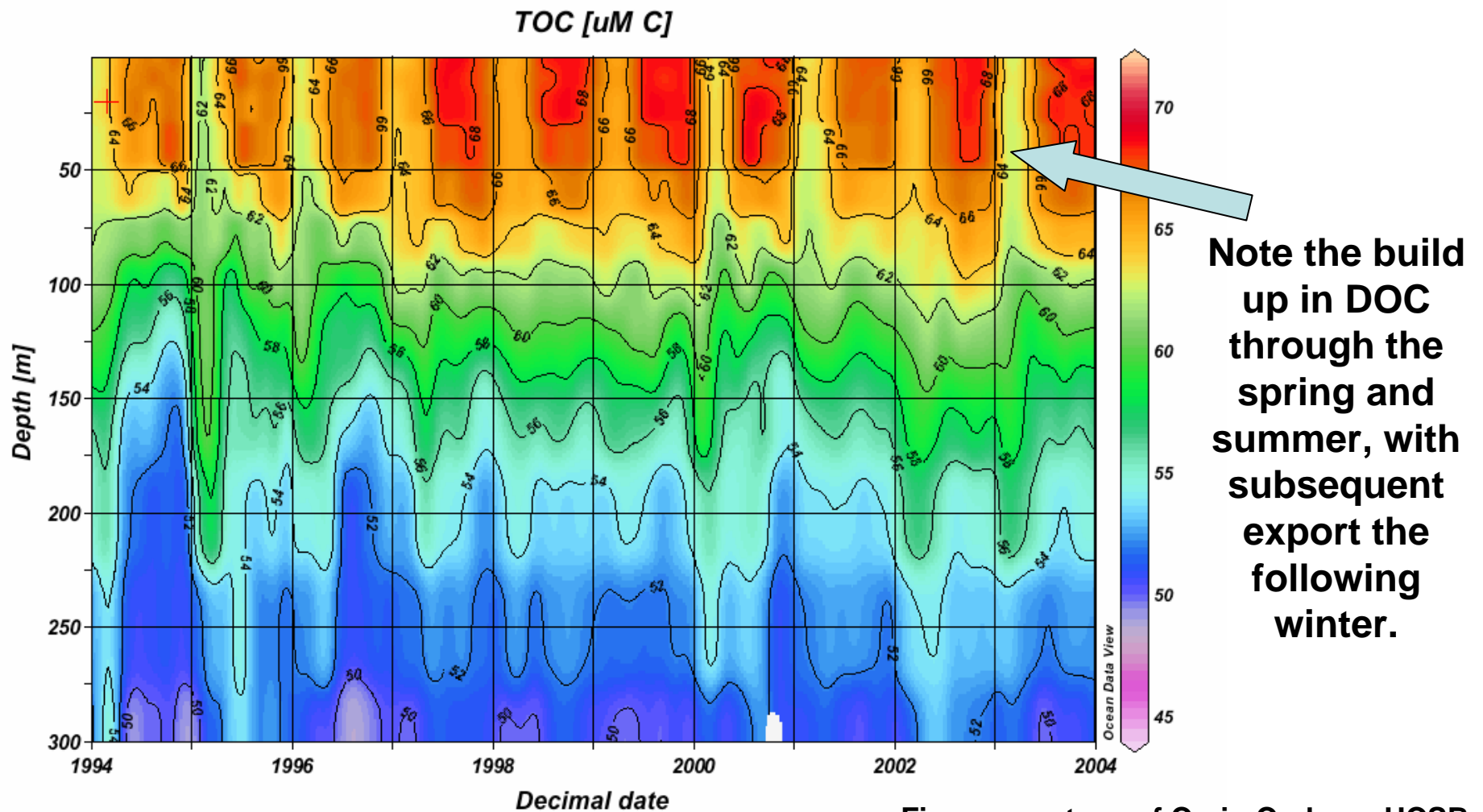


Figure courtesy of Craig Carlson, UCSB

TOC Profiles at BATS

DOC Profiles at BATS

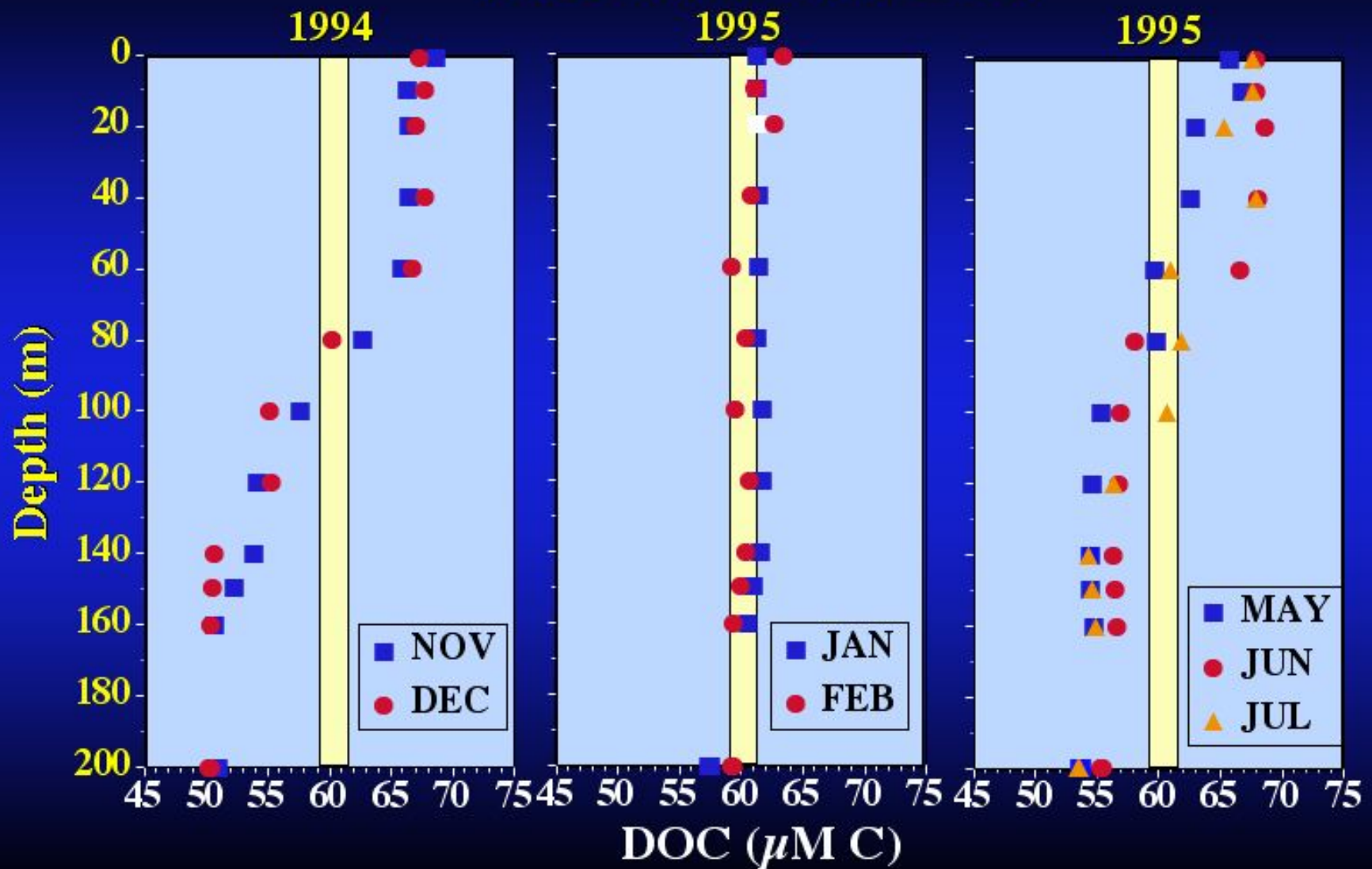


Figure courtesy of Craig Carlson, UCSB

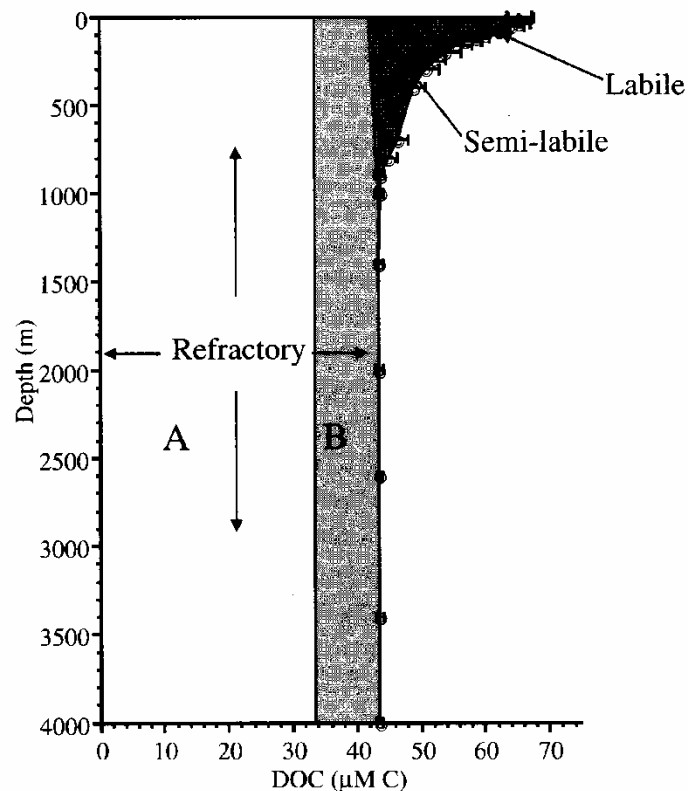


Figure 5 Conceptual cartoon of the various pools of refractory, semilabile, and labile DOC in the open ocean. This figure is based on the mean profile for all DOC data collected at the Bermuda Atlantic Time-series Study (BATS) site in the Northwestern Sargasso Sea. The magnitude and distribution of the various pools of lability will vary depending on the location of the study site and the degree of thermal stratification of the water column (see Hansell, Chapter 15). The refractory pool is divided into two broad pools based on the deep ocean gradient observed by Hansell and Carlson (1998a). They observed the lowest concentration of DOC ($34 \mu\text{M C}$) in the north Pacific and used this concentration to represent refractory DOC which turns over on time scales of greater than ocean mixing (A, white box). The deep DOC concentrations in excess of the $34 \mu\text{M C}$ represents the fraction of the biologically refractory pool that turns over on time scales of ocean mixing (i.e., centuries; B, light gray box).

**Typical DOC profile :
elevated in near surface
water, decreasing
through the thermocline,
stable at depth.**

- **Labile pools cycle over
time scales of hours to
days.**
- **Semi-labile pools persist
for weeks to months.**
- **Refractory material
cycles over on time
scales ranging from
decadal to multi-
decadal...perhaps
longer...**

Contribution of different sources to marine DOM

Sources of DOM to ocean ecosystems

1. Direct algal excretion
2. Zooplankton (sloppy feeding, excretion)
3. Viral lysis
4. Bacterial release
5. Solubilization of POM

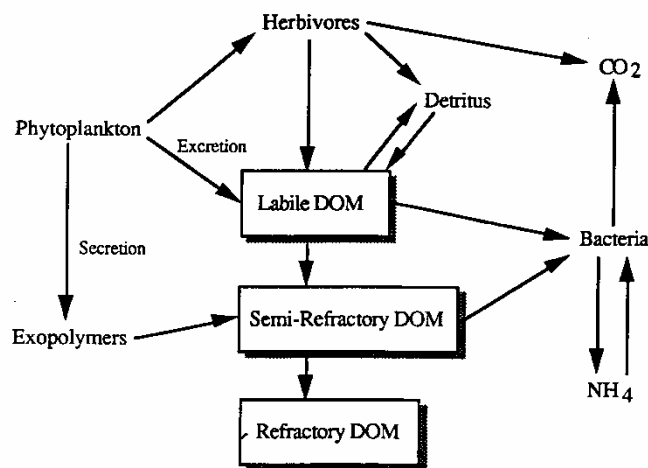
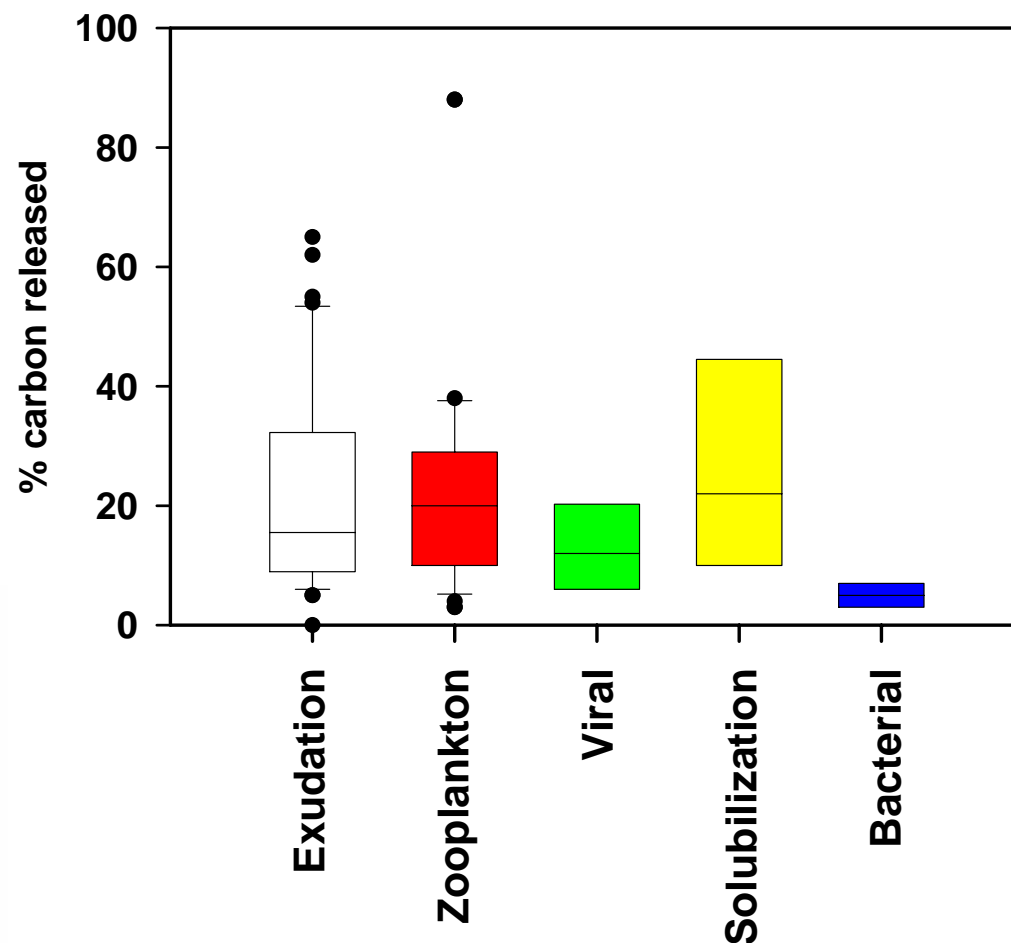


Figure 1 Three major pools of dissolved organic matter (DOM) and the processes contributing to them.



Exudation % ¹⁴C primary production, zooplankton % carbon ingested, solubilization % C released from aggregates, bacterial % release from ¹⁴C labeled organic substrate.
Sources: Nagata (2001), Carlson (2002).

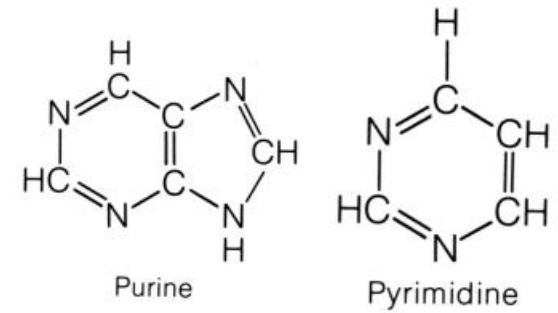
Hydrogen

Amino


Carboxyl

R-group (variant)

**Identified
DOM
compound
classes**




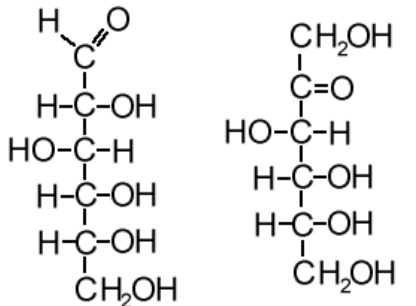
Chitin



The diagram shows a segment of a chitin polymer chain. It consists of two N-acetylglucosamine (GlcNAc) units linked by a β -1,4-glycosidic bond. Each unit is a six-membered ring in a chair conformation. The nitrogen atom at the C2 position of each ring is part of an amide group, with a hydrogen atom (NH) and an acetyl group (H₃C-C=O) attached. The acetyl group is shown with the methyl carbon (H₃C) and the carbonyl carbon (C=O) connected by a single bond. The glycosidic bond connects the C4 of one unit to the C1 of the next unit. The entire structure is labeled 'Chitin' at the top.

The diagram shows a segment of a peptide backbone. It consists of two amino acid residues. The first residue has a nitrogen atom (NH) and a carbonyl group (C=O). The second residue has a nitrogen atom (NH) and a carbonyl group (C=O). The backbone is connected by peptide bonds. Two regions are highlighted with gray boxes: the first box encloses the NH and C=O of the first residue, and the second box encloses the NH and C=O of the second residue. The side chains are labeled R and R'.

Lipids

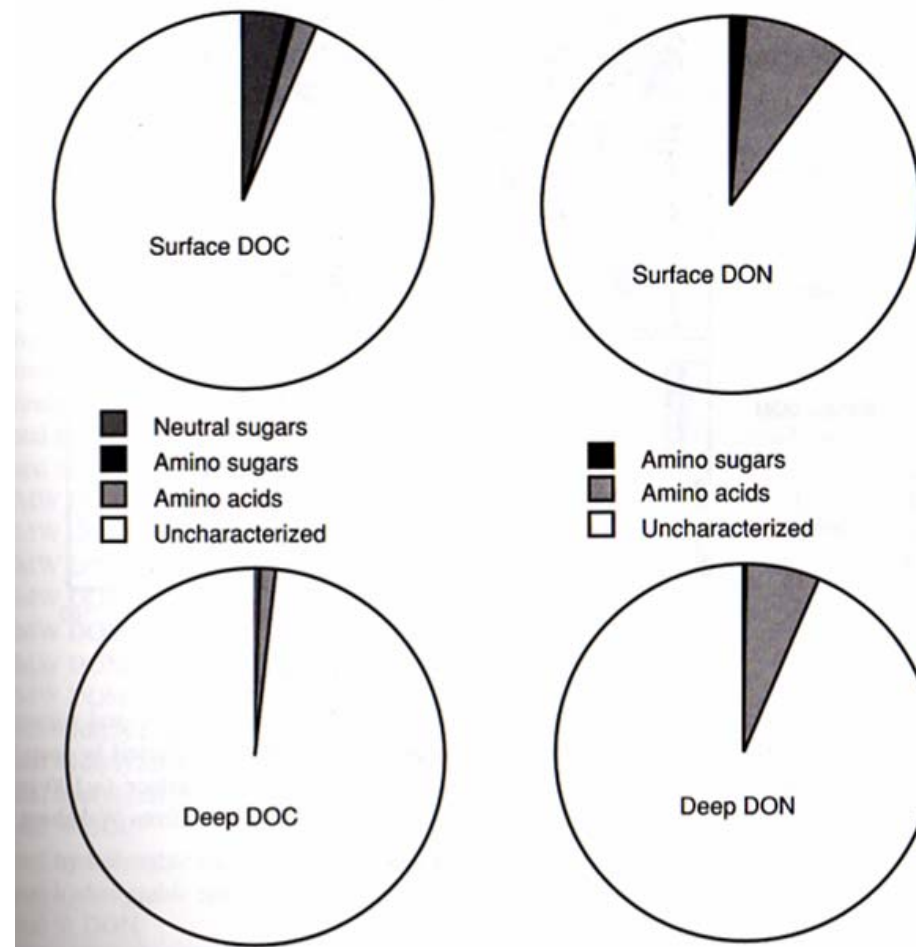
CCCCCCCCCCCC(=O)O

Monosaccharides

The diagram shows a linear chain of six repeating units. Each unit consists of a hexagonal ring (representing a cyclohexane ring) connected to the next unit by an oxygen atom (O). Above each hexagonal ring is a small rectangular block, representing a side chain or substituent. The chain is terminated by oxygen atoms at both ends.

Vitamins

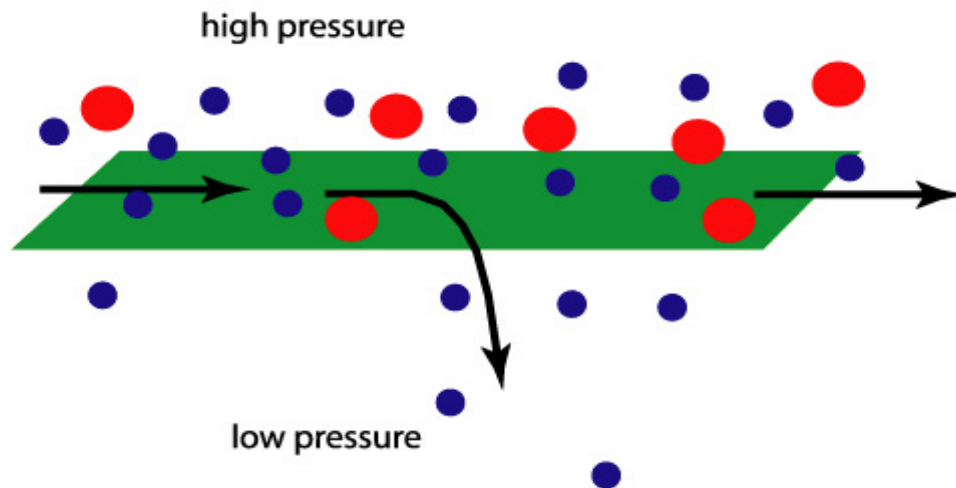
The vast majority of organic matter in the sea remains chemically uncharacterized



Carbohydrates, neutral sugars, amino acids, and amino sugars make up ~20% of the bulk DOC pool in the upper ocean

Isolation of DOM by ultrafiltration

Cross Flow Filtration



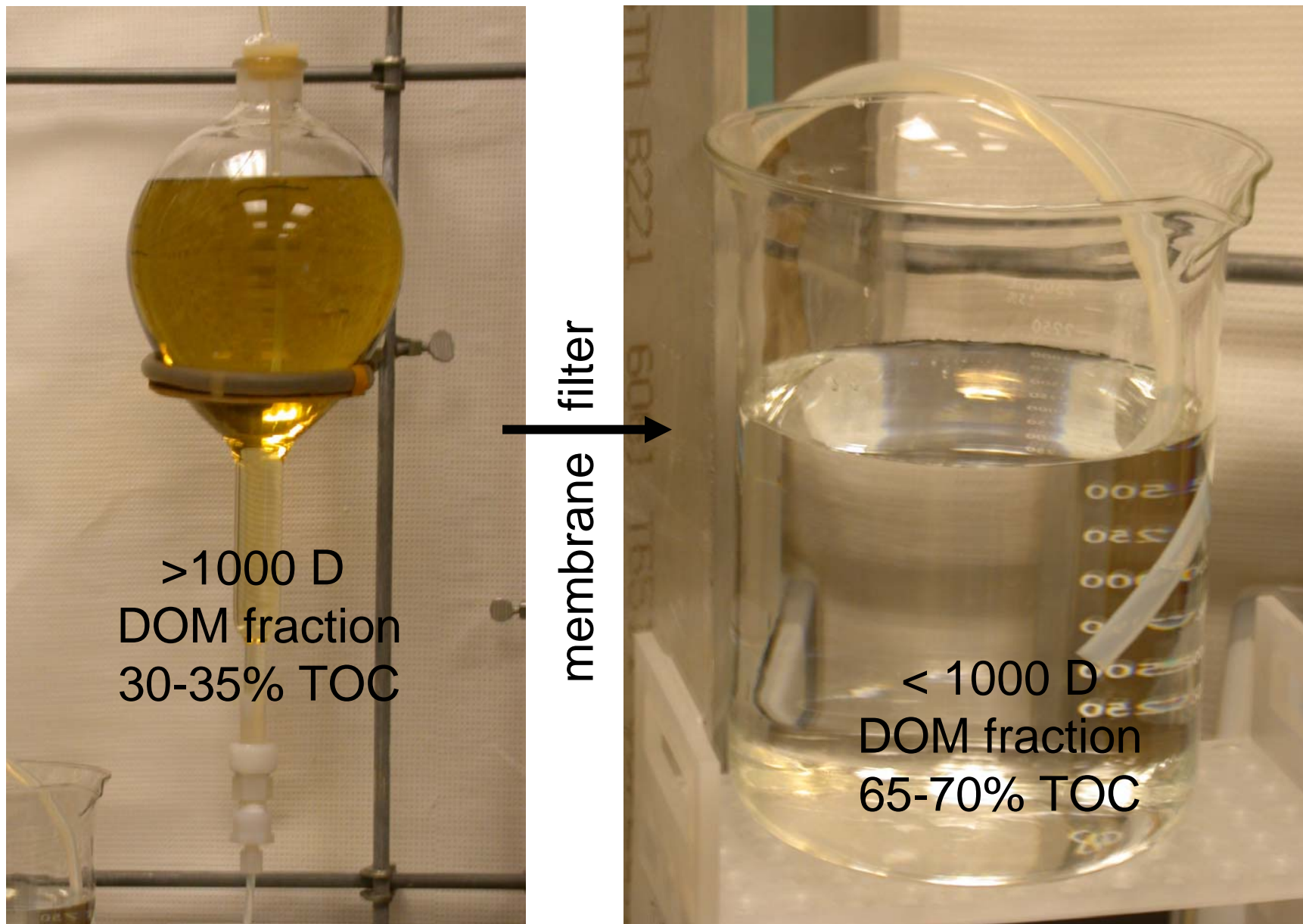
Size selective
concentration of DOM

Typically solutes $> 1\text{ nm}$
are concentrated for
subsequent analyses

Selects for HMW fraction
(about 30-35% TOC)

Some salts collected also

Ultrafiltration high molecular weight DOM (HMWDOM)



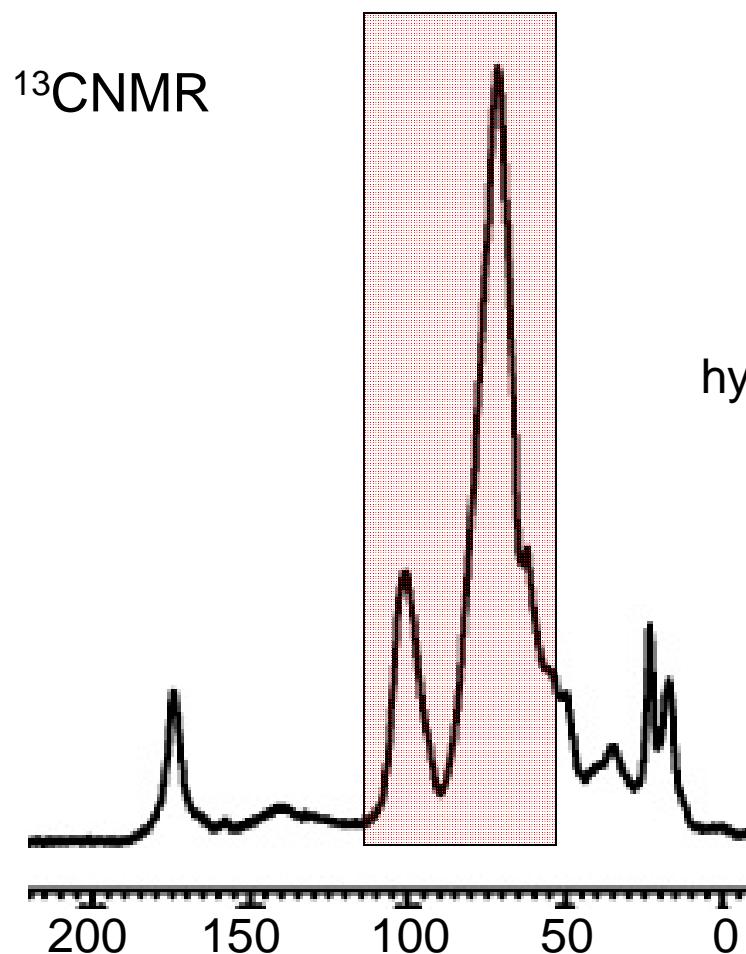
Photos from Dan Repeta

**Final product
30-35% of total DOC**

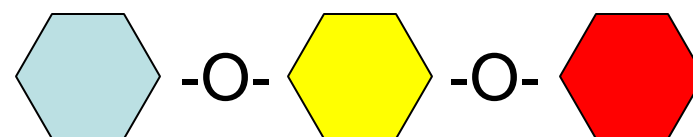


Spectral and chemical analyses of HMWDOC

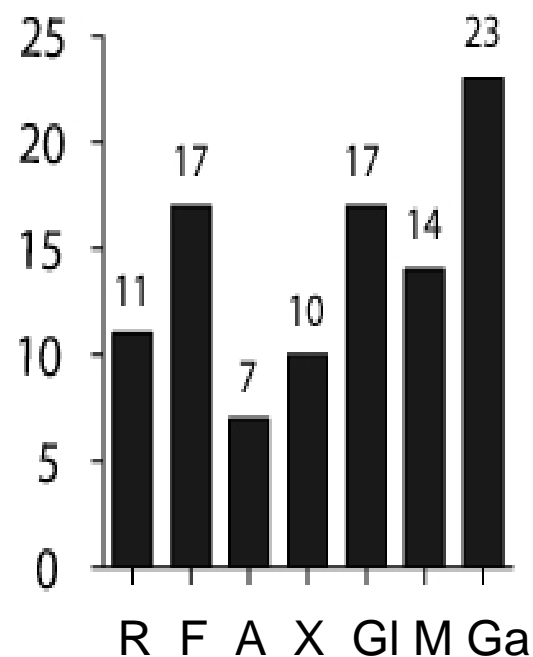
Carbohydrate
50-70% of HMWDOC



Acid
hydrolysis
→

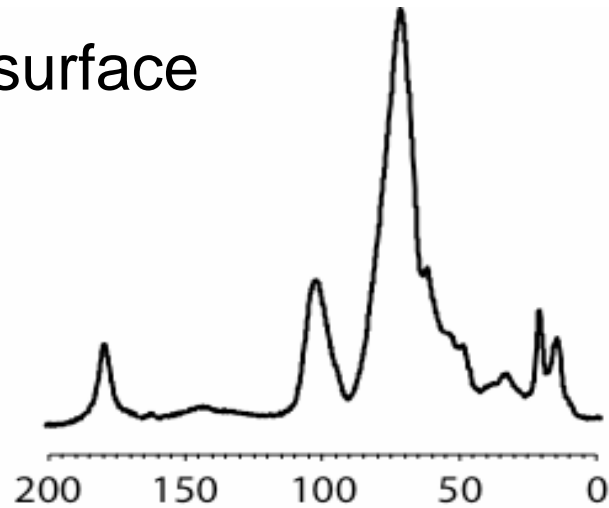


Acid hydrolysis followed by
Monosaccharide analyses
yields 7 major neutral sugars
that represent 5-10% of surface water DOM

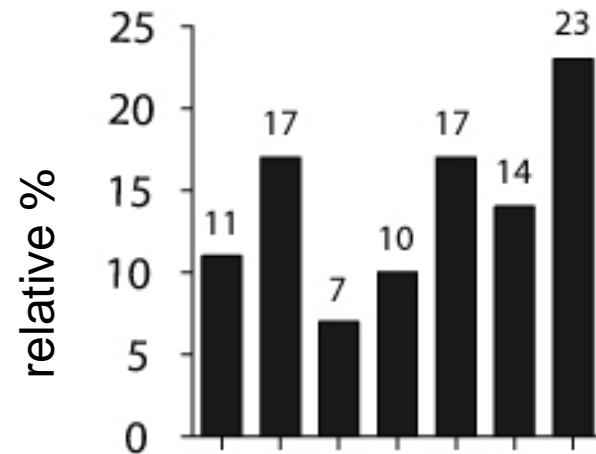


NMR and carbohydrate analyses of deep sea HMWDOC

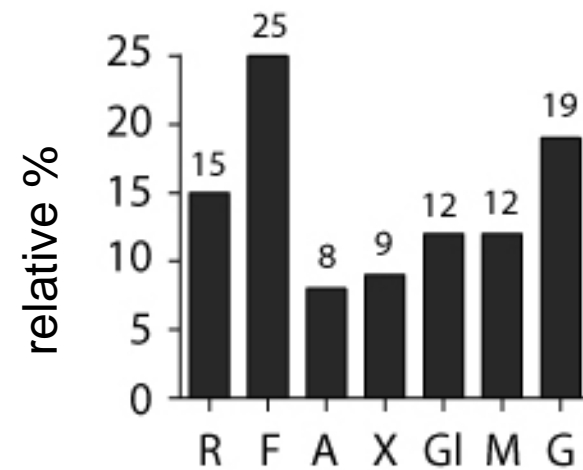
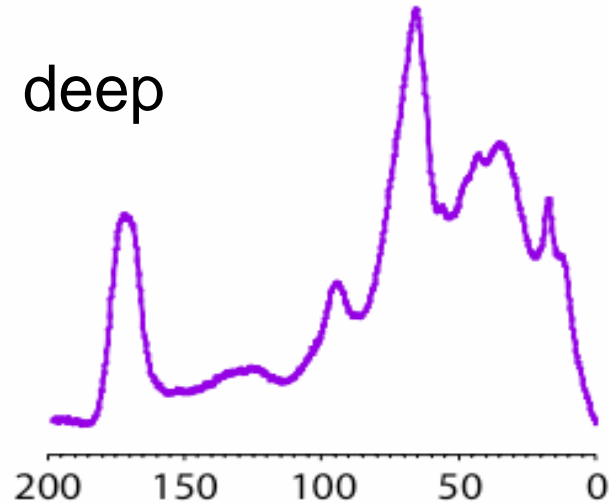
surface

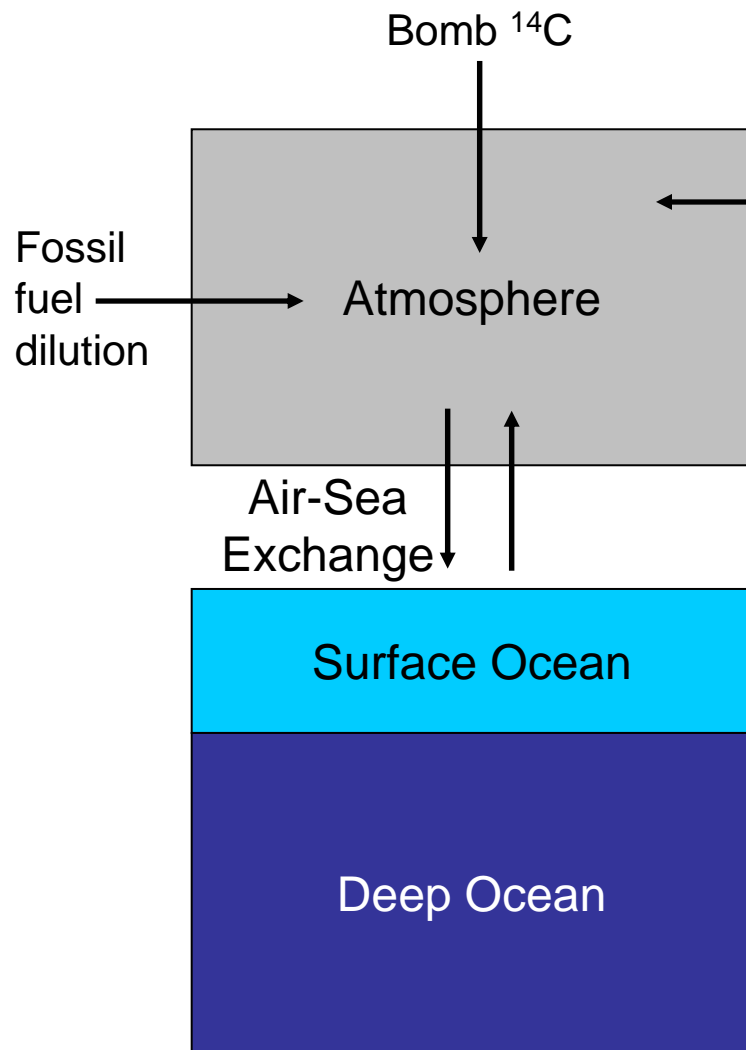


monosaccharide distribution



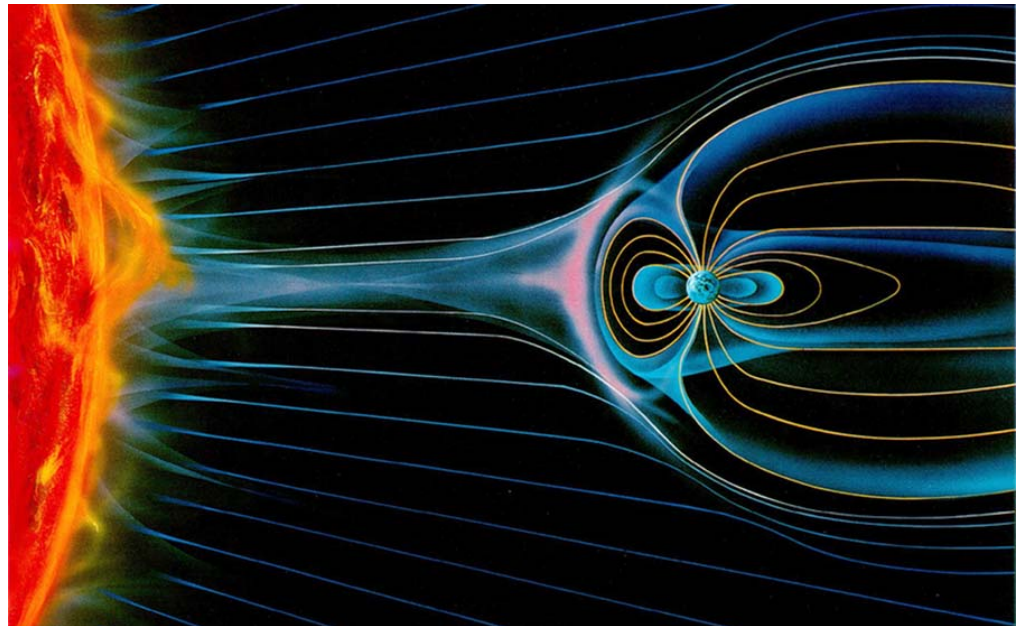
deep





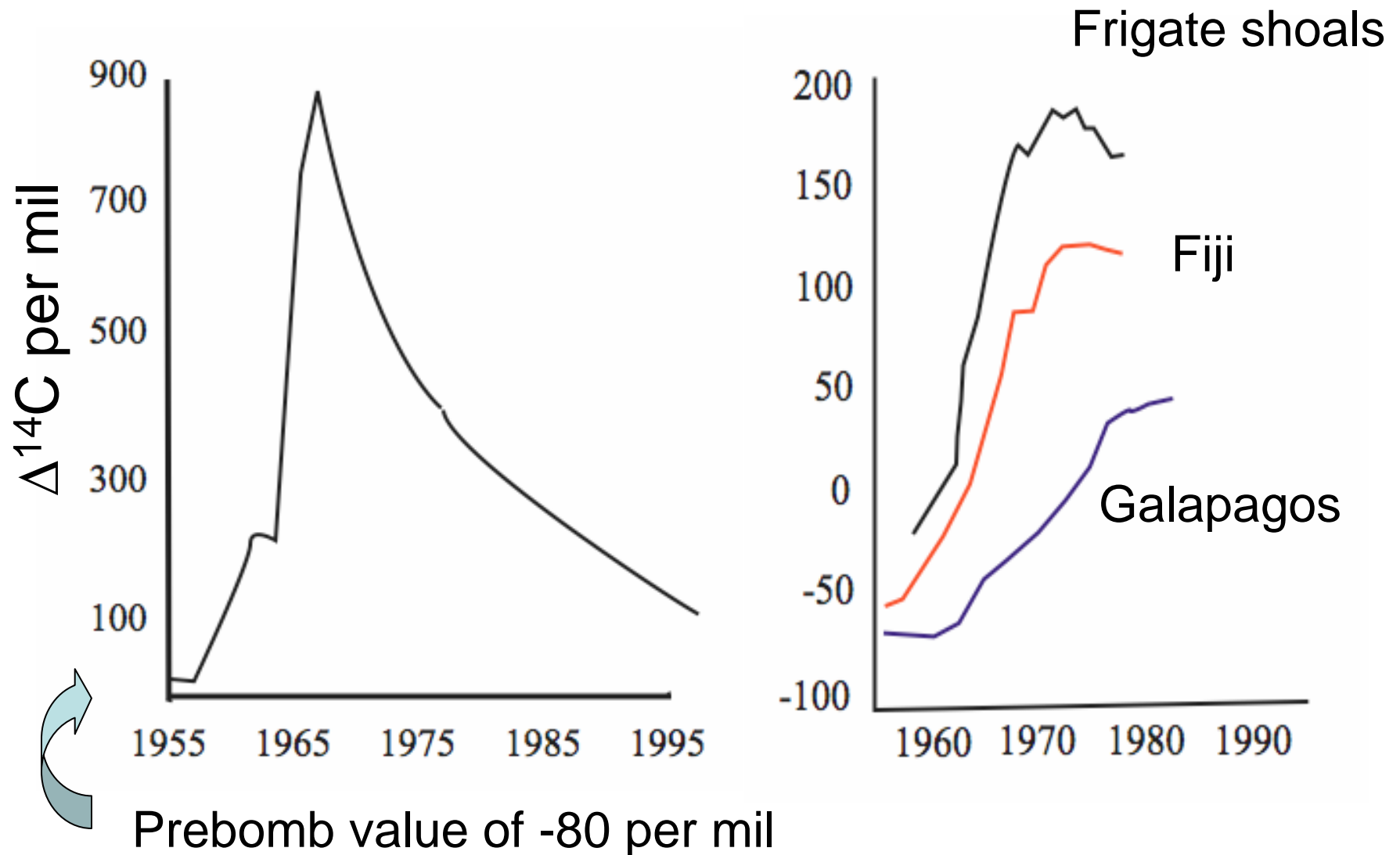
**Factors controlling ^{14}C in
atmospheric and oceanic
reservoirs**

Cosmogenic ^{14}C production



^{14}C half-life is 5730 years

History of radiocarbon in the Atmosphere and ocean



DOC cycling via DO^{14}C

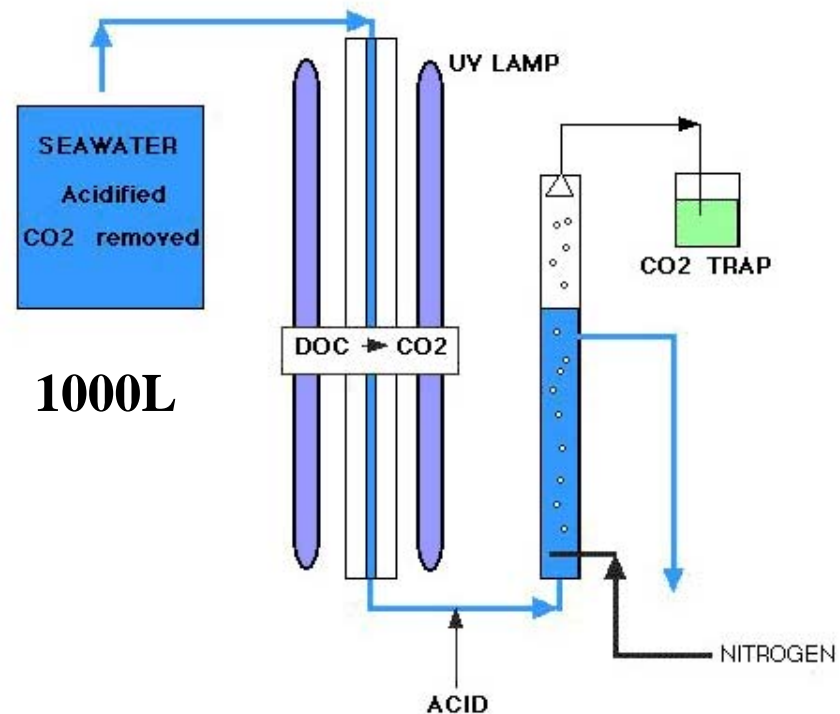
Williams, Oeschger, and Kinney; Nature v224 (1969)

UV photooxidation

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 time¹⁻³. 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.

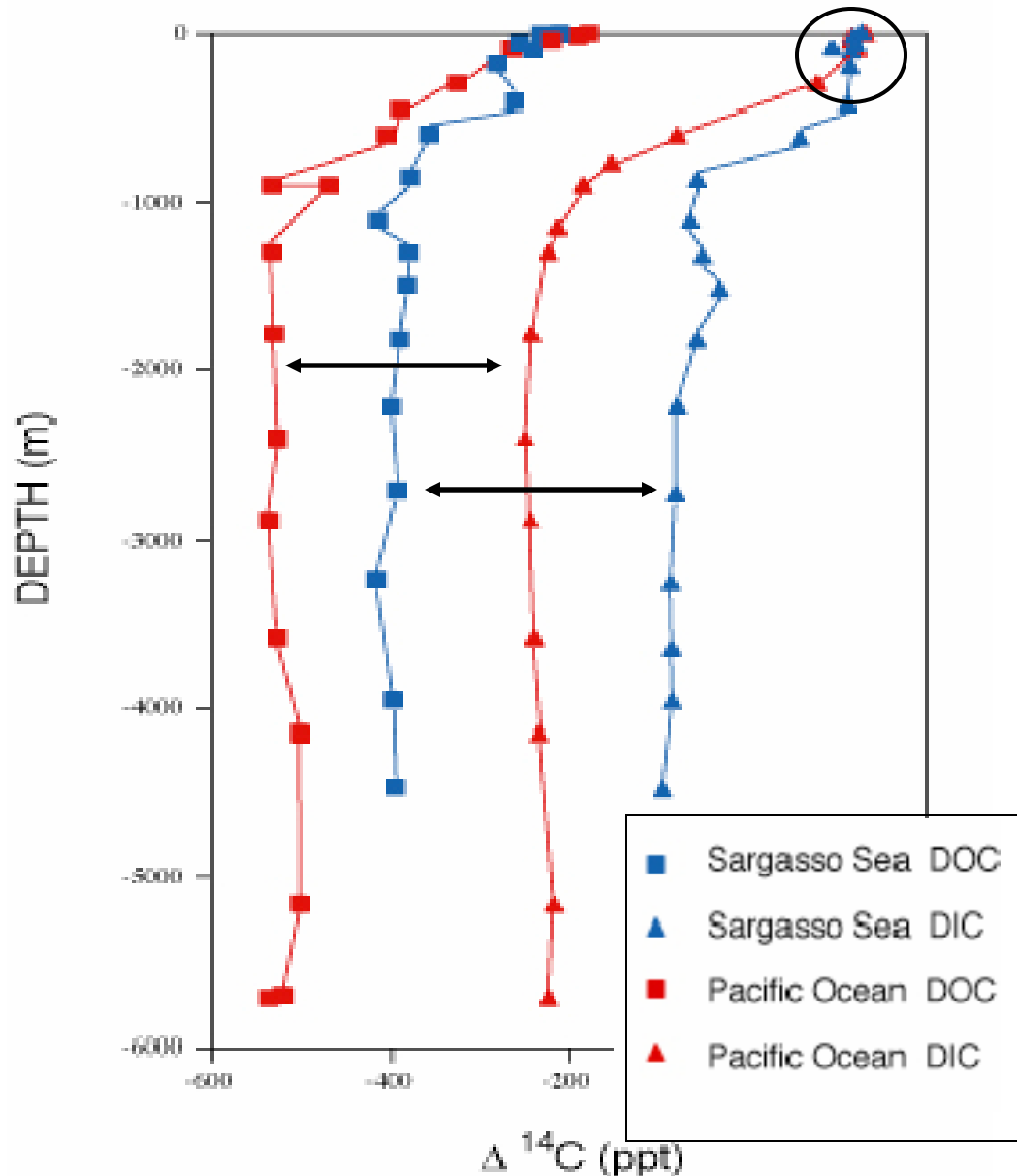
The dissolved organic carbon was converted to carbon dioxide (and subsequently to methane for radiocarbon counting) by photo-oxidation with high energy ultraviolet radiation⁴ (Fig. 1). Seawater was collected with a 100 l. stainless steel sampler and stored in 200 l. pre-leached steel drums lined with 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 $\mu\text{g/L}$. The seawater was acidified to pH 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*.



Depth	$\Delta^{14}\text{C}(\text{‰})$	Age
1880m	-351 ‰	-3470 \pm 330 ybp
1920m	-341 ‰	-3350 \pm 300 ybp

Radiocarbon in the Atlantic and Pacific Oceans

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



DIC ^{14}C in surface waters of the Atlantic and Pacific has the same isotopic value.

DOC is always older than DIC (by 4 kyrs in surface water)

Deep ocean values of DOC are equal to a radiocarbon age of 4000-5000 yrs

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