Chemical Oceanography

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Organic Compounds in the Sea

- Where do they come from?
- **What are they?**
- Why are they important?
- Where do they go?

POC

- Detritus
- Fecal Mat.

DOC

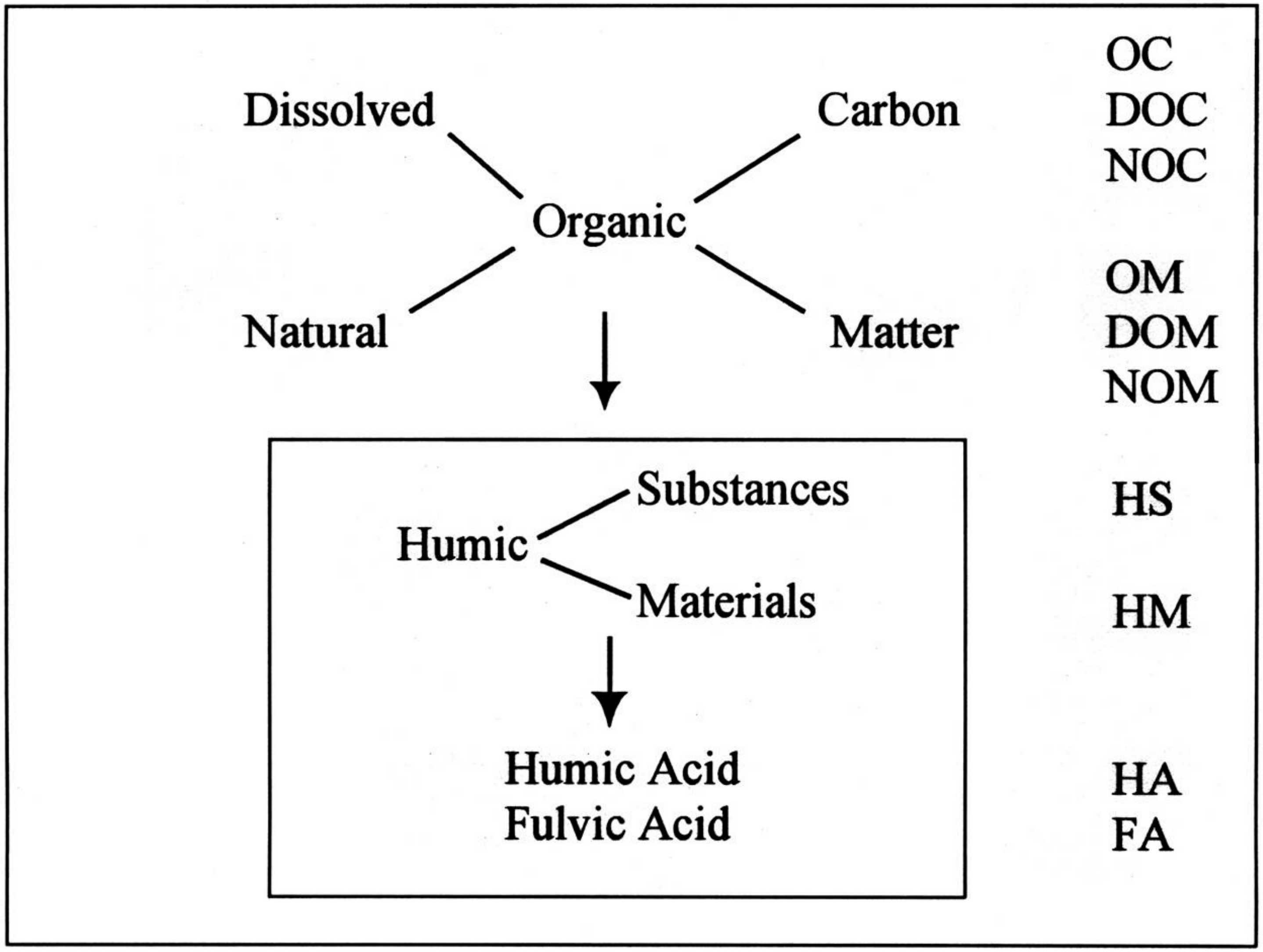
- Biological molecules (lipids, proteins, carbohydrates, etc., etc.)
- Hydrocarbons
- Humic Materials (=other stuff)

Average Concentrations of Organic Compounds in Baltic and North Sea Water

Components	Concentration (μg C liter^{-1})
Free amino acids	10
Combined amino acids	50 (to 100?)
Free sugars	20
Combined sugars	200
Fatty acids	10
Phenols	2
Sterols	0.2
Vitamins	0.006
Ketones	10
Aldehydes	5
Hydrocarbons	5
Urea	10
Uronic acids	18
Approximate identified total	340 μg C liter^{-1}
Approximate total	4000 μg C liter^{-1}

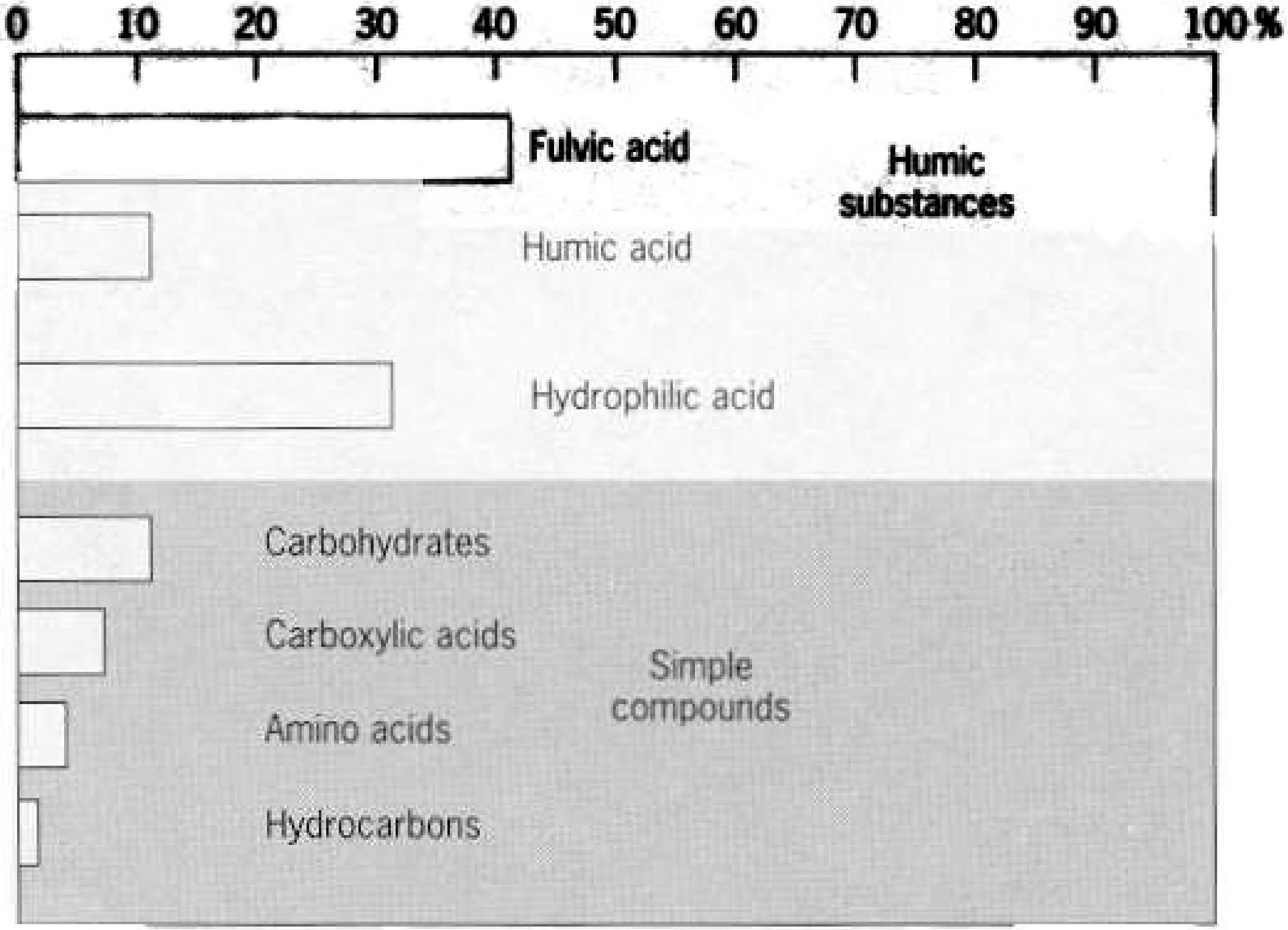
What is this stuff?

Morel, 1983



Dissolved
Carbon
Organic
Natural
Matter
OC
DOC
NOC
OM
DOM
NOM
Humic
Substances
Materials
HS
HM
Humic Acid
Fulvic Acid
HA
FA

Ryan (2000)

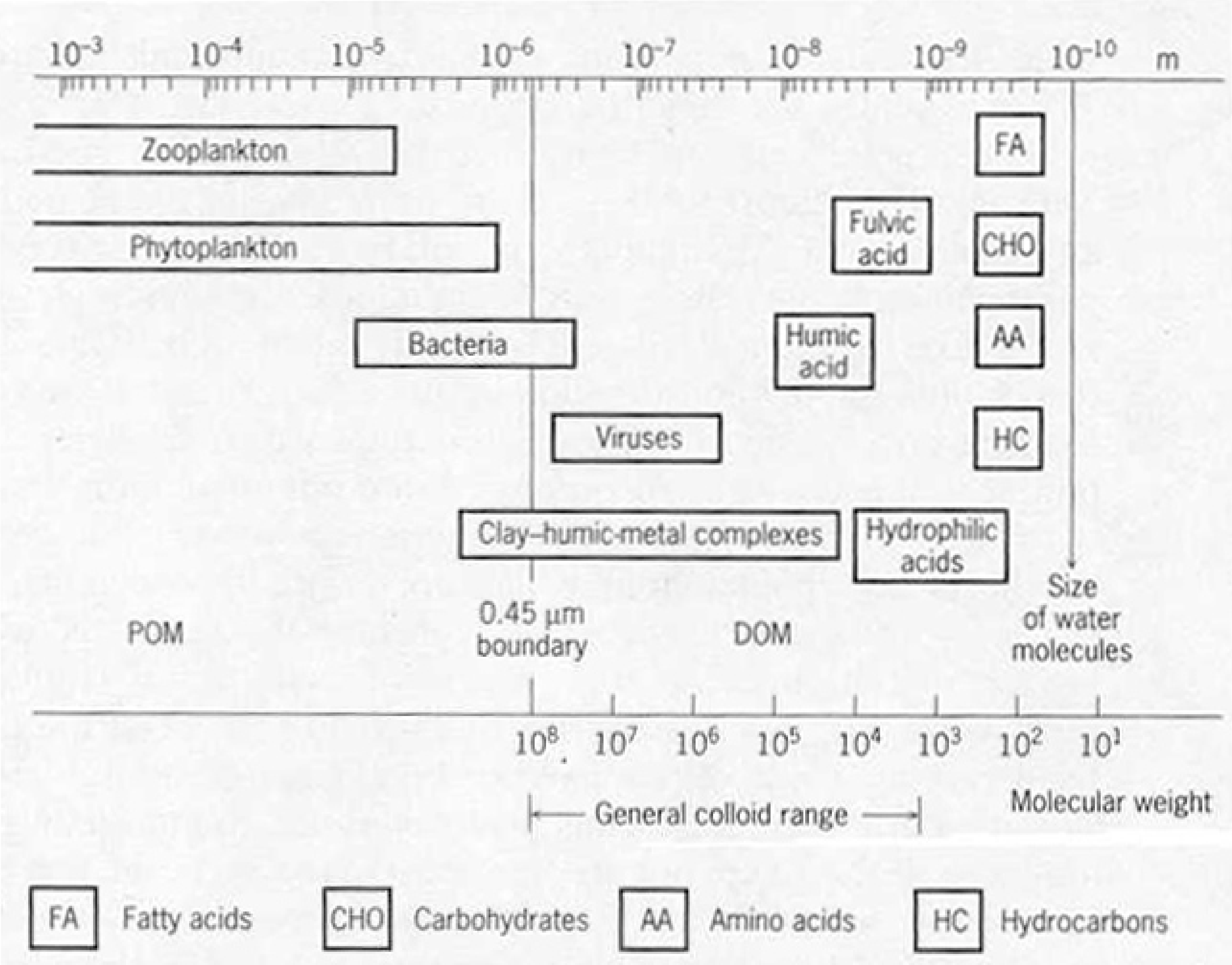


Libes, 1992

FIGURE 23.13. **Composition of dissolved organic carbon in average river water with a DOC concentration of 5 mg/L. *Source*: From *Organic Geochemistry of Natural Waters*, E. M. Thurman, copyright © 1985 by Kluwer Academic Publishers, Dordrecht, The Netherlands. Reprinted by permission.**

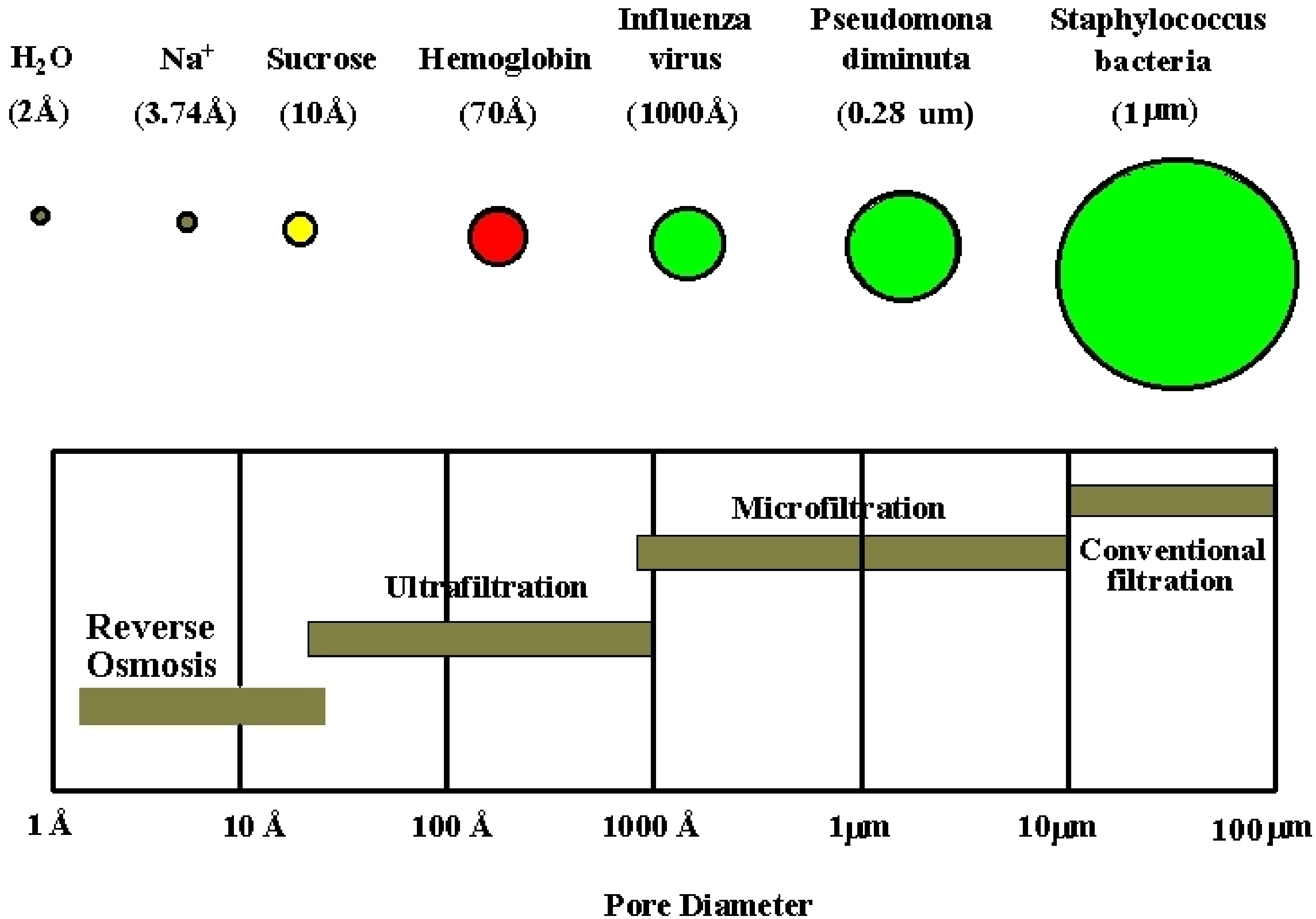
Humic Materials or Humic Substances

- Complex organic molecules of natural origin
- Much is known about properties/importance
- Some is known about structural components
- Little is known about exact chemical nature or exact structure – because:
  - Complexity
  - Heterogeneity
  - Concentrations
  - Deficiencies in analytical techniques
  - Interfering species

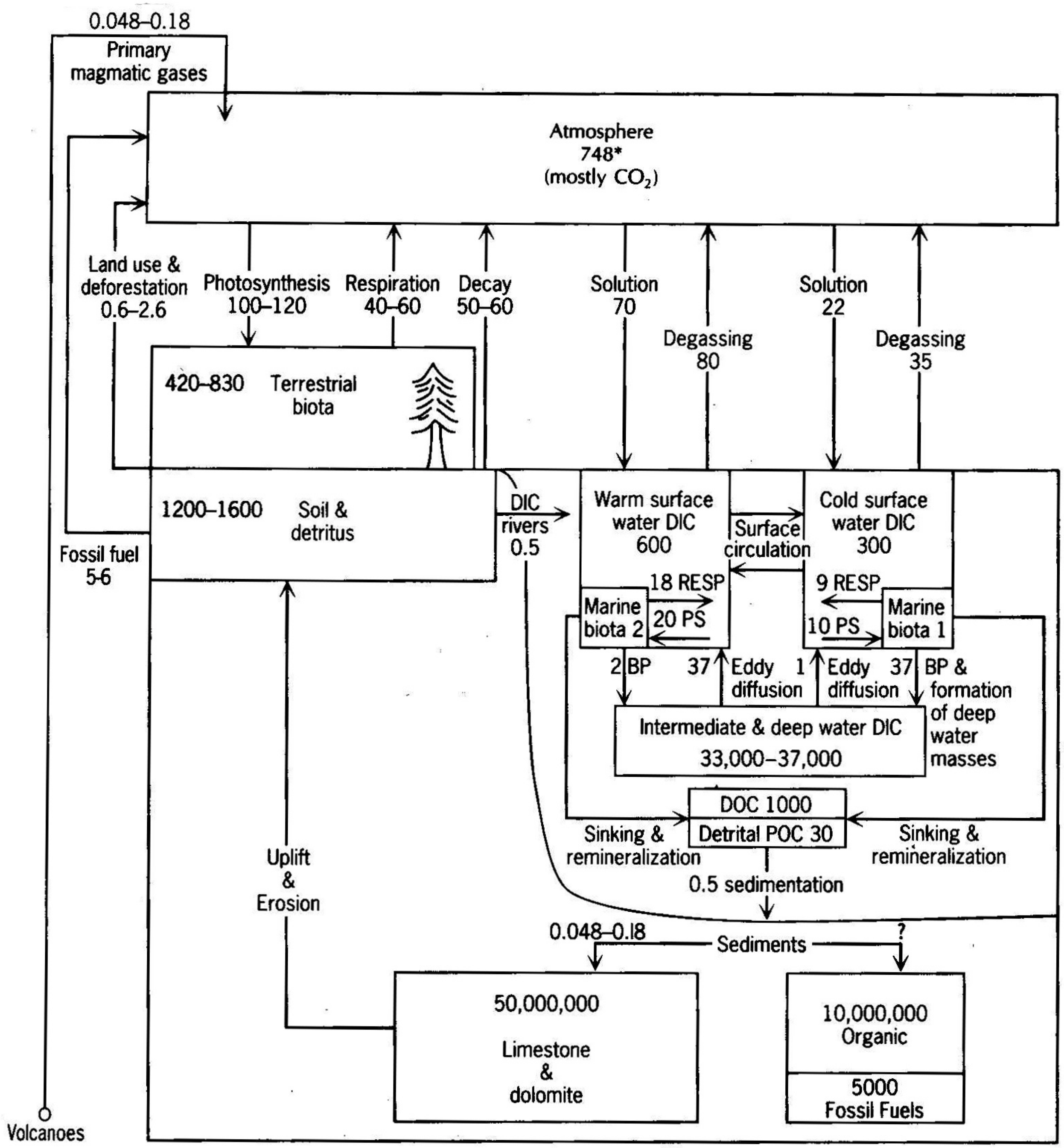

10^{-3} 10^{-4} 10^{-5} 10^{-6} 10^{-7} 10^{-8} 10^{-9} 10^{-10} m
Zooplankton
Phytoplankton
Bacteria
Viruses
Clay–humic-metal complexes
Fulvic acid
Humic acid
Hydrophilic acids
FA
CHO
AA
HC
Size of water molecules
POM
0.45 μm boundary
DOM
10^8 10^7 10^6 10^5 10^4 10^3 10^2 10^1
General colloid range
Molecular weight
FA Fatty acids
CHO Carbohydrates
AA Amino acids
HC Hydrocarbons

Libes, 1992

Pore Size of Filtration Processes



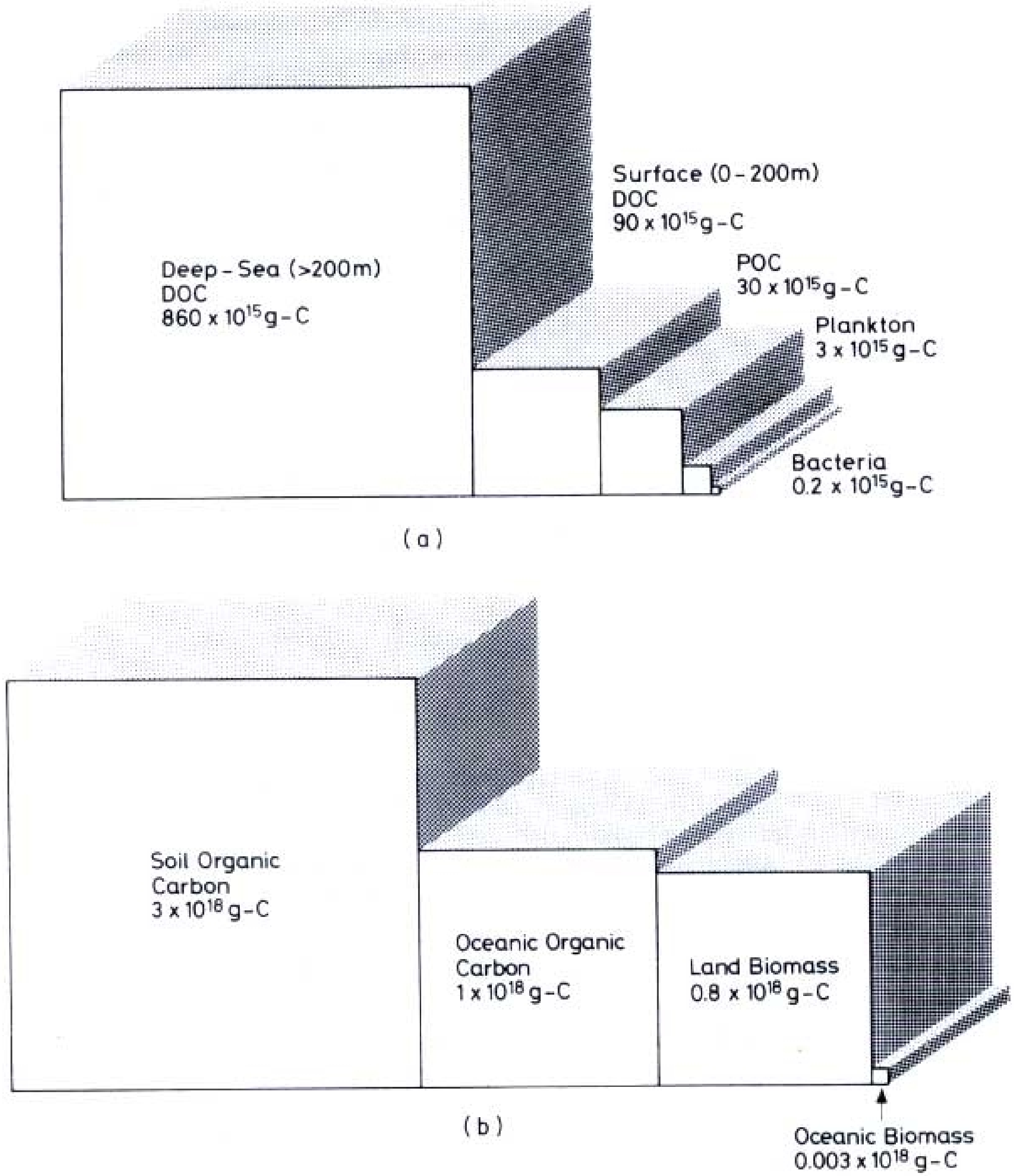
Millero, 1996



Carbon Cycle
Libes, 1992

Inventories in
10^{15} g C = BMT

Fluxes (arrows)
10^{15} g C/yr



Distribution of Organic Carbon

(a) Major compartments in the global ocean

(b) Major compartments for the planet

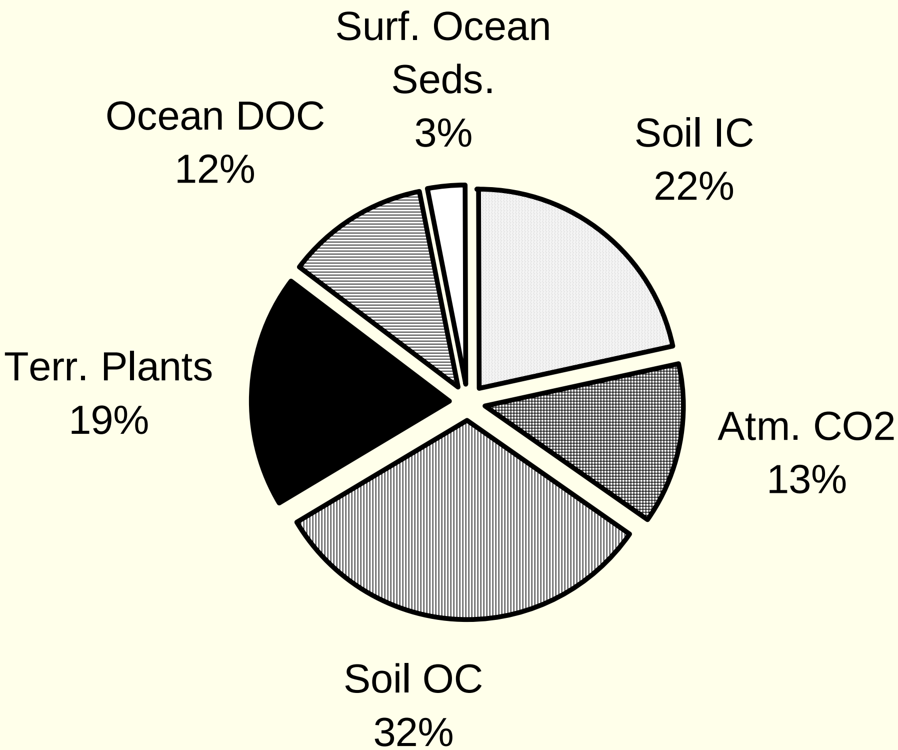
Cauwet, 1978

Major reservoirs of organic and inorganic carbon

Reservoir type	Amount (10^{18} g C)
Sedimentary Rocks	
• Inorganic (Carbonates)	60,000
• Organic (e.g. kerogen, coal)	15,000
Active (surficial) pools	
Inorganic	
• Marine DIC	38
• Soil Carbonate	1.1
• Atmospheric CO_2	0.66
Organic	
• Soil humus *	1.6
• Land plant tissues	0.95
• Seawater DOC	0.60
• Surface marine sediments	0.15

After Hedges, 1992; * pre-anthropogenic values.

Active Carbon Reservoirs (excluding Ocean DIC)



Organic Compounds in the Sea

- Where do they come from?
- What are they?

Bio & Geo
- Hydrocarbons

Bio
- Carbohydrates (polysaccharides), sugars
- Lipids, fats, waxes, oils, fatty acids
- Pigments
- Nucleic acids, RNA, DNA
- Amino acids, polypeptides, proteins, enzymes
- Low molecular weight carboxylic acids

?
- Humic Substances

Organic Carbon Inputs to SW

- Allochthonous = formed externally (*ex situ*)
- Autochthonous = formed internally (*in situ*)

Most Marine Humic Material is formed *in situ* through a combination of biotic & abiotic processes

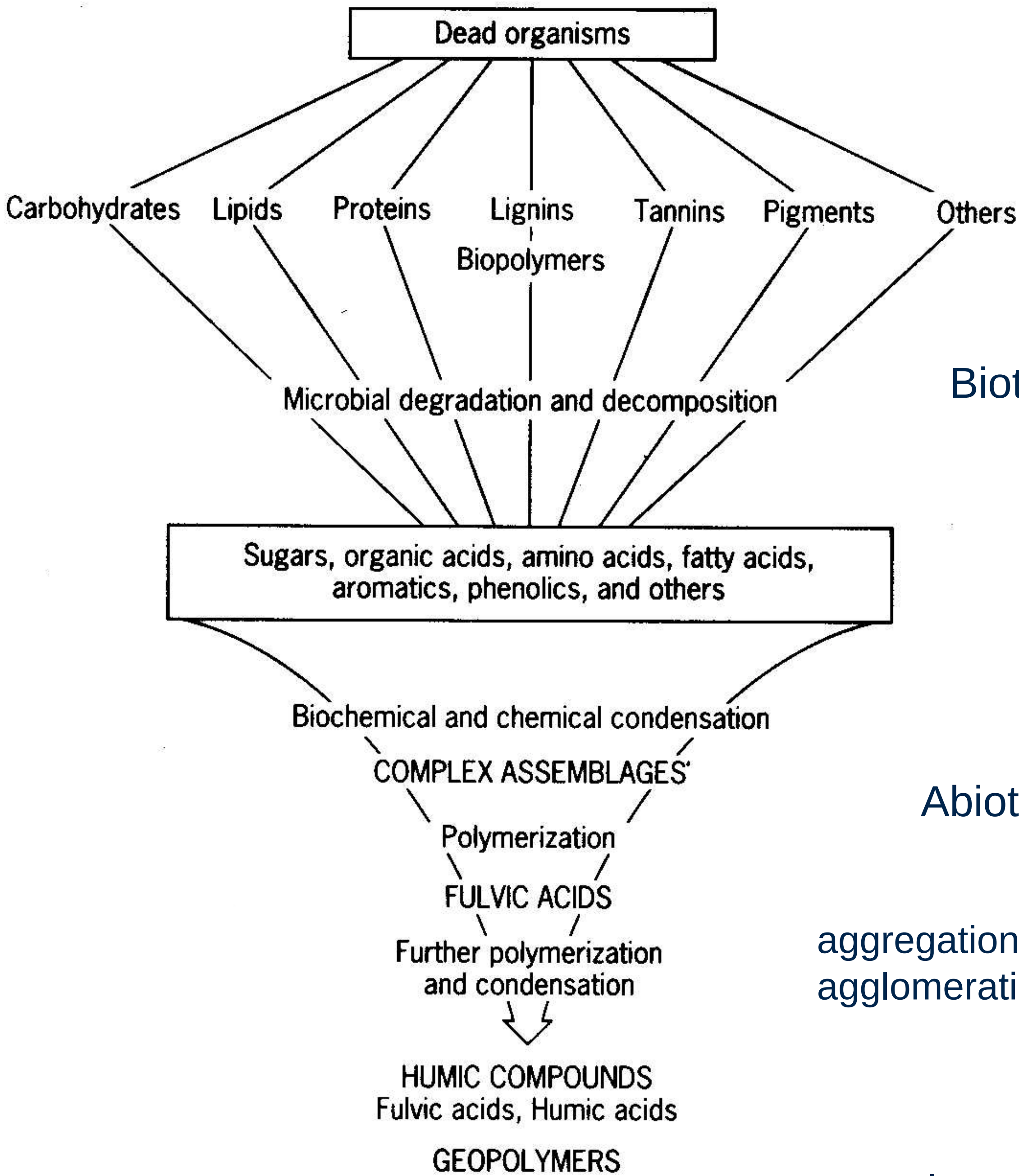
Some Humic Material (i.e., coastal) is introduced from terrestrial sources (formed on land)

Transformation of DOC

- Biological molecules are **labile** = readily broken down or degraded → fast
- By-products of this breakdown (substances not completely remineralized) can react with other organic compounds in a process called **Humification** or **Early Diagenesis**
- This results in fairly non-labile **Humic Materials**
- Humics may degrade slowly or be removed to the sediments (**refractory or non-labile**)

Transformation of DOC

- These processes occur in water column, in sediments, and in soils
- Humification is the first step, fast, aerobic
- Fossilization or carbonification occur more slowly on geologic time scales, anaerobicly, after burial in sediments
- Diagenesis, Catagenesis, Metagenesis



Biotic

Abiotic

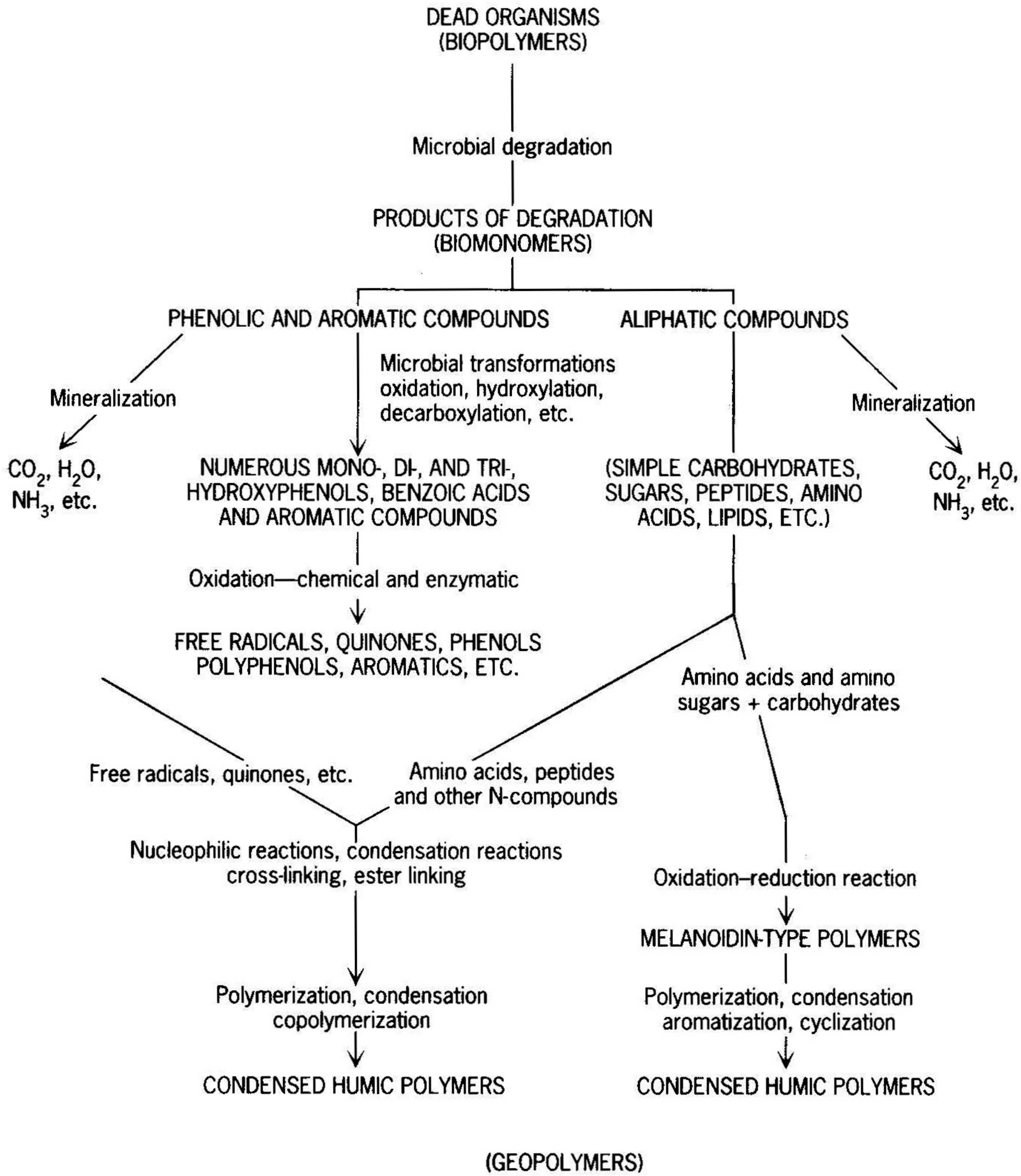
aggregation
agglomeration

Macromoloecules

Hydrocarbons, Fats, Waxes
Oils, Sterols, Vitamins, etc.

Humification of
Organic Matter
(possible scheme)

Libes, 1992



Humification of Organic Matter (another scheme)

Libes, 1992

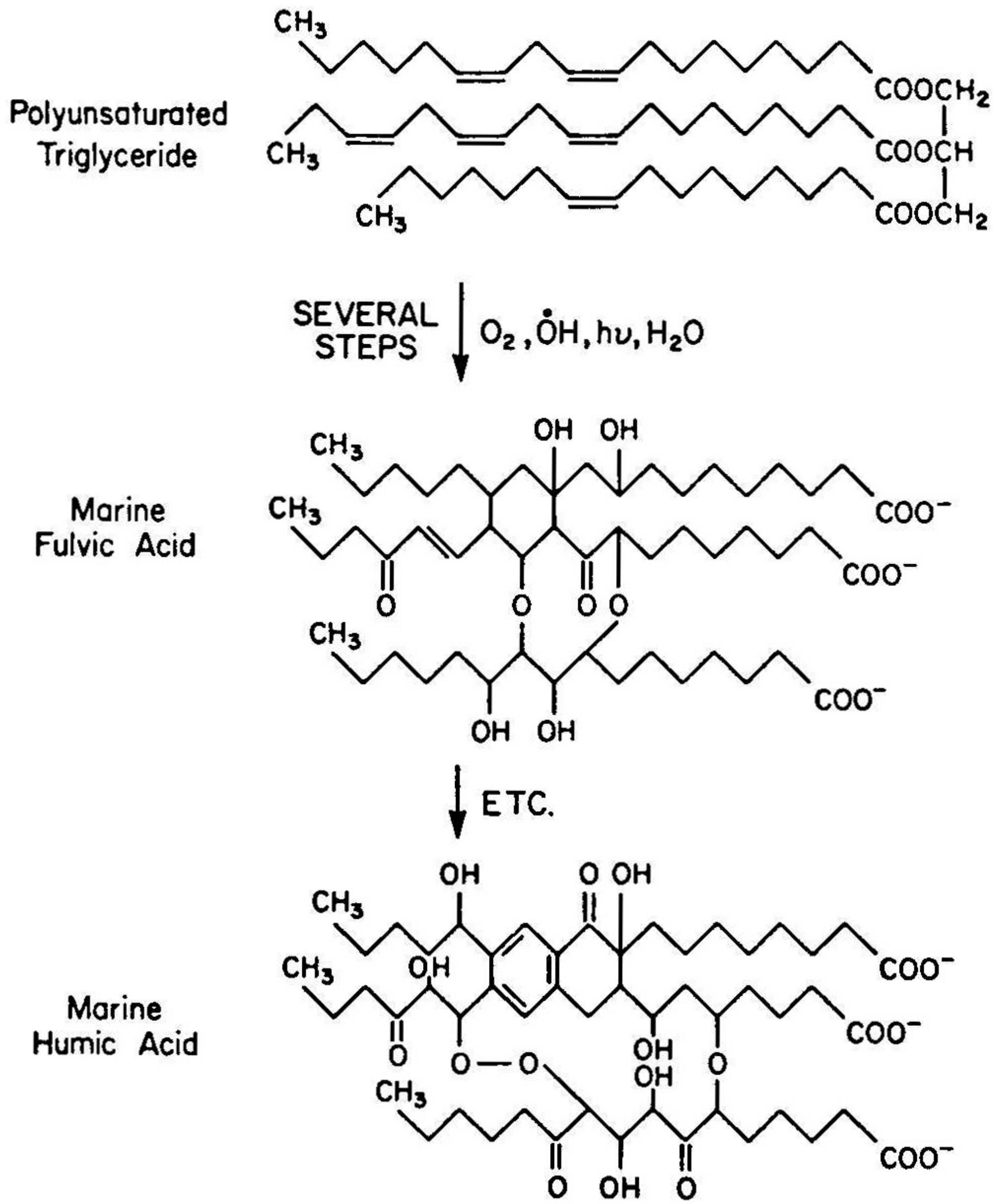
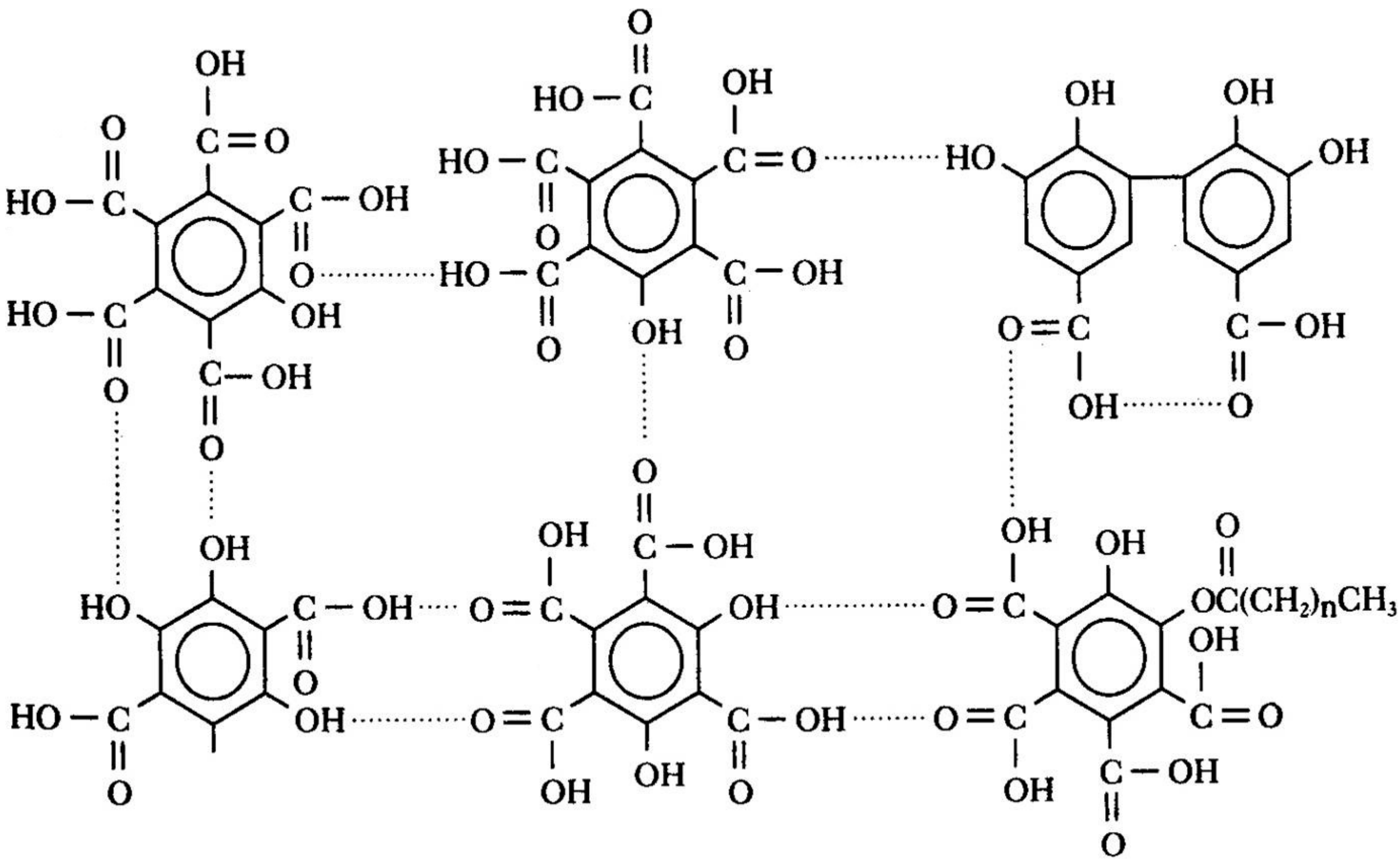
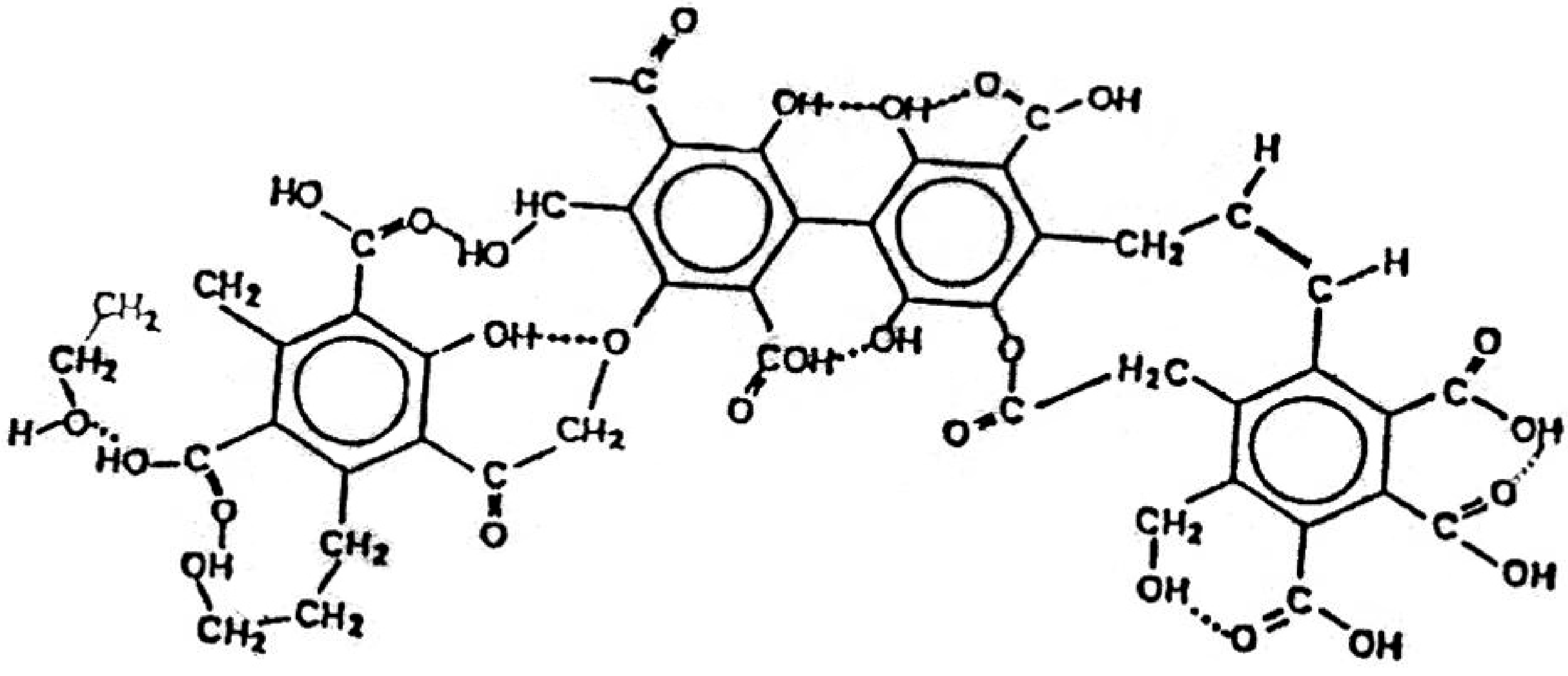


Figure 6.13 A possible pathway for the formation of marine humic acids from a triglyceride. From Harvey et al., 1983.

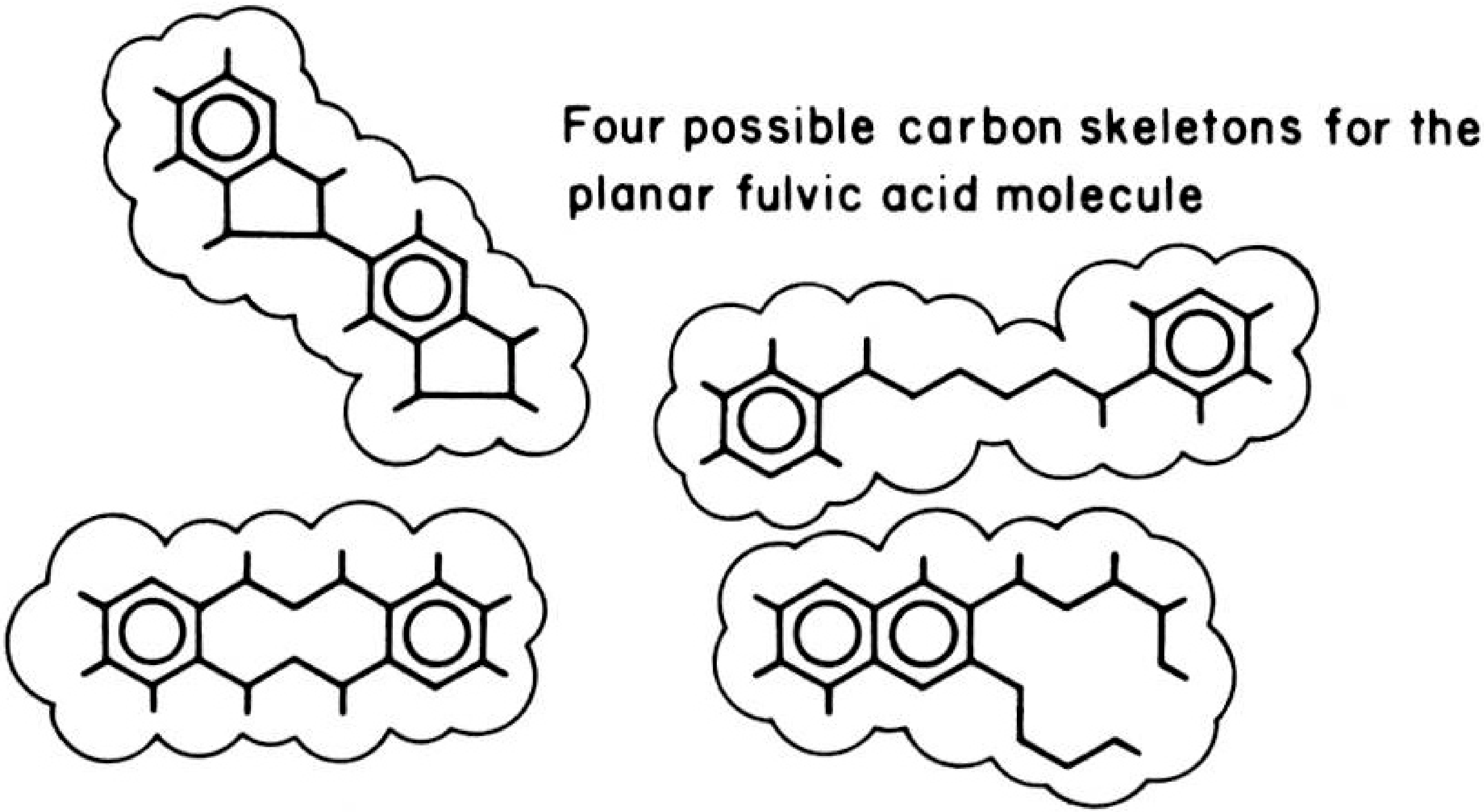
Morel & Hering, 1993



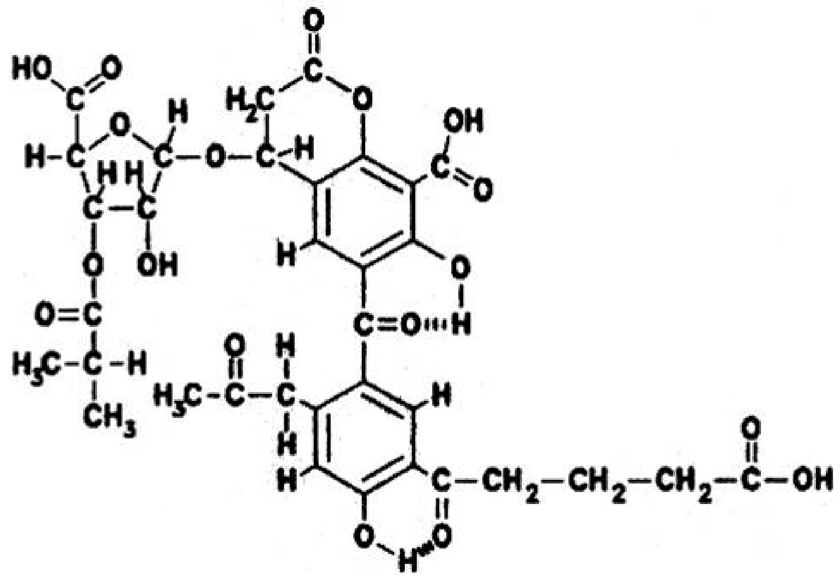
Humic Structure Proposed by Schnitzer (Rashid 1985)

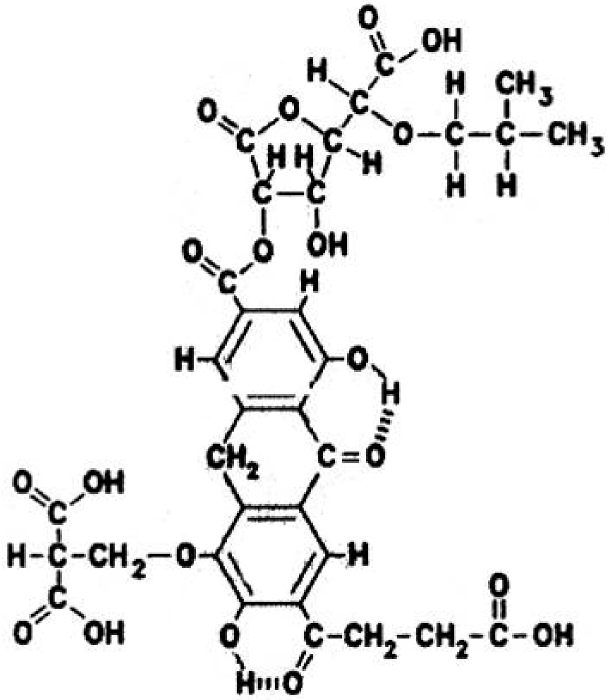


Structure Attributed to Gamble et al. (1985)

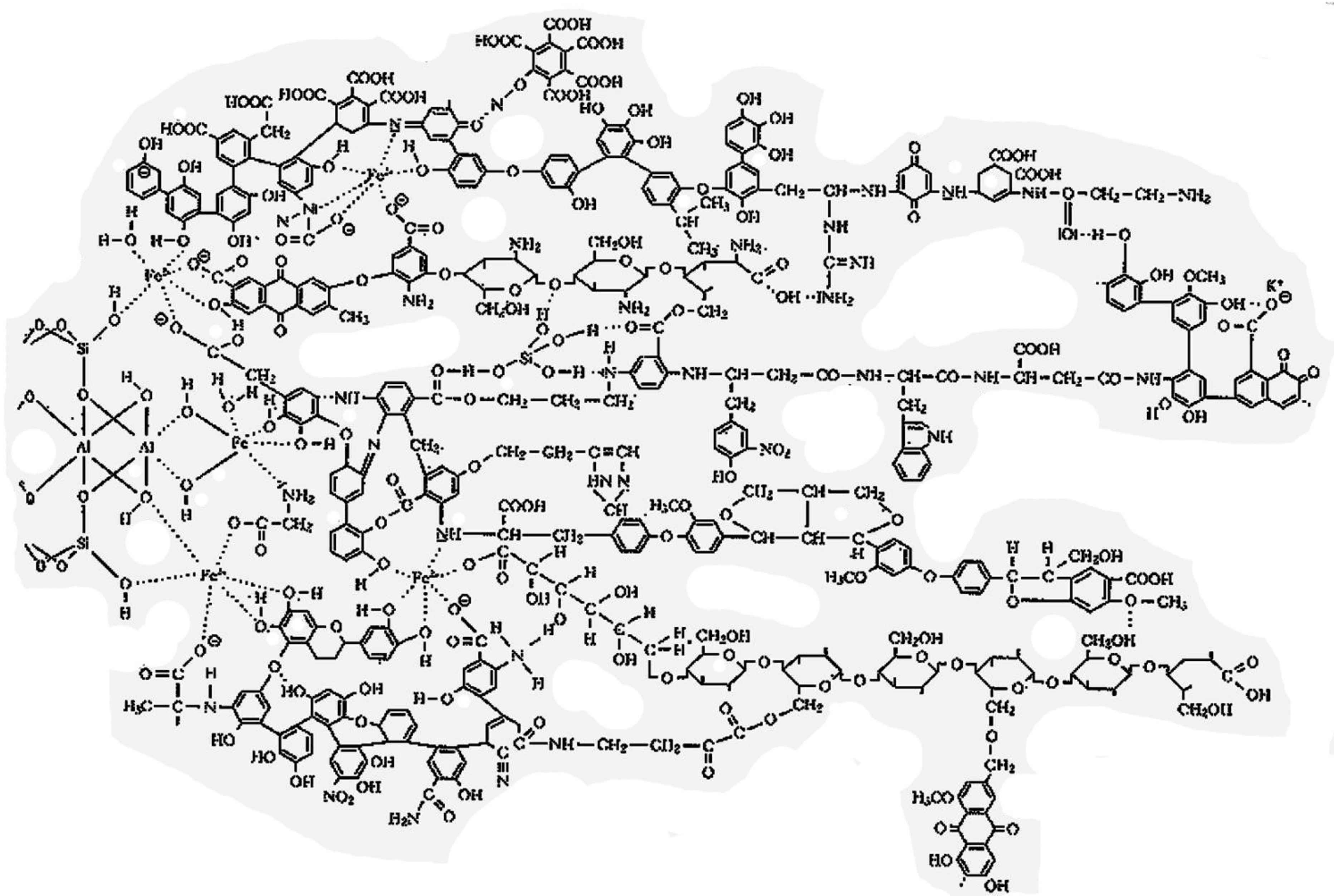


Morel & Hering (1993) Based on Aiken et al. (1985)

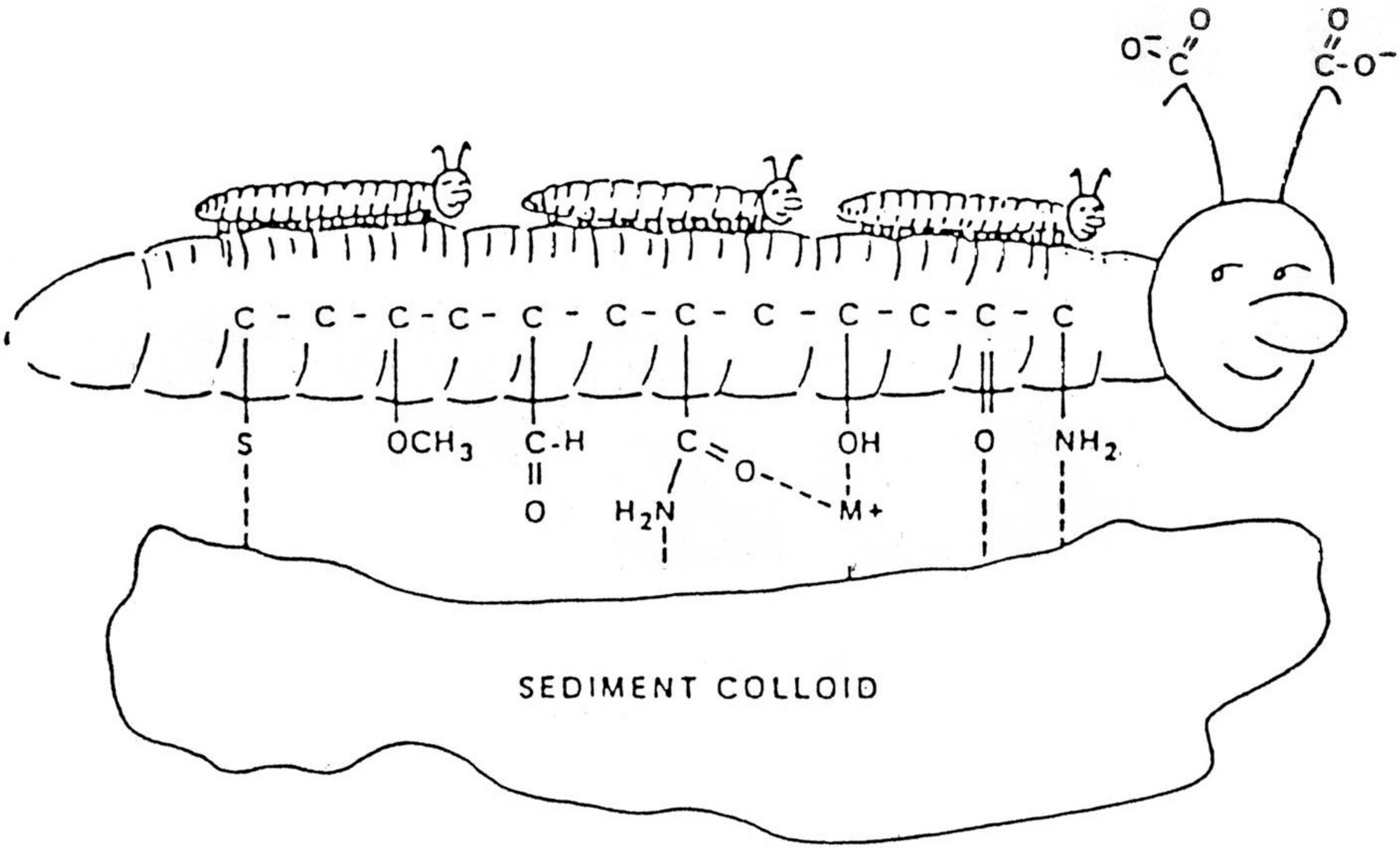




Possible Structural Units Set Forth by Averett, Leenheer, McKnight & Thorn (1989) From Morel & Hering, 1993

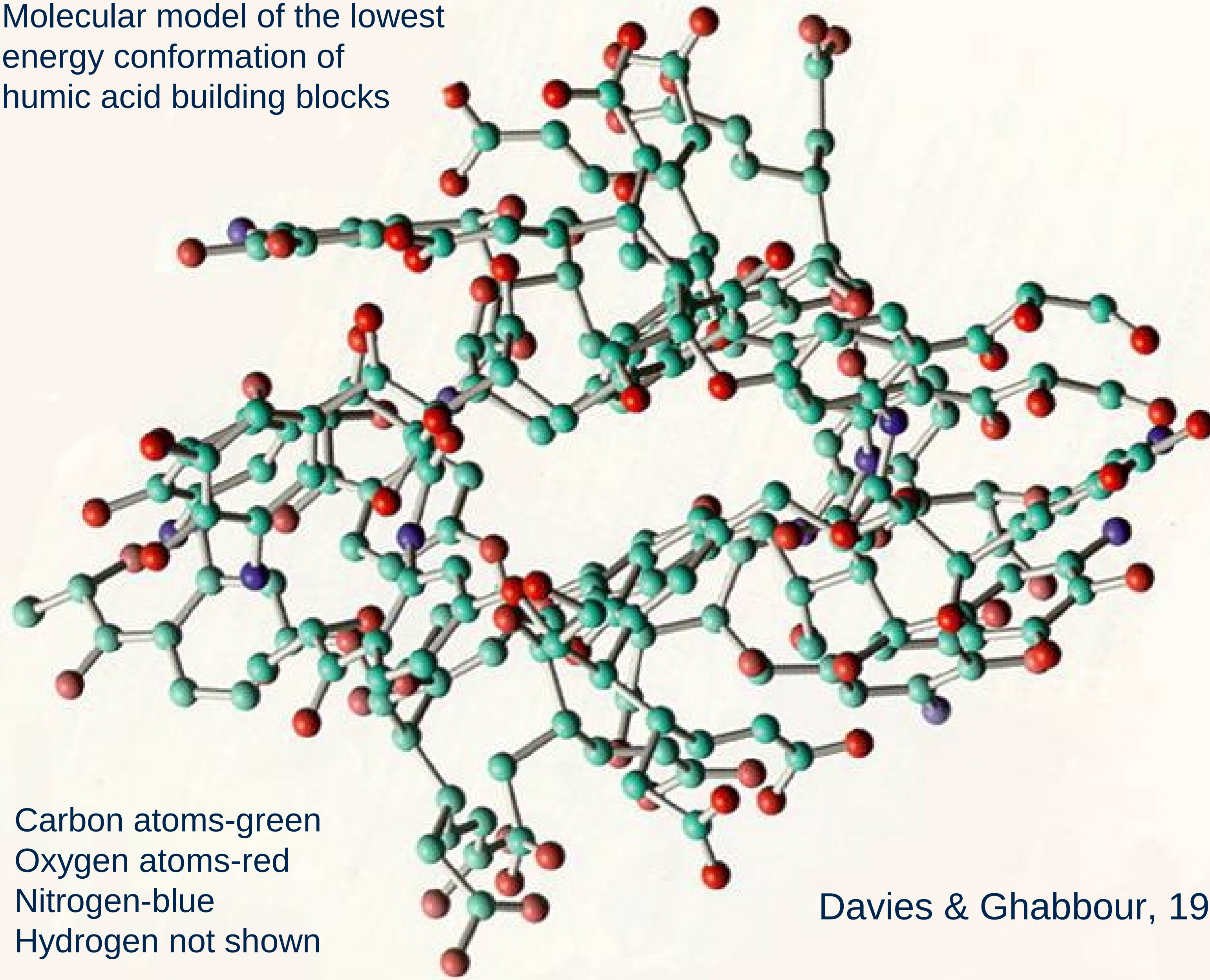


Kleinhempel reprinted from Albrecht Thaer Archiv (1970)



Organic Solute Macromolecule (ORSMAC) Leenheer (1985)

Molecular model of the lowest energy conformation of humic acid building blocks



Carbon atoms-green
Oxygen atoms-red
Nitrogen-blue
Hydrogen not shown

Davies & Ghabbour, 1999

Importance of Humic Materials

Global Carbon Reservoir
Take Part in Interfacial Phenomena
Undergo Coagulation and Aggregation
Involved in Photochemical Reactions
Contain Radicals
Known Reducing Agents
Methylate Metals
Form Chlorinated Species, THMs DBPs
Detoxify Metals
Limit Bioavailability of Metals
Alter Solubility
Influence
Bind Metals & Organic Pollutants
Terminal Electron Transport Acceptor for Bacteria

Estuarine, Coastal and Shelf Science (1983) **16,** 431–440

The Removal of Dissolved Humic Acid During Estuarine Mixing

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College of Marine Studies, University of Delaware, Lewes, Delaware, USA

Received 2 February 1982 and in revised form 28 May 1982

Keywords: humic acids; dissolved organic compounds; estuaries

A simple method for the determination of dissolved humic acid based on carbon analysis is presented. This method was used to measure the distribution of dissolved humic acids in seven coastal plain estuaries located in the middle-Atlantic United States. Results indicate that 100% of the dissolved humic acid was removed during estuarine mixing, although concurrent measurements of dissolved organic carbon showed either production or conservative behavior in regions of the estuary where humic acid removal was observed. It is apparent from these observations that removal of dissolved humic acid is a minor part of the estuarine transport of dissolved organic carbon.

Laboratory experiments carried out by mixing river water with sea water demonstrated that salt-induced removal of dissolved humic acid was insignificant in two of three estuaries studied. These results suggest *in situ* removal of dissolved humic acid may not be universally caused by increasing estuarine salinity.

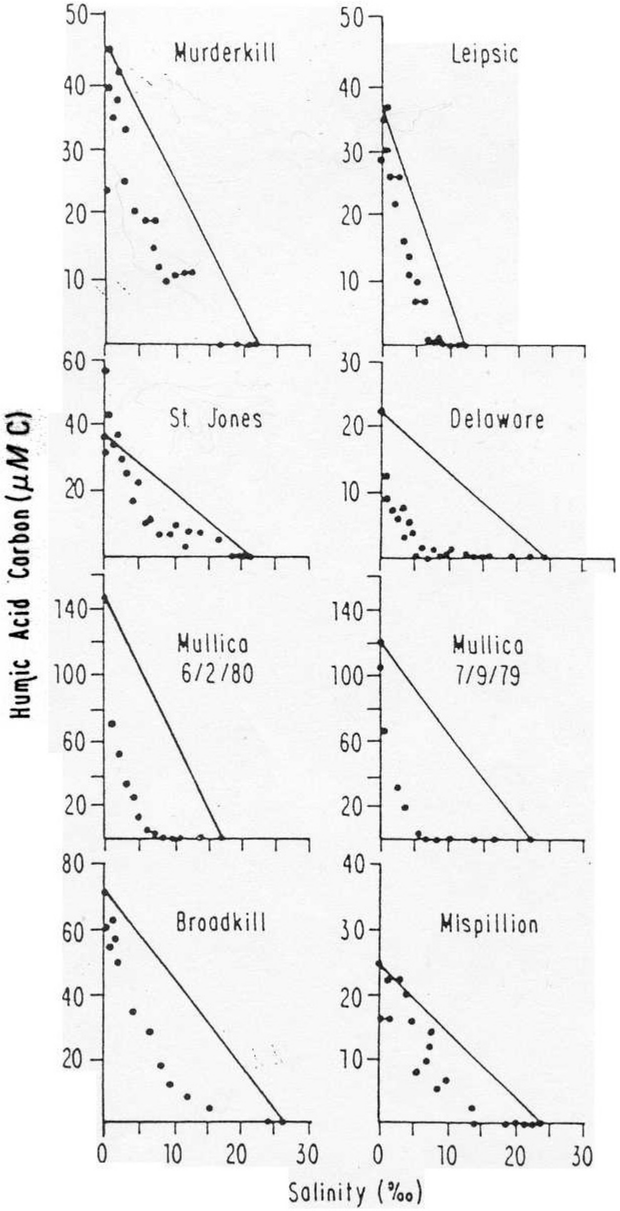


Figure 3. Humic acid carbon as a function of salinity. The standard error of the mean is 5%.

Fox, 1983

Photochemistry

CDOM = Chomophoric (Colored) Organic Matter

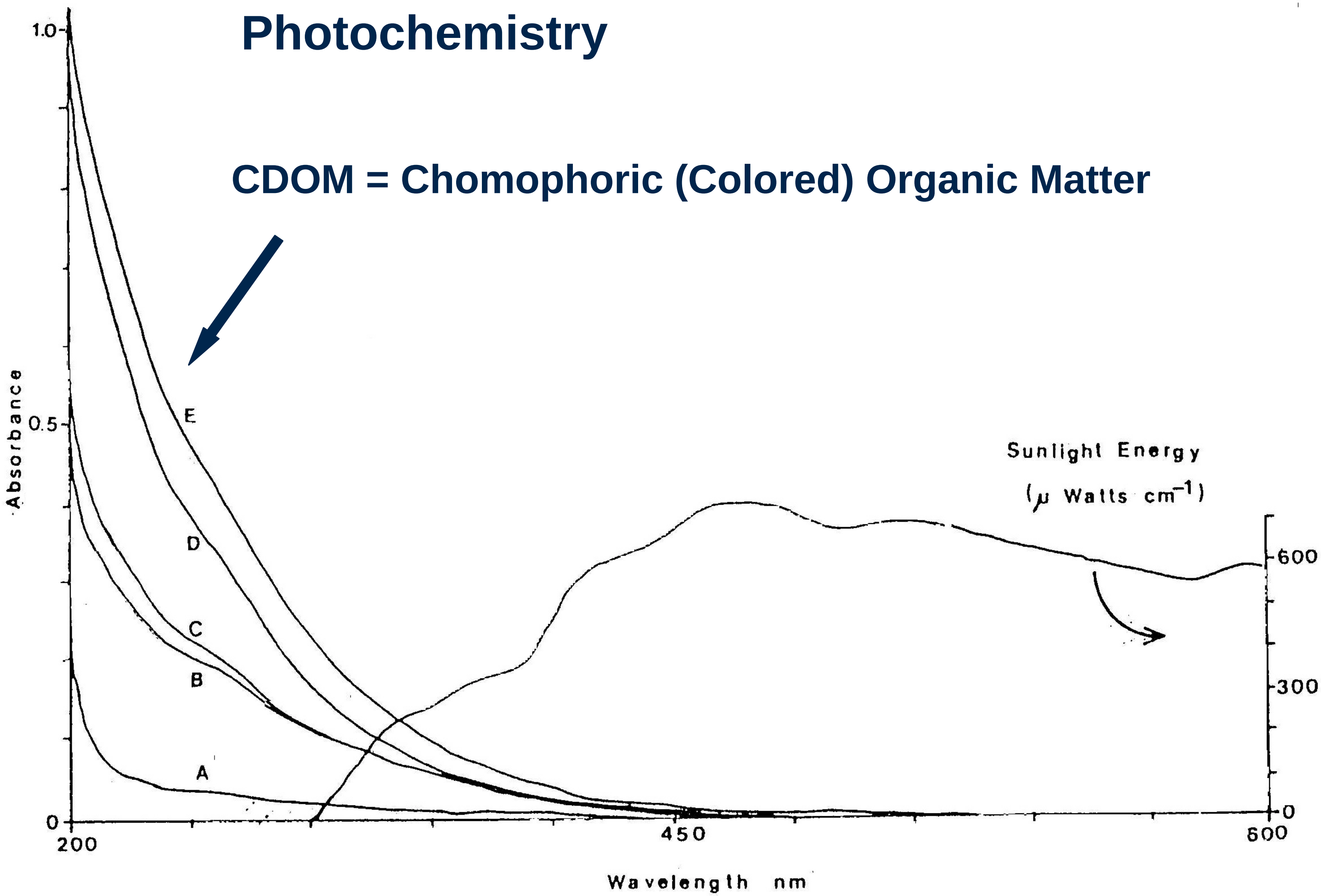
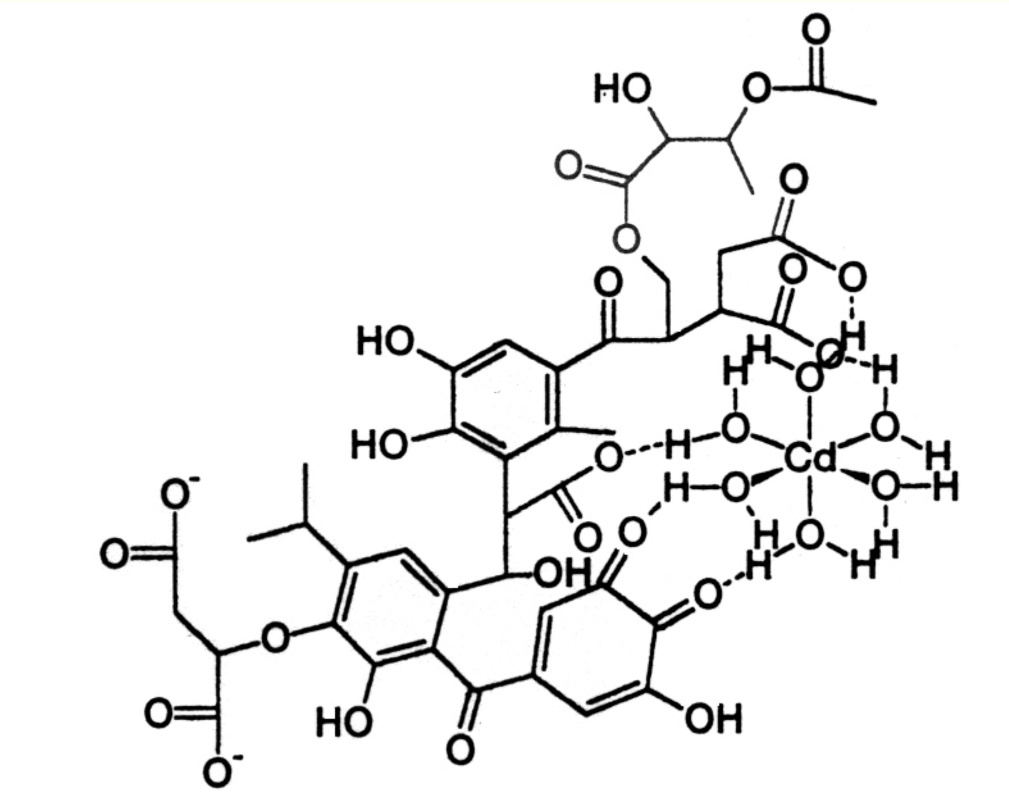
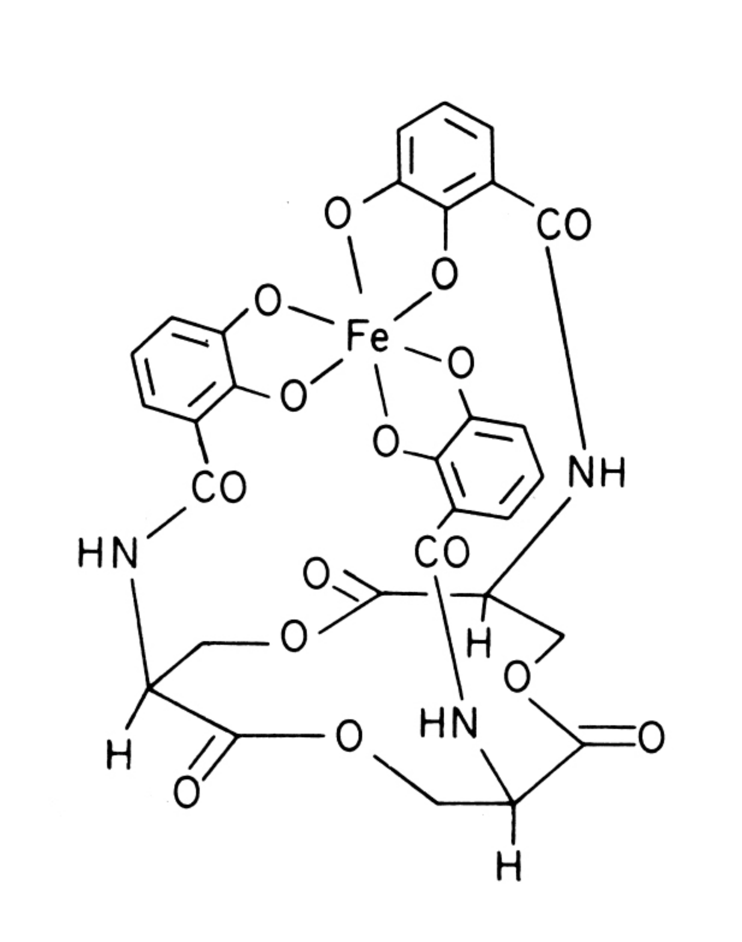


Figure 1. Absorption spectra (pathlength of 1 cm) of several waters and a generalized surface solar energy distribution (adapted from ref. 8). (DOC of waters: A = 3.0, B = 7.8, C = 13.4, D = 13.4, E = 15.4 mg L^{-1}).

Metal Complexation by Humics



Leenheer et al. (1998)



Morel (1983)

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