

Organic Compounds in Sea Water

OCN 623 – Chemical Oceanography

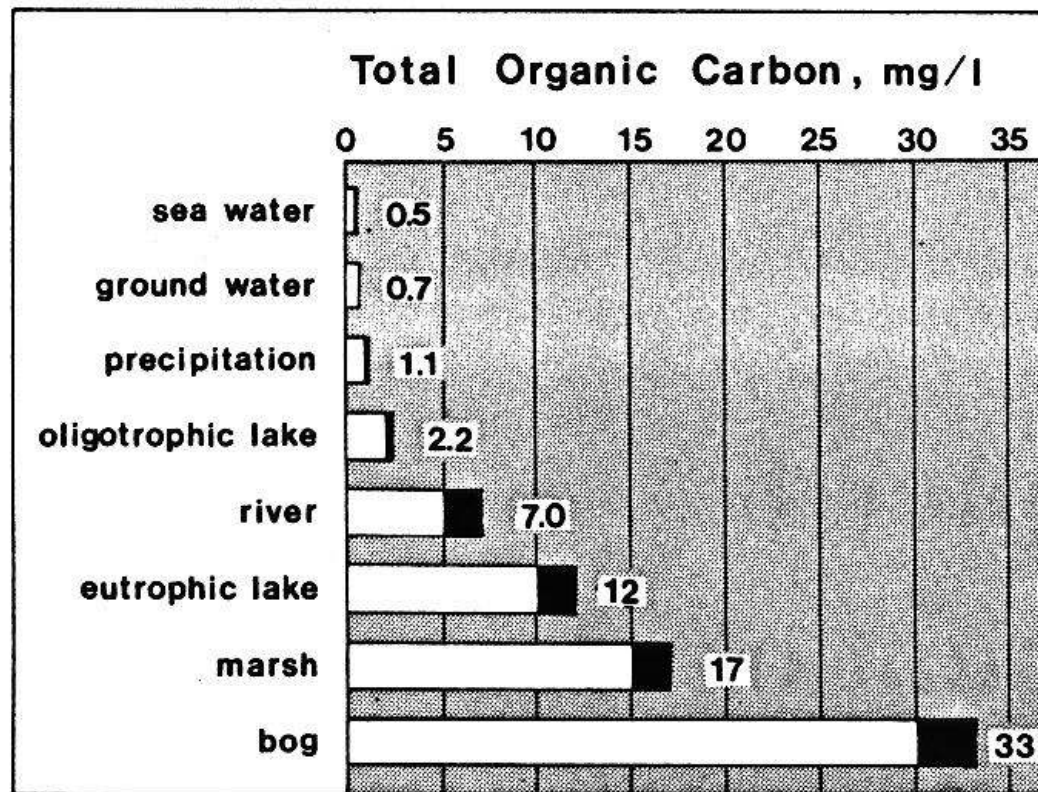
14 February 2013

Reading: Libes, Chapters 22 & 23 (much detail on subject)

Note: You can skim the details on compound classes

Outline

1. Basic considerations
 - DOM in aquatic environments
 - Size fractionation
2. Organic matter processing in the water column
 - Sources and sinks of marine organic matter
 - Colored dissolved organic matter & photo-oxidation
3. From water column to fossil fuel
 - Particle fluxes in water column
 - Sediment processing & preservation
4. Additional info
 - Analytical methods
 - Organic matter polarity



Dissolved Organic Carbon

Particulate Organic Carbon

Operational
definitions!

Figure 1.1 Approximate concentrations of dissolved and particulate organic carbon in natural waters. Thurman (1985).

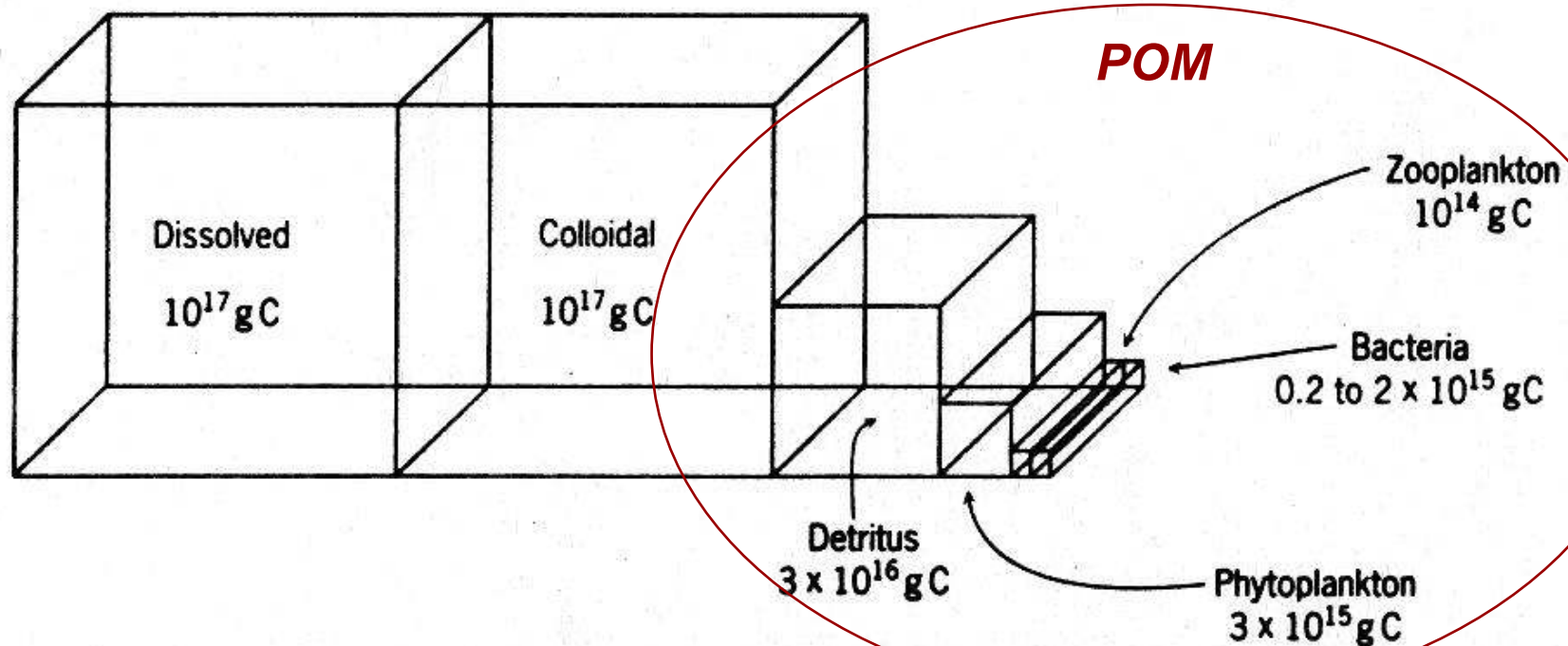


FIGURE 23.2. Distribution of organic carbon in the oceans. *Source:* After G. Cauwet, reprinted with permission from *Oceanologica Acta*, vol. 1, p. 101, copyright © 1978 by Gauthiers-Villars, Montrouge, France.

Organic Matter Size Fractionation

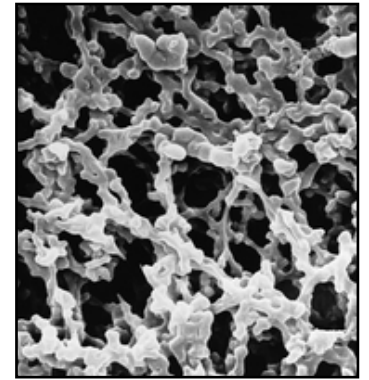
(or, what do we mean by *dissolved* vs. *particulate*?)

Operational definitions based on filter retention:

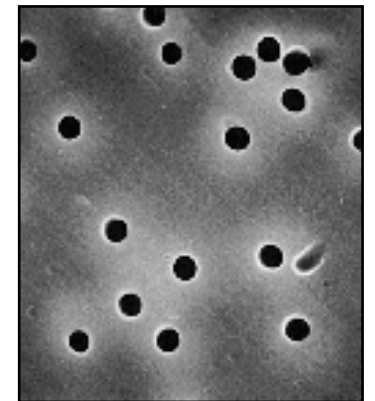
1. *Particulate organic matter (POM)*

Membrane filtration (e.g., Millipore)

Micropore filtration (e.g., Nuclepore)



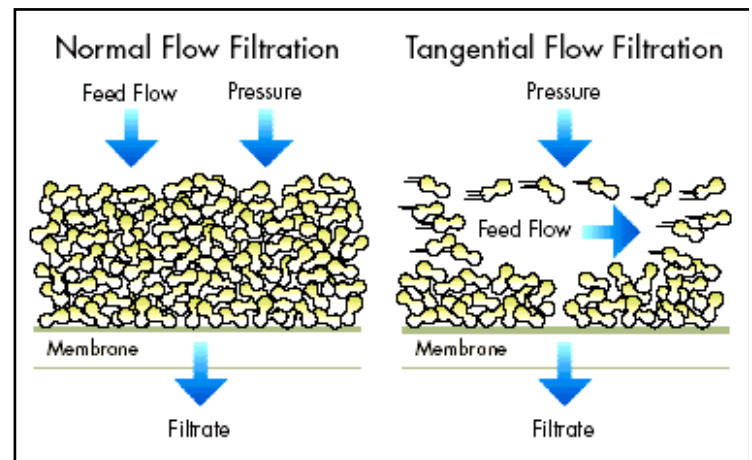
www.millipore.com



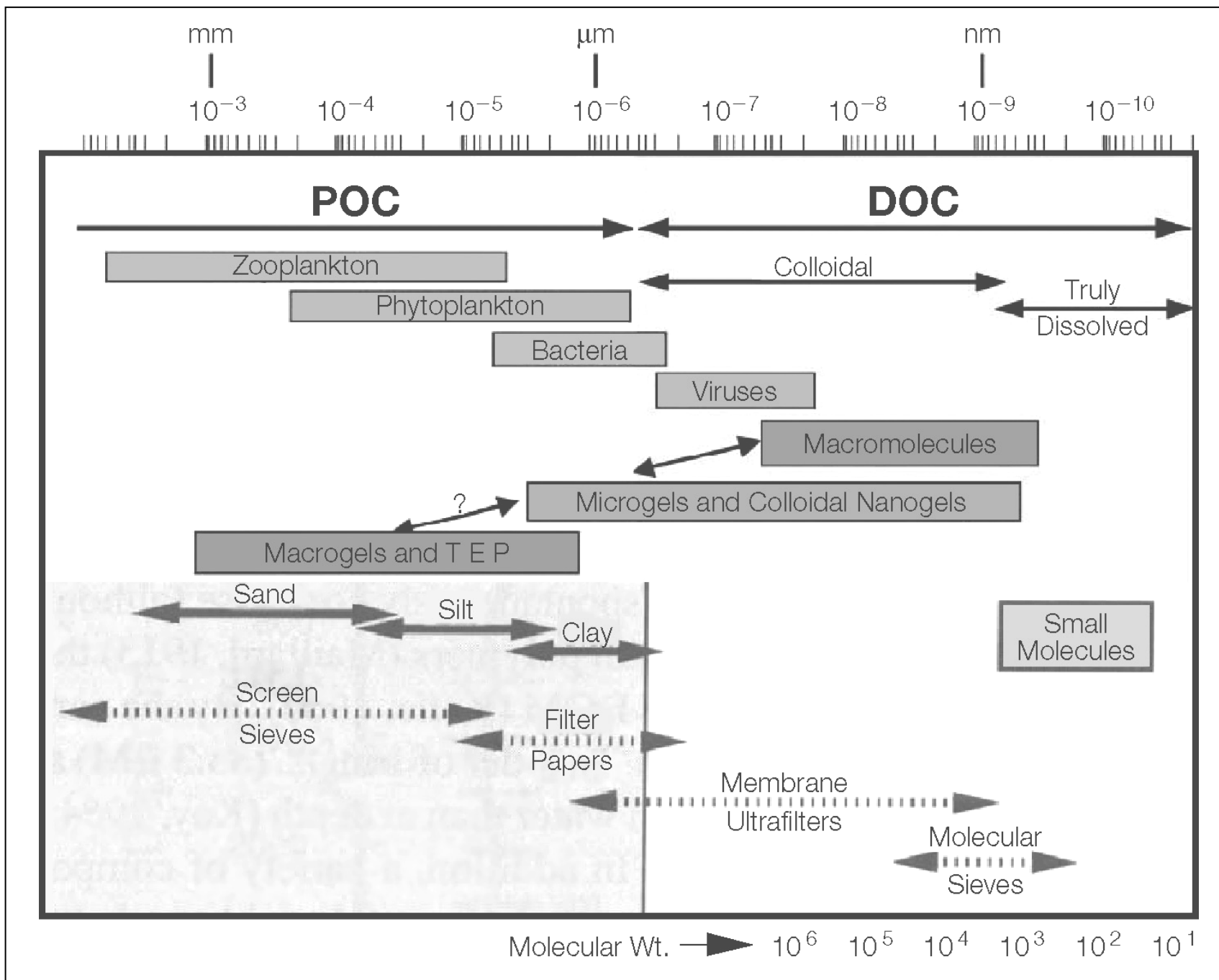
www.2spi.com

2. *Colloidal organic matter (COM)*

Tangential flow ultra-filtration (e.g., Amicon)



www.millipore.com



3. *Dissolved organic matter (DOM)*

a. *Dissolved organic carbon (DOC)*

- Oceanic concentrations = $\mu\text{g-C/L}$ to mg-C/L
- Turnover time: days to centuries, depending on compound
- Very fast during blooms, when large amounts of DOC are excreted
- Typical upper ocean DOC turnover time: 3 - 40 days.


b. *Dissolved organic nitrogen (DON)*

- Oceanic concentrations = $\mu\text{g-N/L}$
- Much shorter turnover time

c. *Dissolved organic phosphorus (DOP)*

- Oceanic concentrations = ng-P/L to $\mu\text{g-P/L}$
- Presumably very fast turnover time

Note: If you are using mass/vol units, be sure you specify if you mean mass of atoms or mass of molecules!



C/N Ratio Inversely Related to OM Lability

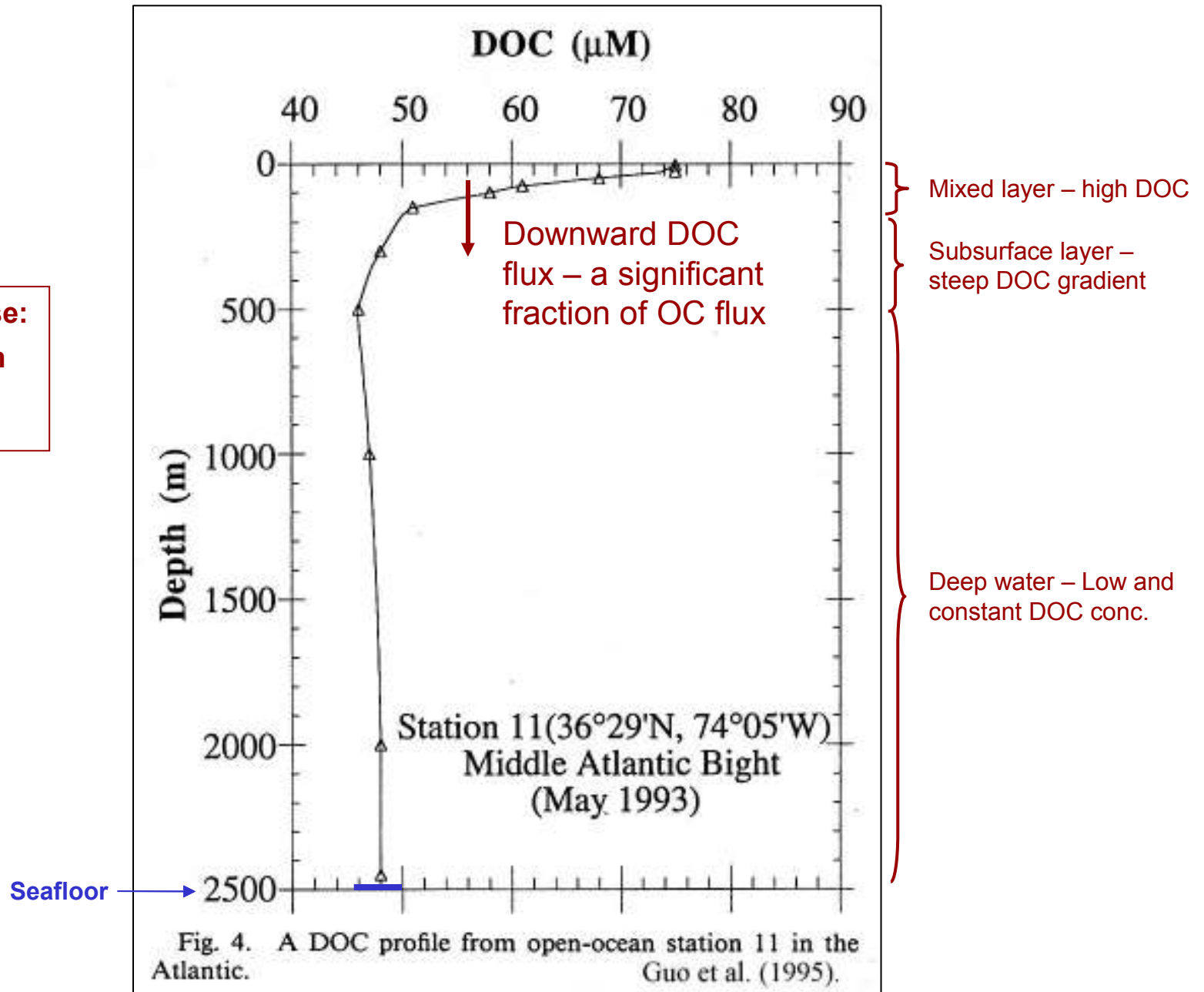
Table 9.1 Approximate carbon-to-nitrogen ratios in some terrestrial and marine producers.^a

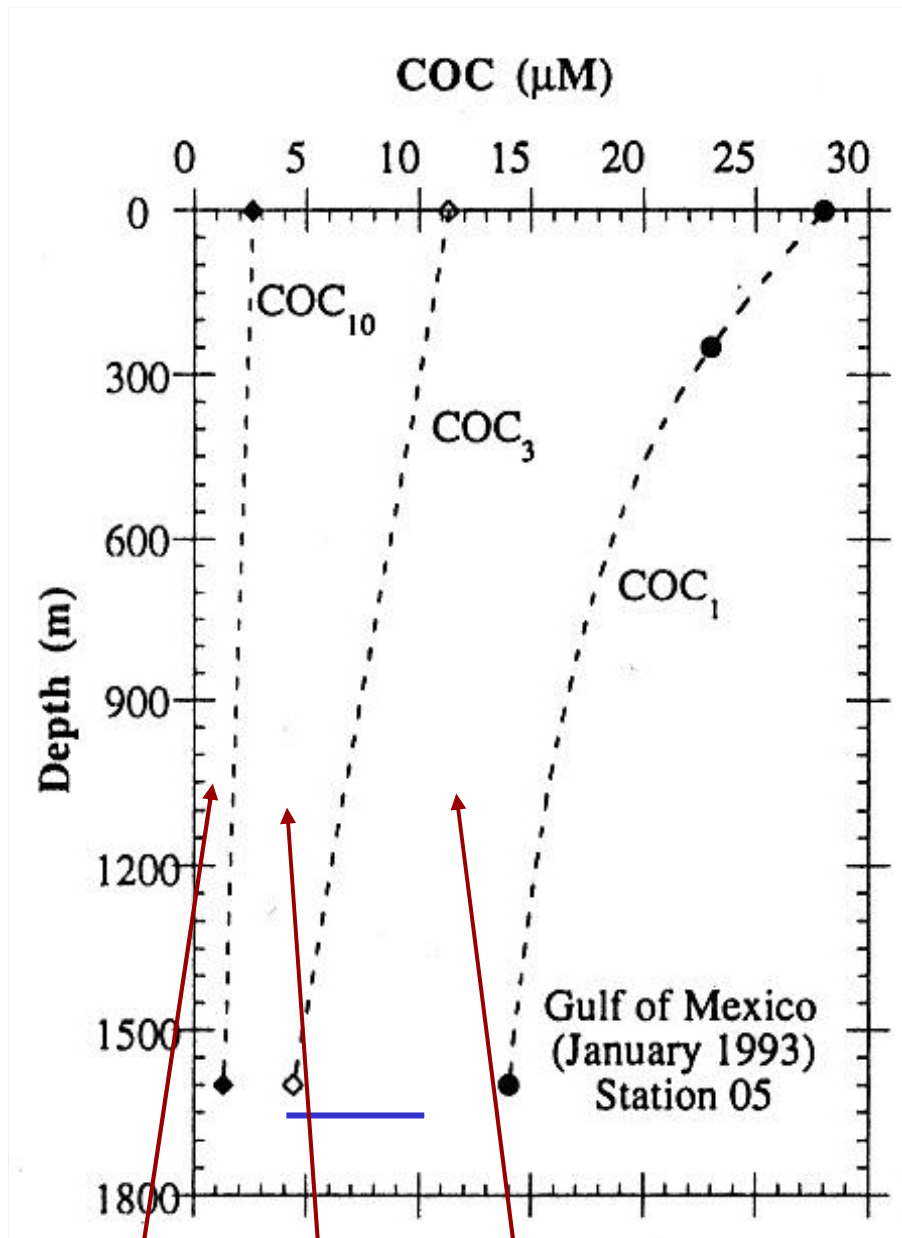
	C/N
Terrestrial	
Leaves	100
Wood	1000
Marine vascular plants	
<i>Zostera marina</i>	17–70
<i>Spartina alterniflora</i>	24–45
<i>S. patens</i>	37–41
Marine macroalgae	
Browns (Fucus, Laminaria)	30 (16–68)
Greens	10–60
Reds	20
Microalgae and microbes	
Diatoms	6.5
Greens	6
Blue–greens	6.3
Peridineans	11
Bacteria	5.7
Fungi	10

^aData compiled in Fenchel and Jørgensen (1977), Alexander (1977), and Fenchel and Blackburn (1979), and data of Valiela and Teal (1976).
Modified from Valiela (1995).

DOC Dynamics and Size Fractionation

DOC in this case:
Passes through
Whatman GF/F
filter (0.7 μm)





Filter water first thru a 0.2 μm filter to obtain DOC, then thru a series of **ultrafilters to measure colloidal organic carbon**:

COC₁₀ = 10 kDa - 0.2 μm (>200 L, 8 h)

COC₃ = 3 kDa - 0.2 μm (>200 L, 8 h)

COC₁ = 1 kDa - 0.2 μm (1000 L, 12 h)

1 Dalton = mass of 1 hydrogen atom
= 1.67×10^{-24} g

10 kDa - 0.2 μm

3 - 10 kDa

1 - 3 kDa

(Guo *et al.*, 1995)

Sources And Sinks Of Marine Organic Matter

1. ***Autochthonous*** vs. ***Allochthonous*** organic matter

(locally produced vs. imported)

Greek roots: "*auto*" = self

"*allo*" = other

"*chthonous*" = earth, ground

2. In general, the major source of open ocean OM is planktonic primary producers (**autochthonous**)

Most OM exported from coastal waters (**allochthonous**) is consumed in stratified continental shelf waters during the summer

3. OM abundance in the open ocean is controlled by grazing:
 - ~85% of primary production is recycled through consumers
 - ~15% is released from primary producers by extracellular release
 - This extracellular release supplies ~50% of microbial growth requirements

4. Humic materials – Part of *colored dissolved organic matter (CDOM)* – “Gelbstoffe”
 - Mostly terrestrial in origin (e.g., brown rivers)
 - Product of random polymerization
 - Refractory
 - Quickly removed from seawater by poorly understood processes

Rainwater

A Frequently Forgotten DOC Source

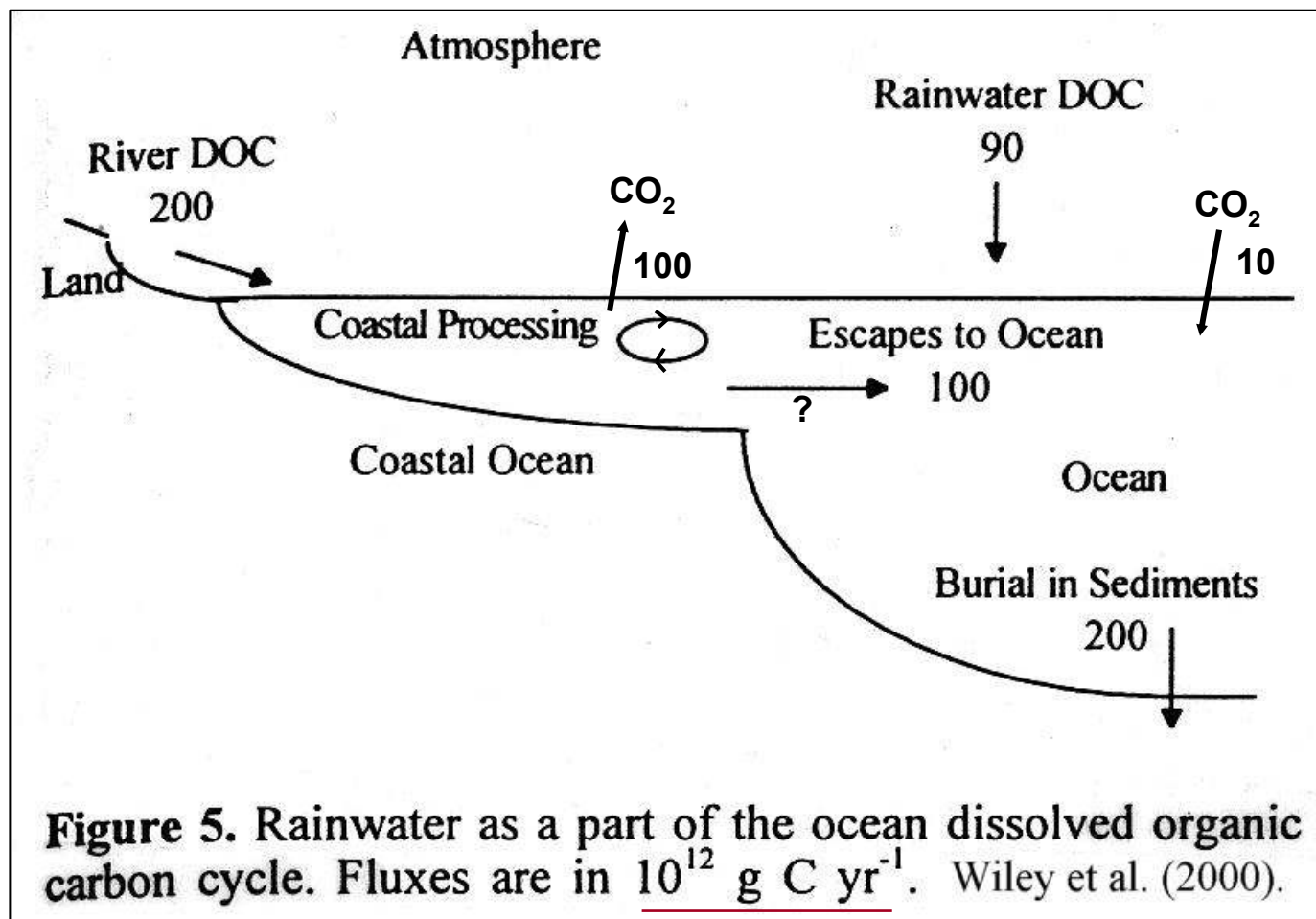


Figure 5. Rainwater as a part of the ocean dissolved organic carbon cycle. Fluxes are in $10^{12} \text{ g C yr}^{-1}$. Wiley et al. (2000).

Colored Dissolved Organic Matter - CDOM

A Very Operational Class of Organic Compounds

- Adsorption of **UV** and **visible** light by CDOM:
 - Controls UV penetration
 - Impacts phytoplankton and other microbial activity
 - A primary reactant in the photoproduction of CO_2 , CO , H_2O_2 , OCS (carbonyl sulfide)
 - Can affect remote observations of ocean chlorophyll and primary production
- **Coastal regions:**
 - Mostly terrestrial humic and fulvic acids (from plant-matter breakdown) from rivers and runoff
 - CDOM decreases with distance from coast, as does DOM

- Open ocean:
 - Composition in open ocean is largely unknown
 - <5% from terrestrial sources
 - DOM from microbial excretion / lysis must be altered to become CDOM
 - Summertime bleaching of CDOM -- lowers CDOM conc but has negligible effect on DOM conc
 - Significant variations in CDOM concs occur in the upper ocean over seasonal-to-interannual timescales
 - CDOM and DOM concs vary *inversely* over large space scales

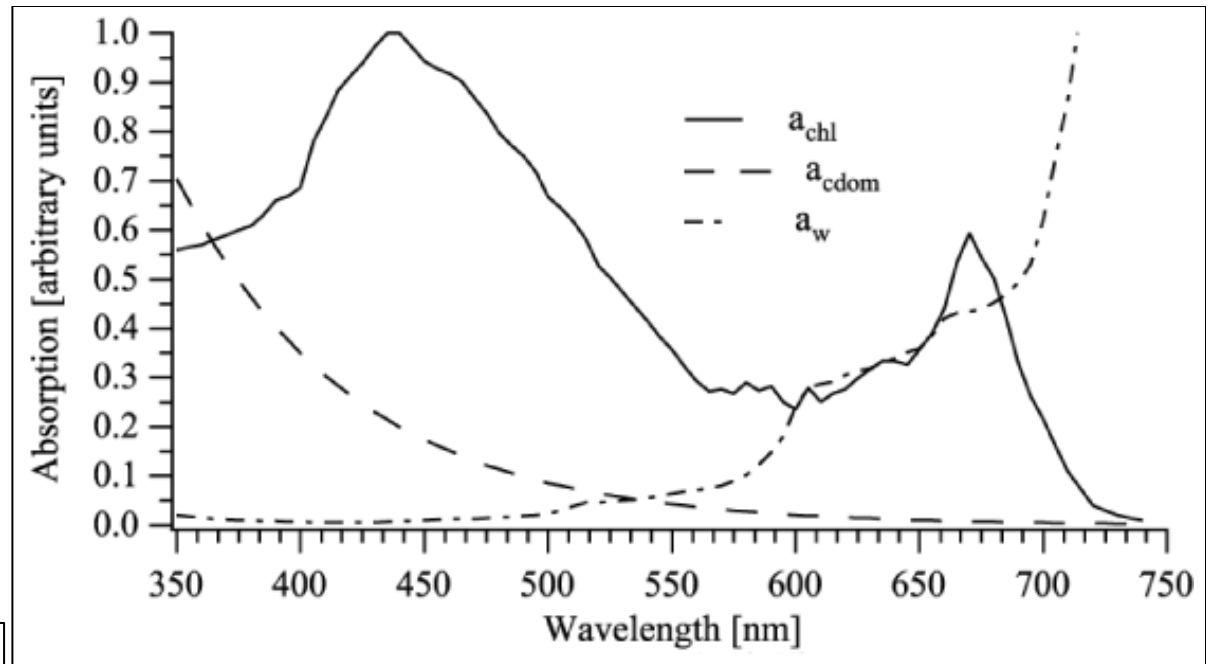
Nelson, N.B., D.A. Siegel, Chromophoric DOM in the Open Ocean. In: *Biogeochemistry of Marine Dissolved Organic Matter*, D.A. Hansell, C.A. Carlson (eds.), Academic Press, 2002.

Absorption spectra:

a_{chl} - chlorophyll absorbance

a_{cdom} - CDOM absorbance

a_w - pure water absorbance



Sargasso Sea - July

Absorption vs. depth:

O - CDOM

Δ - Particulate matter (mostly phytoplankton)

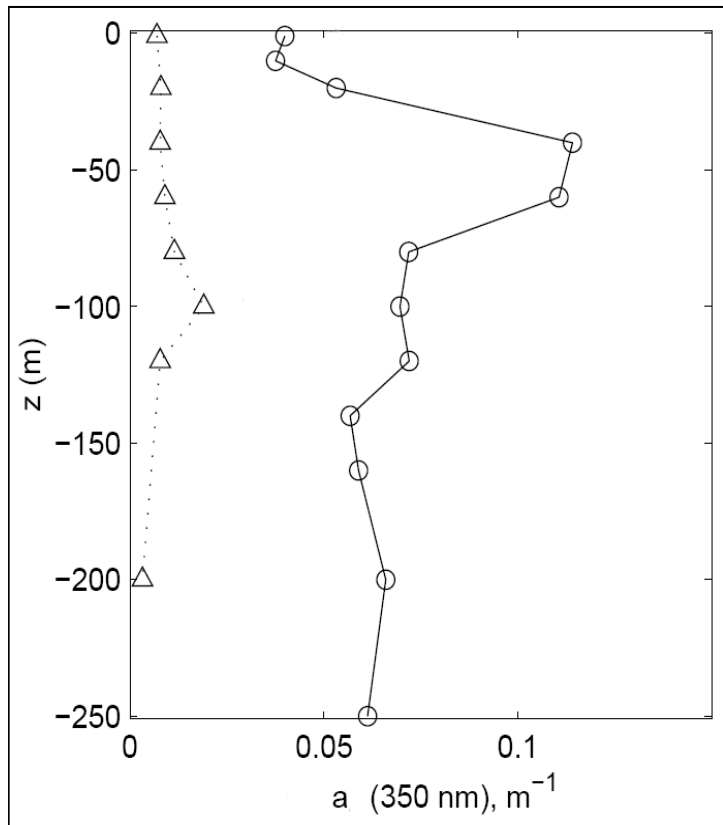
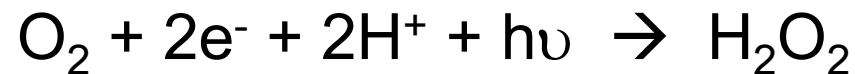


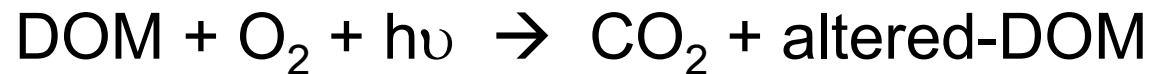
Photo-chemistry in the Upper Ocean

Two main processes:

- H_2O_2 (hydrogen peroxide) production:



- DOM oxidation:



Similar rate of O_2 consumption by each process

Table 1. Biologically available compounds formed via photochemical processes from aquatic DOM.

Compound	MW	Structure	Reference
<u>Low MW Organic Compounds</u>			
Acetaldehyde	44	$\text{H}_3\text{C}-\overset{\text{H}}{\underset{ }{\text{C}}}=\text{O}$	Mopper and Stahovec 1986 Mopper et al. 1991 Kieber et al. 1990
Acetate	59	$\text{H}_3\text{C}-\overset{\text{O}^-}{\underset{ }{\text{C}}}=\text{O}$	Wetzel et al. 1995 Dahlén et al. 1996
Acetone	58	$\text{H}_3\text{C}-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{CH}_3$	Mopper and Stahovec 1986
Citrate	189	$\begin{array}{c} \text{O} \\ \\ -\text{O}-\text{C}-\text{CH}_2-\text{C}-\text{O}^- \\ \\ \text{O}^- \end{array} \begin{array}{c} \text{O} \\ \\ \text{C}-\text{O}^- \\ \\ \text{O}^- \end{array} \text{CH}_2-\text{C}-\text{O}^-$	Wetzel et al. 1995
Formaldehyde	30	$\text{H}_2\text{C}=\text{O}$	Mopper and Stahovec 1986 Mopper et al. 1991 Kieber et al. 1990
Formate	45	$\text{HC}=\overset{\text{O}^-}{\underset{ }{\text{C}}}=\text{O}$	Wetzel et al. 1995 Dahlén et al. 1996
Glyoxal	58	$\text{HC}-\overset{\text{O}}{\underset{ }{\text{C}}}-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{H}$	Mopper and Stahovec 1986 Mopper et al. 1991

Glyoxalate	73	$\text{HC}-\overset{\text{O}}{\underset{ }{\text{C}}}-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{O}^-$	Kieber and Mopper 1987 Mopper et al. 1991 Kieber et al. 1990
Levulinate	115	$\text{H}_3\text{C}-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{O}^-$	Wetzel et al. 1995
Malonate	102	$^-\text{O}-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{O}^-$	Dahlén et al. 1996
Methylglyoxal	72	$\text{HC}-\overset{\text{O}}{\underset{ }{\text{C}}}-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{CH}_3$	Mopper and Stahovec 1986
Oxalate	88	$^-\text{O}-\overset{\text{O}}{\underset{ }{\text{C}}}-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{O}^-$	Dahlén et al. 1996
Propanal	59	$\text{H}_3\text{C}-\text{CH}_2-\overset{\text{O}}{\underset{ }{\text{C}}}=\text{H}$	Mopper and Stahovec 1986
Pyruvate	87	$\text{H}_3\text{C}-\overset{\text{O}}{\underset{ }{\text{C}}}-\overset{\text{O}}{\underset{ }{\text{C}}}-\text{O}^-$	Kieber and Mopper 1987 Kieber et al. 1989 Mopper et al. 1991 Wetzel et al. 1995

Carbon Gases

Carbon Monoxide	28	CO	Mopper et al. 1991 Jones 1991 Valentine and Zepp 1993 Schmidt and Conrad 1993 Miller and Zepp 1995
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Nutrients

Ammonium	17	NH_4^+	Bushaw et al. 1996
Phosphate	95	PO_4^{3-}	Francko and Heath 1982

Moran and Zepp (1997)

Table 3. Estimated formation of biologically labile photoproducts from DOM in seawater from the continental shelf of the southeastern U.S. during exposure to 1 h of noontime summer sunlight at 32°N latitude. Calculations were made by normalizing for light intensity, length of exposure, and light absorption properties of the DOM among a number of studies. Daily production rates given in the text were calculated by assuming 7.6 h of noontime sunlight per day.

Compound	Production (nM (C or N) h ⁻¹)	Reference
Low-MW organic compounds		
Acetaldehyde	11	Kieber et al. 1990 Mopper et al. 1991 Mopper and Stahovec 1986
Acetate	5	Wetzel et al. 1995
Formaldehyde	14	Kieber et al. 1990 Mopper and Stahovec 1986
Formate	1	Wetzel et al. 1995
Glyoxal	6	Mopper et al. 1991 Mopper and Stahovec 1986
Glyoxylate	22	Kieber et al. 1990 Mopper et al. 1991
Levulinate	46	Wetzel et al. 1995
Propanal	3	Mopper and Stahovec 1986
Pyruvate	12	Mopper et al. 1991
Carbon gases		
Carbon monoxide	108	Mopper et al. 1986 Valentine and Zepp 1993 Miller and Zepp 1995
Nutrients		
Ammonium	17	Bushaw et al. 1996

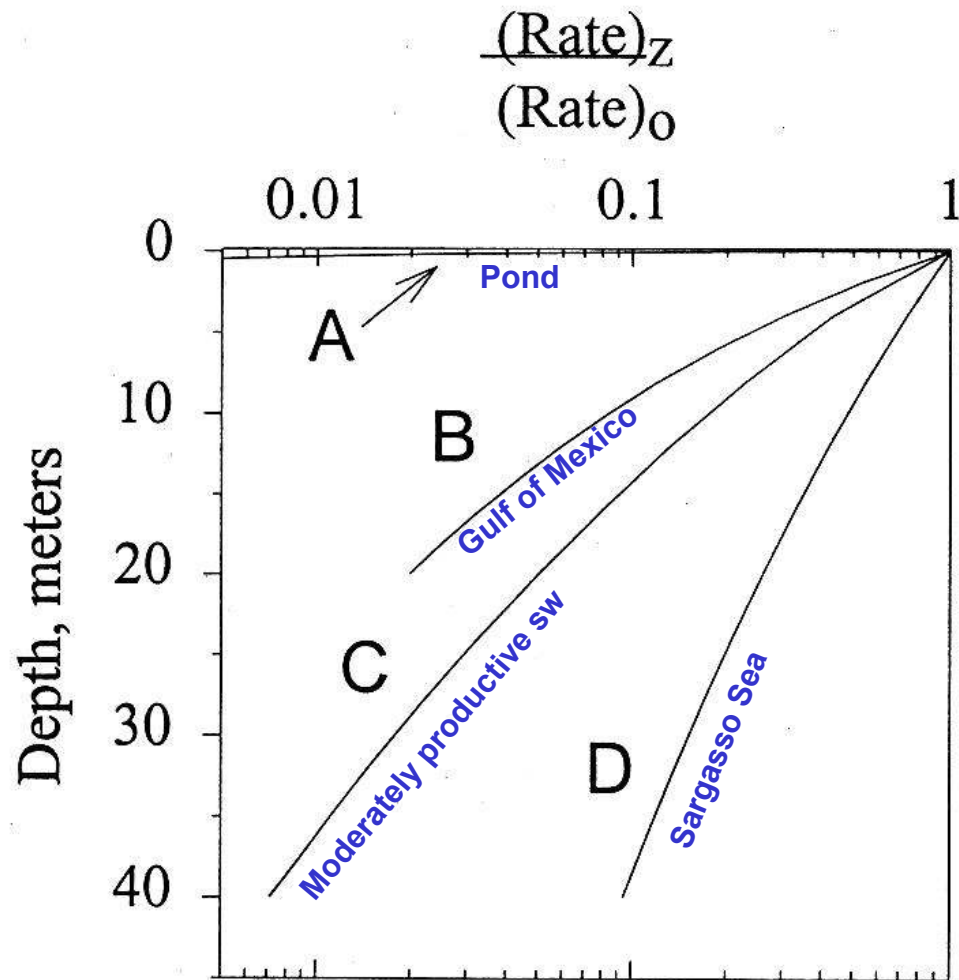


Fig. 3. Depth profiles of relative rates of formation of biologically available DOM photoproducts for representative marine and freshwater ecosystems. Estimates of diffuse attenuation coefficients for the boreal pond sample (A) were based on an absorption spectrum obtained on a Shimadzu spectrophotometer using a 0.2- μm filtered water sample. Diffuse attenuation coefficients for water from the Gulf of Mexico (B), moderately productive seawater (C), and the Sargasso Sea (D) are from Smith and Baker (1979). The assumed action spectrum is based on that of Valentine and Zepp (1993) for CO photoproduction.

Moran and Zepp (1997).

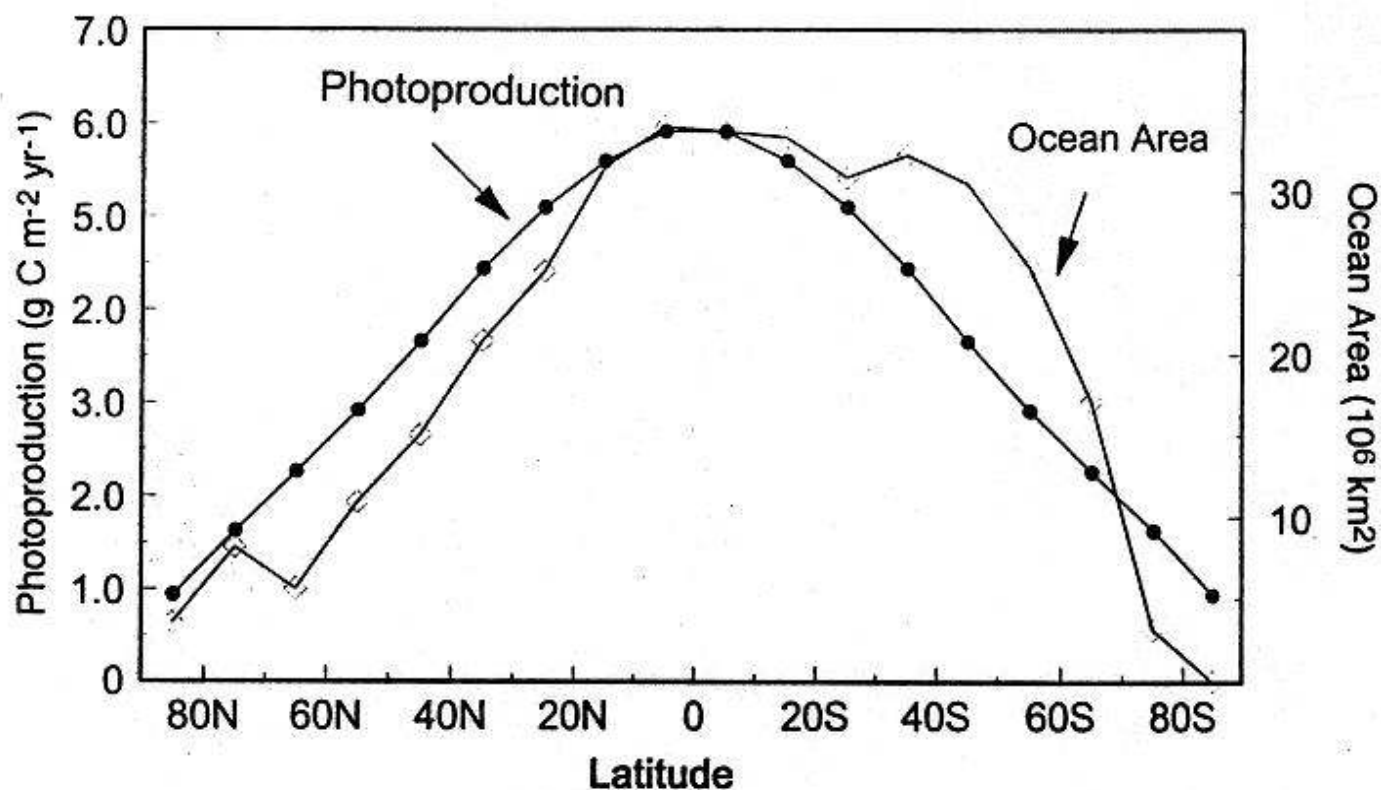


Fig. 4. Estimated depth-integrated photochemical formation of biologically available carbon photoproducts from DOM and surface area of the ocean for 10° latitude bands. Photoproduction calculations assume particle-free water of sufficient depth for all sunlight to be absorbed, the action spectrum of Valentine and Zepp (1993), and cloud-free skies. Ocean area is from Sverdrup et al. (1942). Annual depth-integrated production for 10° increments in latitude are based on fluxes that were computed for each month using a previously described model (Valentine and Zepp 1993) and recent total ozone data (Harris et al. 1995).

Moran and Zepp (1997).

Eastern Pacific Sediment Trap Data

Percent of Particulate Organic Matter (POM)

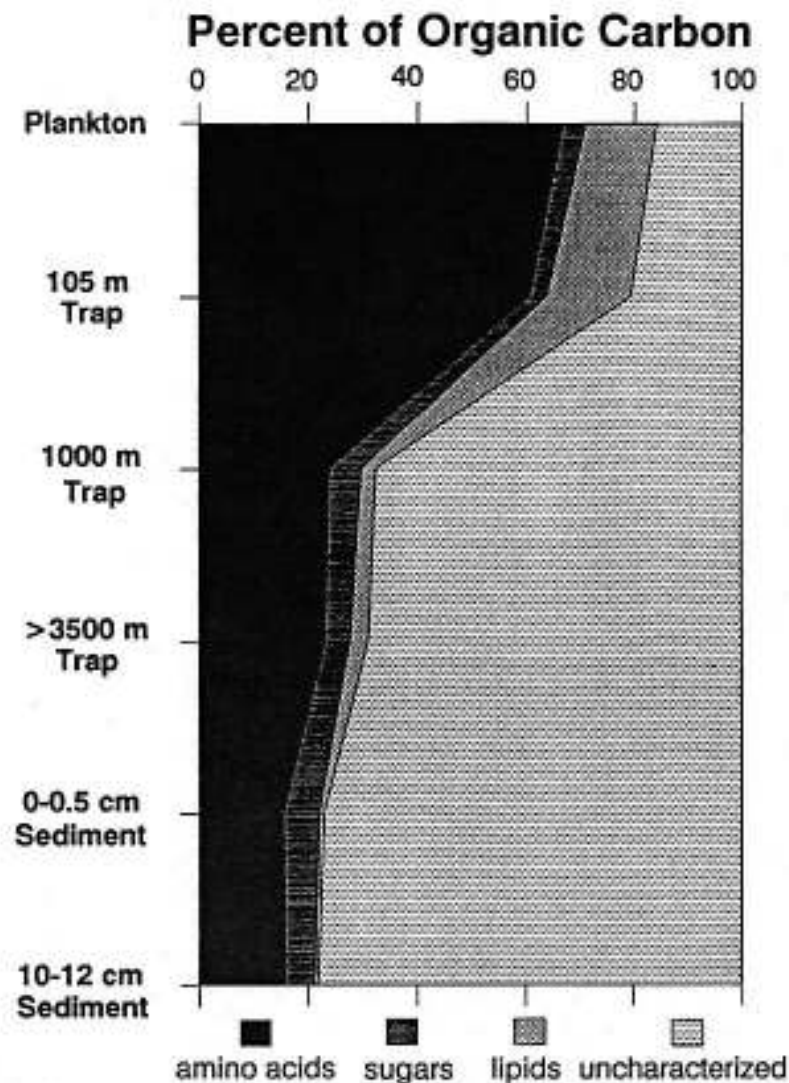


Fig. 2. Cumulative biochemical class distributions (compound class-C as percent of total C_{org}). Values at 9°N, 5°N, and the equator have been averaged; values for the 105-m traps represent means for the two surveys. Carbon contents were calculated directly for amino acids and sugars, while the measured lipids were estimated to be 85% C. Chlorophyll and its degradation products are included with lipids but are quantitatively negligible. Residual "uncharacterized" carbon was obtained as the difference between total C_{org} and the sum of carbon in amino acid + sugar + lipid.

Particulate Organic Matter Fluxes

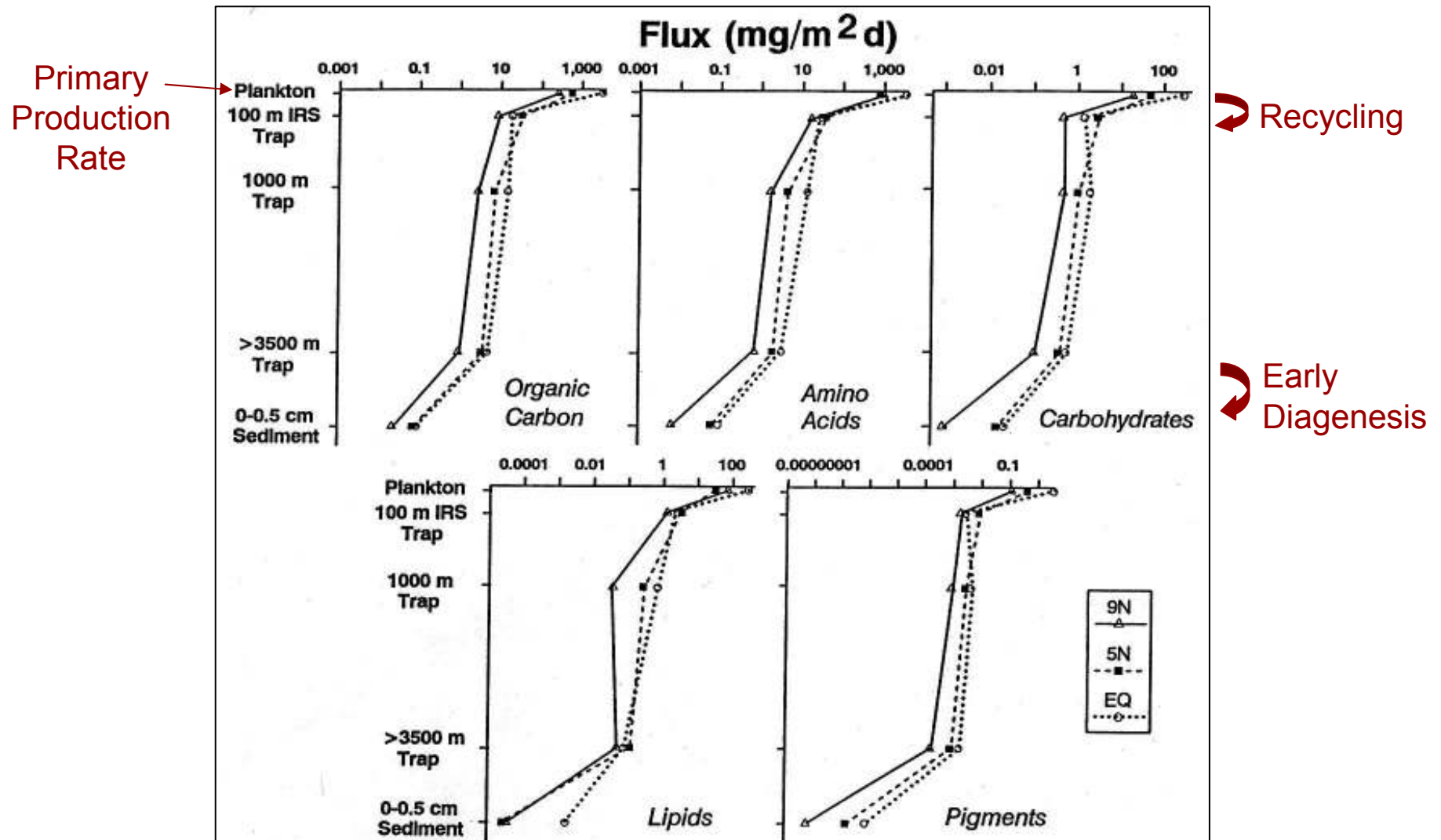


Fig. 1. Fluxes ($\text{mg}/\text{m}^2 \text{d}$) of organic carbon and biochemical classes at 9°N , 5°N , and the equator. Compound class fluxes are in mg of compound, not mg C . Fluxes for net-plankton are derived from primary production rates (Barber et al., 1996) and our measurements of biochemical content of net-plankton. Floating sediment trap fluxes at 5°N and the equator are means of two surveys (there was only 1 measurement at 9°N). Fluxes into surface sediments were calculated using the sediment C_{org} content and accumulation rates (DeMaster et al., 1997) and our biochemical measurements. There are no accumulation rate data for 10–12 cm sediments.

Fig 23.5
in text

Organic Matter Processing

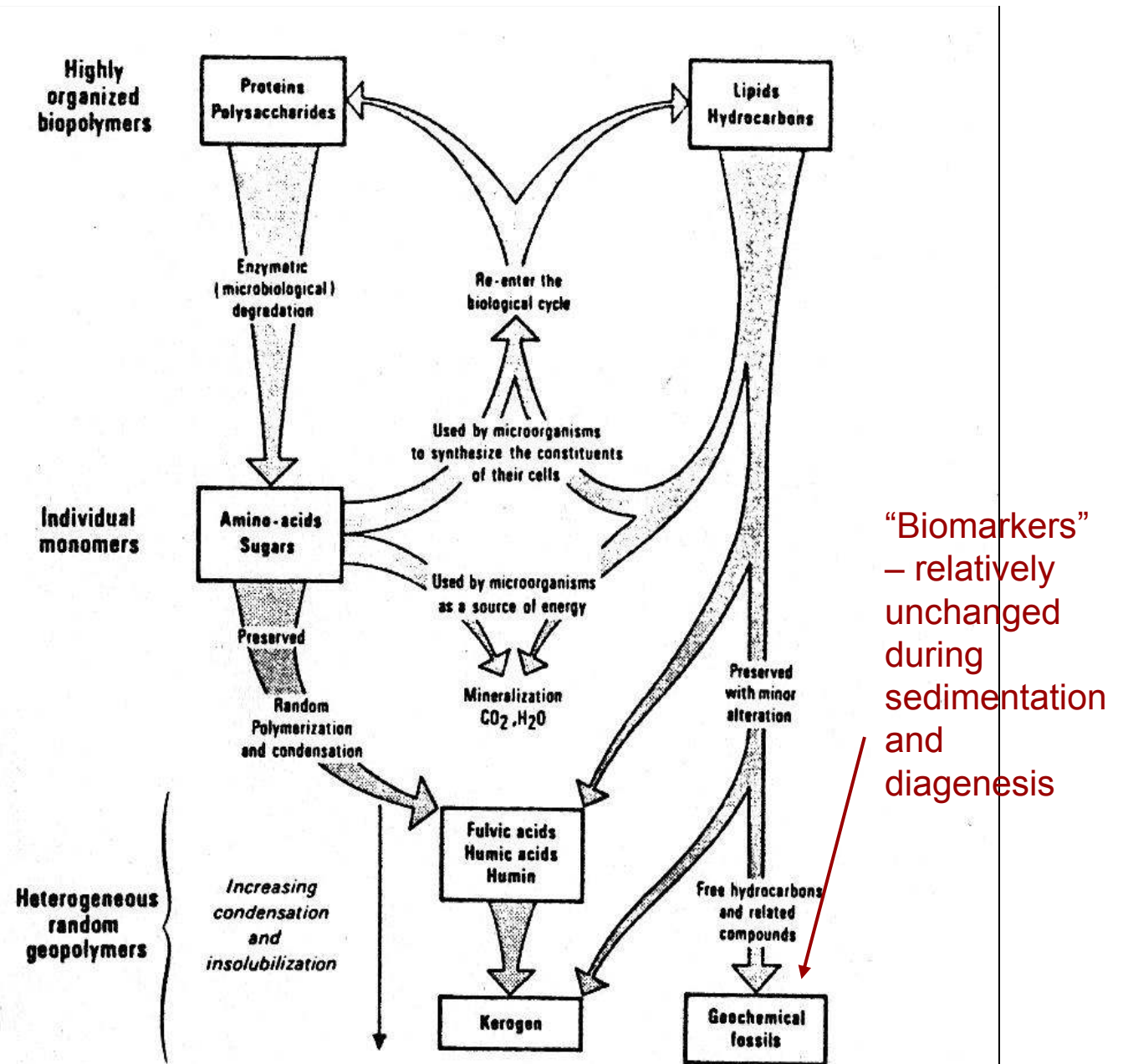
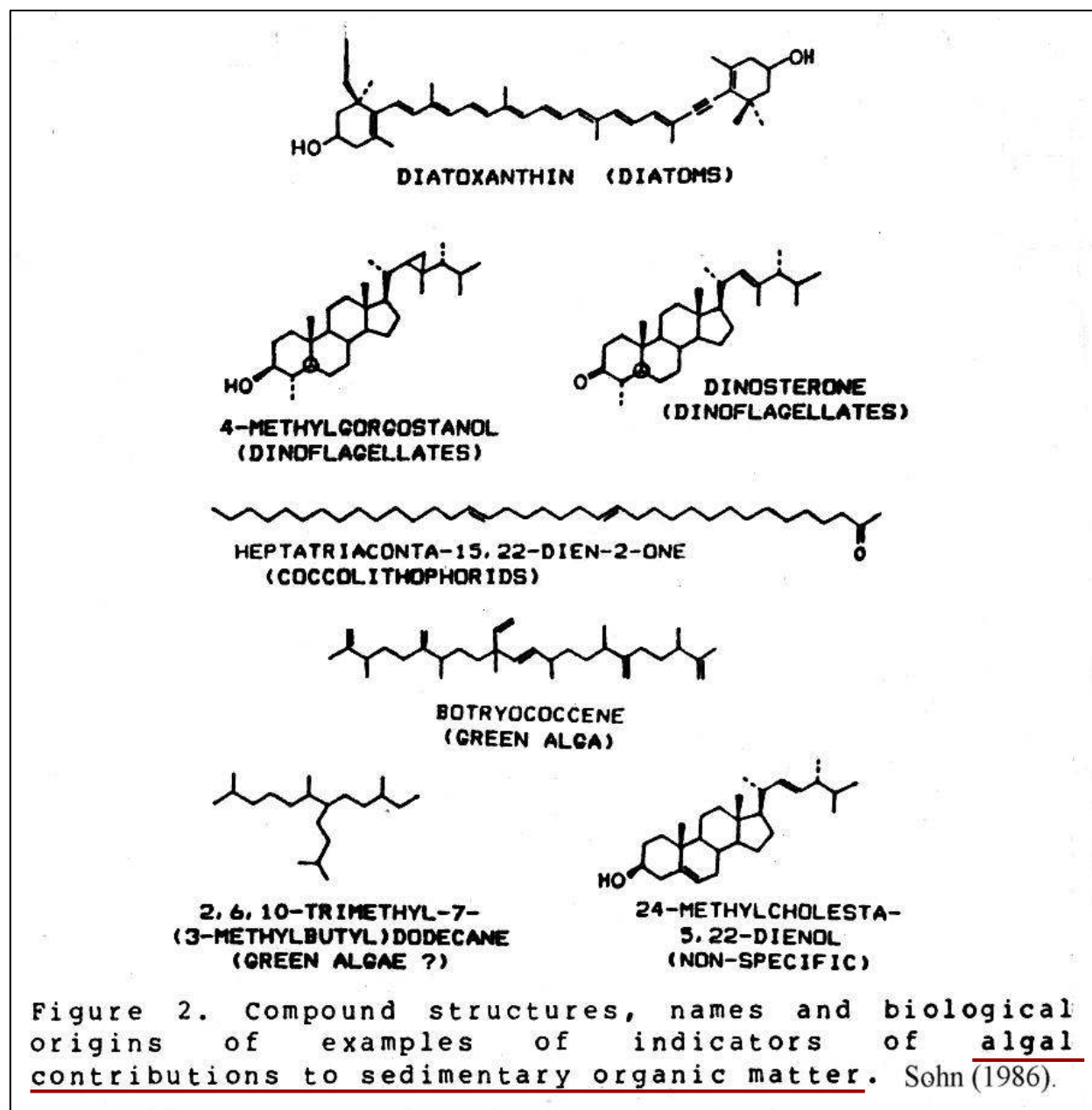


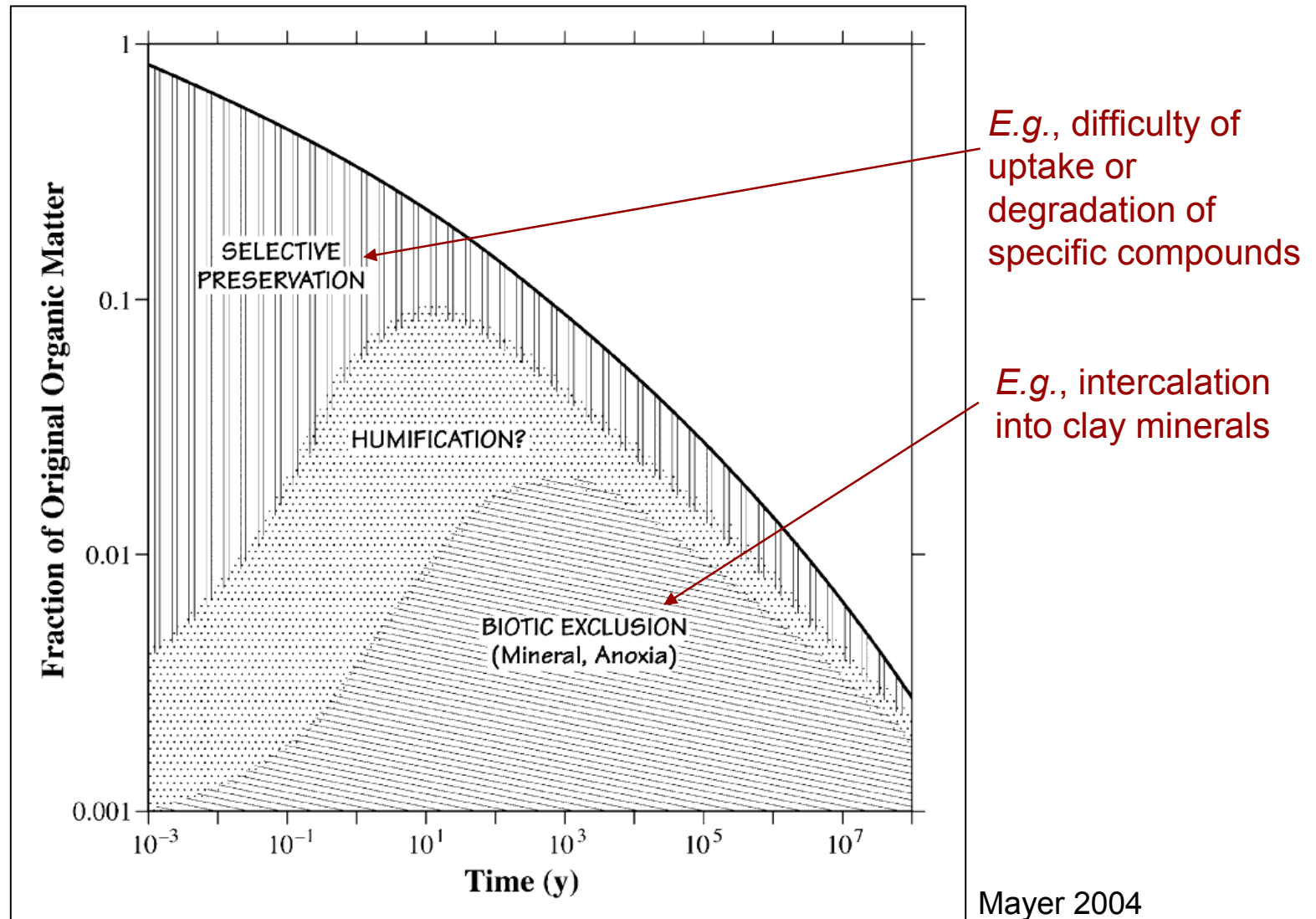
Fig. II.2.10. Fate of organic material during sedimentation and diagenesis, resulting in two main organic fractions: kerogen and geochemical fossils Tissot and Welte.

A Few Examples of Biomarkers



OM Protection in Sediment

A Succession of Mechanisms



A succession of preservation methods as the OM ages

Analytical Methods - Organics in Seawater

1. Bulk analysis:

- Oxidize or combust DOC to CO_2 (detect with IR spectrophotometer or coulometer),

Three methods commonly used:

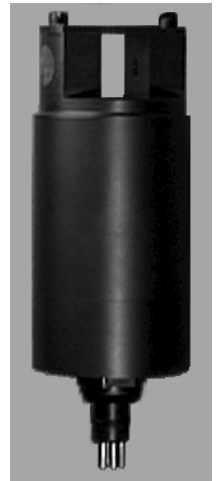
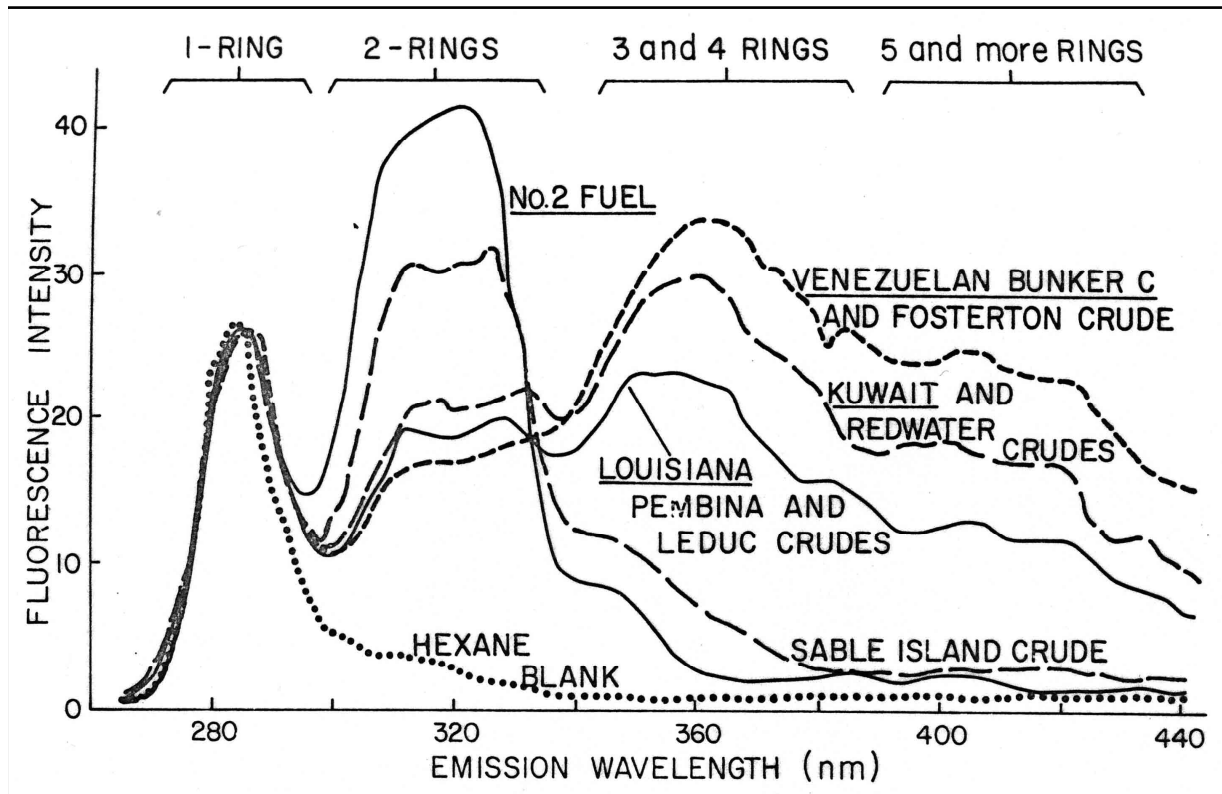
- a. UV-oxidation (traditional)
- b. Persulfate oxidation (traditional)
- c. High temperature catalytic oxidation (recent)

- Oxidize DON to N_2 (chemiluminescence detector) or
Hydrolyze DON to DIN (colorimetric analysis)
- Hydrolyze DOP to DIP (colorimetric detector)

Note: DOC, DON, DOP - Must be corrected for pre-existing DIC,
DIN, DIP

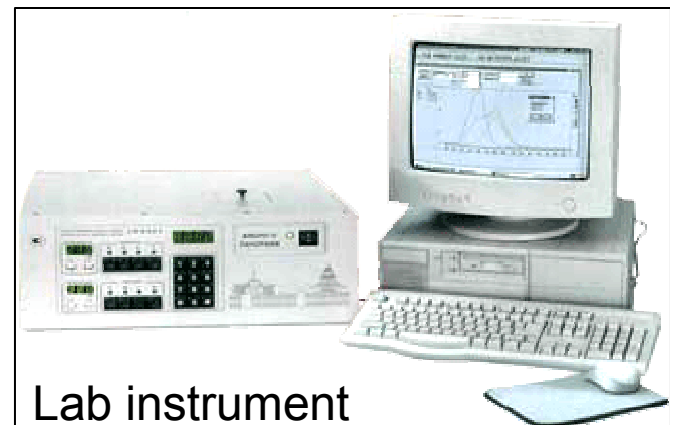
POC: Must corrected for C in carbonate minerals

2. **Fluorescence detection:** Analysis of chromophoric or colored fraction of dissolved organic matter (CDOM)



In situ sensor

VS.



Lab instrument

3. **Molecular analysis:**

Problems:

- Great number of compounds
- Very low concentrations
- Difficult matrix (seawater)

Need to worry about **separation** and **identification**:

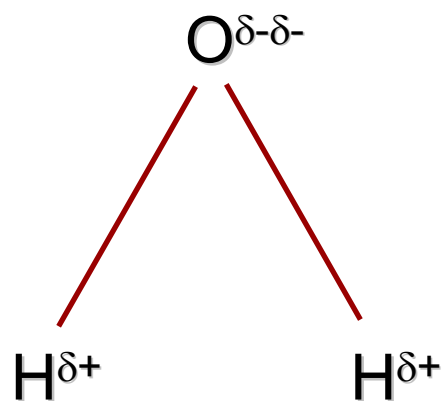
- **Extract and concentrate OM** from seawater (use liquid-liquid or solid-phase extraction)
- **Fractionate OM** into individual compound classes (use chromatography or extraction)
- **Separate individual compounds** in each class (chromatography)
- **Identify compounds:**
 - Mass spectroscopy
 - Nuclear magnetic resonance
 - Infrared spectroscopy
 - X-ray diffraction
 - Ultraviolet-visible light spectroscopy

Has been done for ~30-40% of DOM

Organic Matter Polarity

A Useful Tool For Predicting DOM Behavior

Polar - molecule has a net ionic dipole - thus, dissolves well in polar solvents such as water



Net dipole (sum of two bond dipoles)

(δ^+ and δ^- indicate partial charges)

Non-polar - molecule has no net ionic dipole - "surface active" in polar solvents (*i.e.*, wants to come out of solution)

Organic compounds display a range of polarities:

CH_4 - *methane* (non-polar)

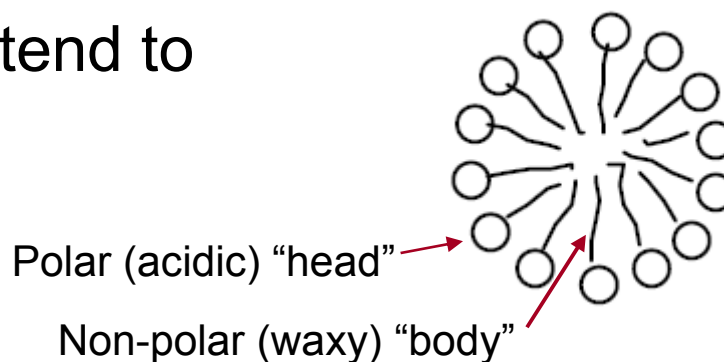
CH_3COOH - *acetate* (polar)

C_{16} - *n-hexadecane* (non-polar)

$\text{CH}_3-(\text{CH}_2)_{16}-\text{COOH}$ - *stearate*

(polar carboxyl group + non-polar wax = "fatty acid")

Fatty acids in water tend to form *micelles*:



Polarity is a Good Predictor of DOM Solubility

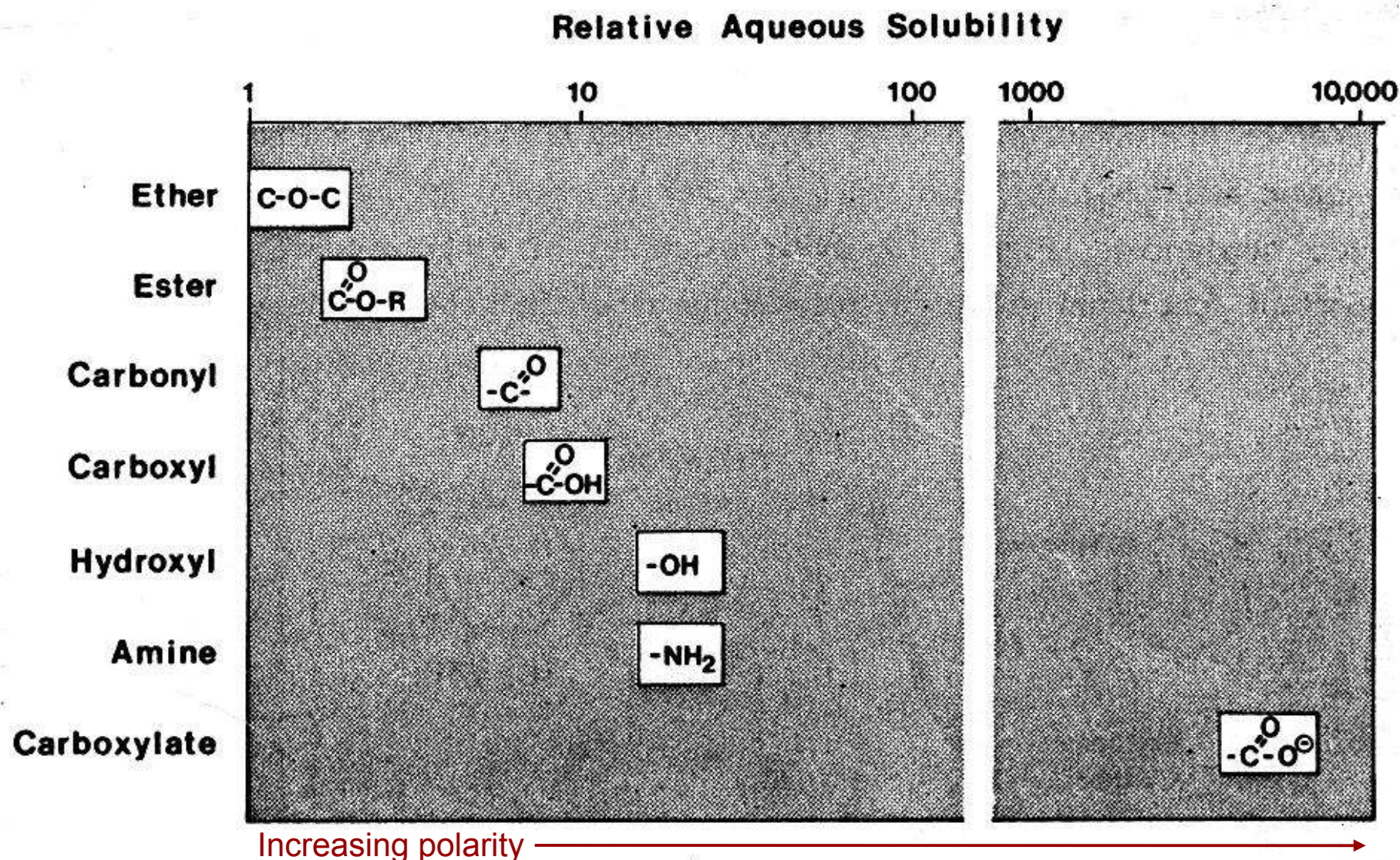


Figure 3.5 Relative aqueous solubility of different functional groups .

Thurman (1985).