Chemical Oceanography

Organic Materials II

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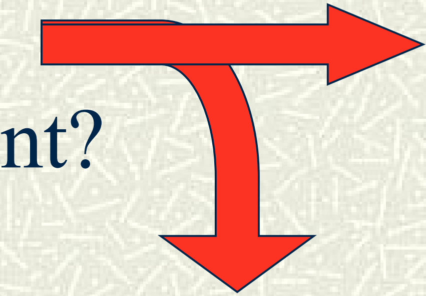
Organic Compounds in Marine Environment

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

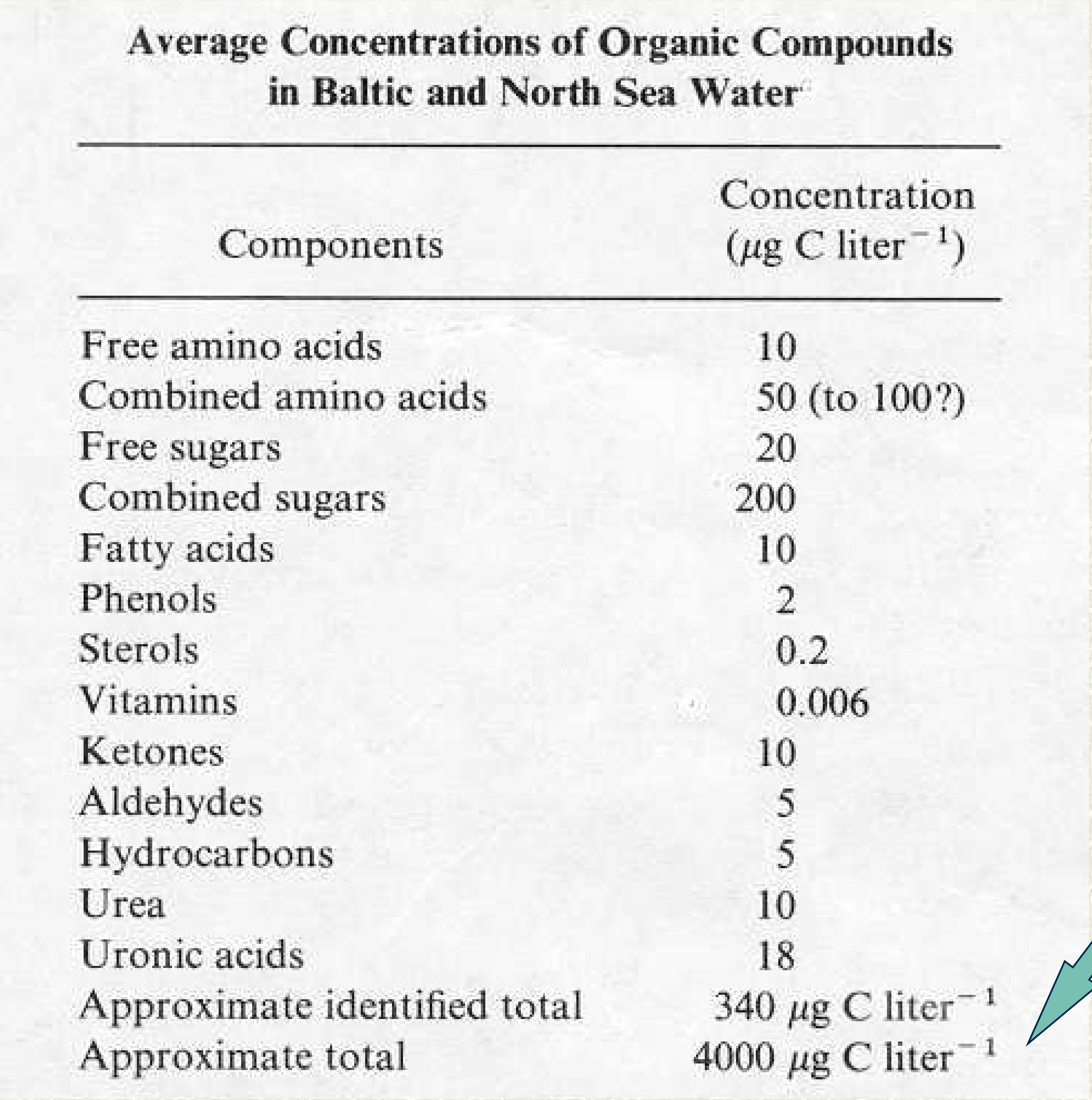


POC

- 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

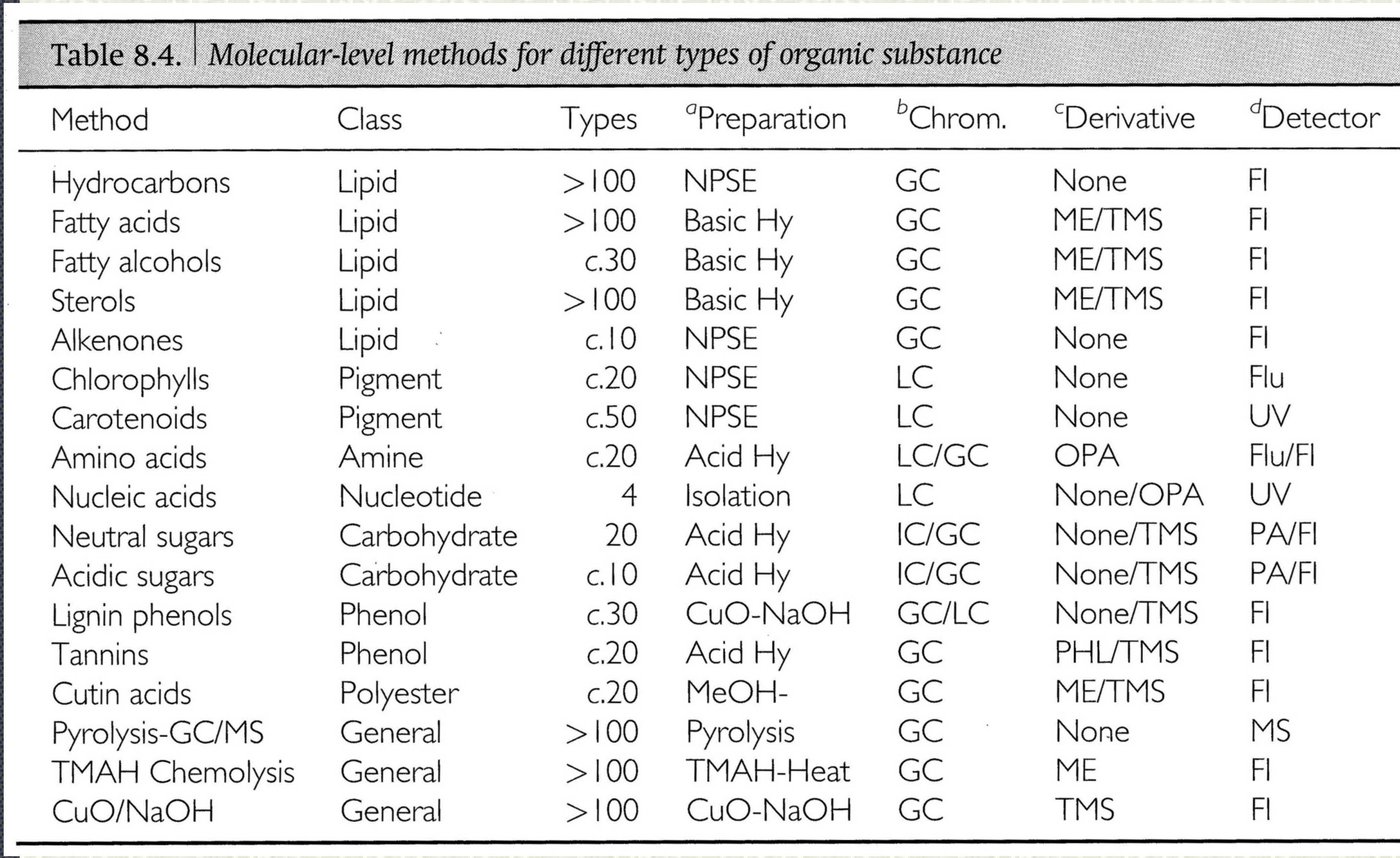


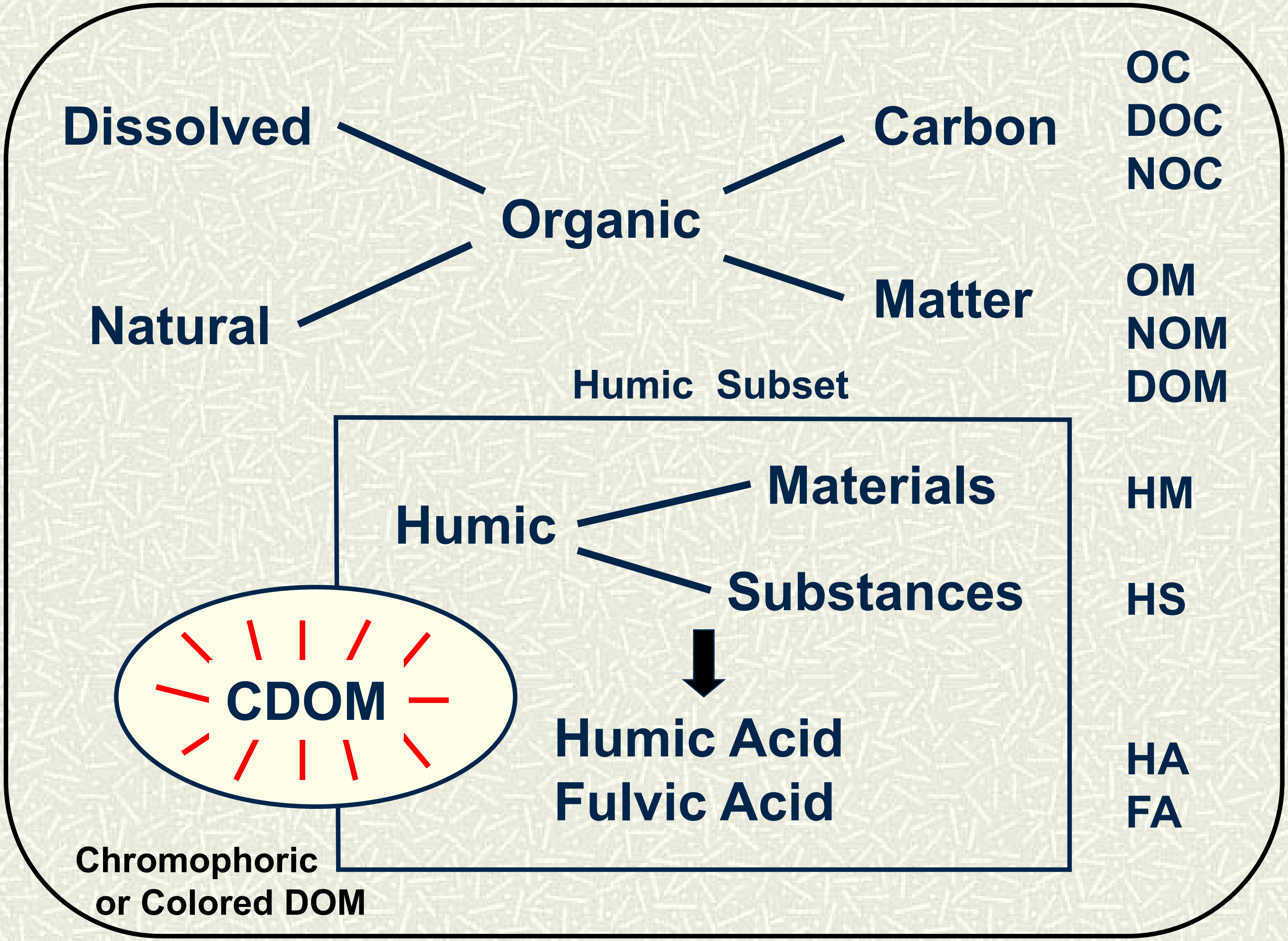
Table 8.4. *Molecular-level methods for different types of organic substance*

Method	Class	Types	[a]Preparation	[b]Chrom.	[c]Derivative	[d]Detector
Hydrocarbons	Lipid	>100	NPSE	GC	None	FI
Fatty acids	Lipid	>100	Basic Hy	GC	ME/TMS	FI
Fatty alcohols	Lipid	c.30	Basic Hy	GC	ME/TMS	FI
Sterols	Lipid	>100	Basic Hy	GC	ME/TMS	FI
Alkenones	Lipid	c.10	NPSE	GC	None	FI
Chlorophylls	Pigment	c.20	NPSE	LC	None	Flu
Carotenoids	Pigment	c.50	NPSE	LC	None	UV
Amino acids	Amine	c.20	Acid Hy	LC/GC	OPA	Flu/FI
Nucleic acids	Nucleotide	4	Isolation	LC	None/OPA	UV
Neutral sugars	Carbohydrate	20	Acid Hy	IC/GC	None/TMS	PA/FI
Acidic sugars	Carbohydrate	c.10	Acid Hy	IC/GC	None/TMS	PA/FI
Lignin phenols	Phenol	c.30	CuO-NaOH	GC/LC	None/TMS	FI
Tannins	Phenol	c.20	Acid Hy	GC	PHL/TMS	FI
Cutin acids	Polyester	c.20	MeOH-	GC	ME/TMS	FI
Pyrolysis-GC/MS	General	>100	Pyrolysis	GC	None	MS
TMAH Chemolysis	General	>100	TMAH-Heat	GC	ME	FI
CuO/NaOH	General	>100	CuO-NaOH	GC	TMS	FI

Emerson & Hedges 2010

Flame Ionization (FI), Fluorescence (Flu), Pulsed Amperometric (PA)
Mass Spectrometry (MS), UV absorption

All Dissolved Organic Compounds



Dissolved

Natural

Organic

Carbon

Matter

OC
DOC
NOC

OM
NOM
DOM

Humic Subset

Humic

Materials

Substances

Humic Acid
Fulvic Acid

HM

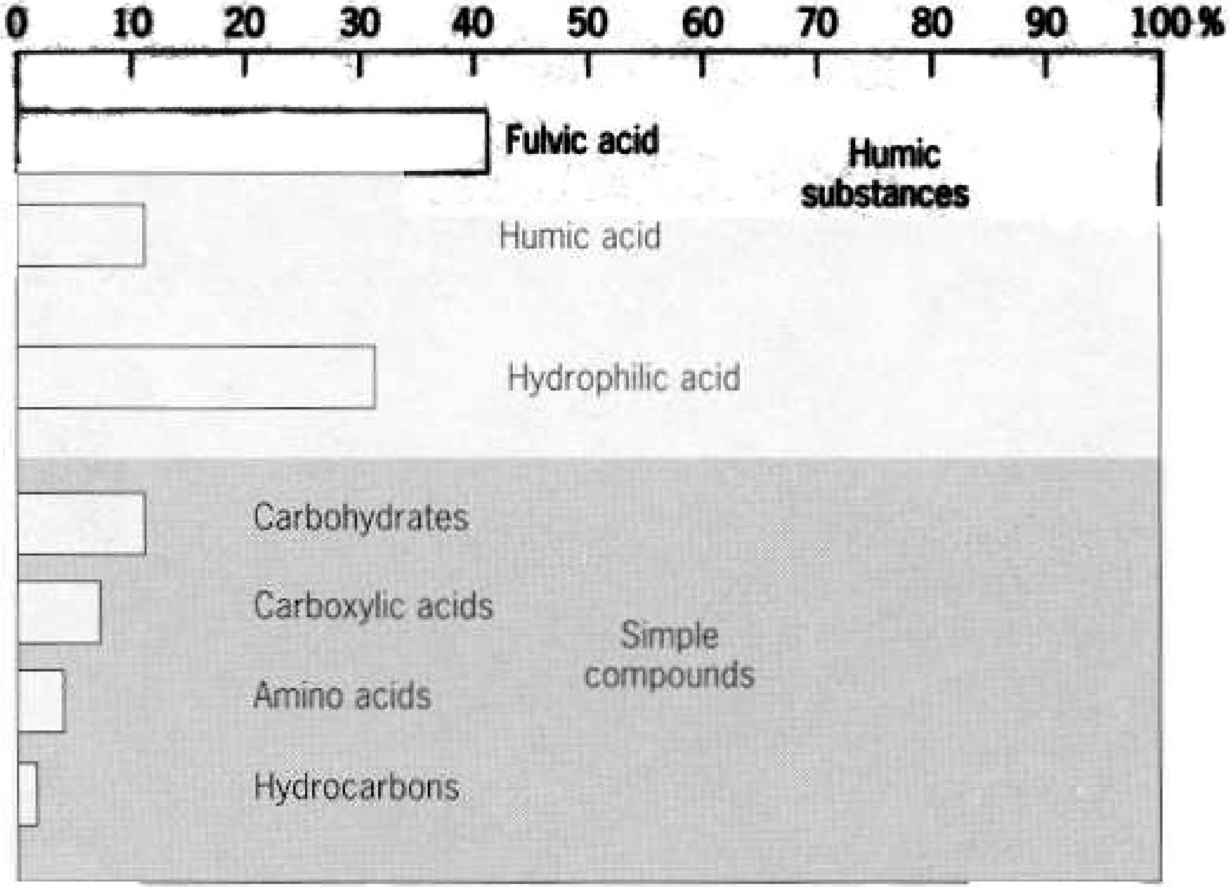
HS

HA
FA

CDOM

Chromophoric
or Colored DOM

Ryan &
Zhu 2013



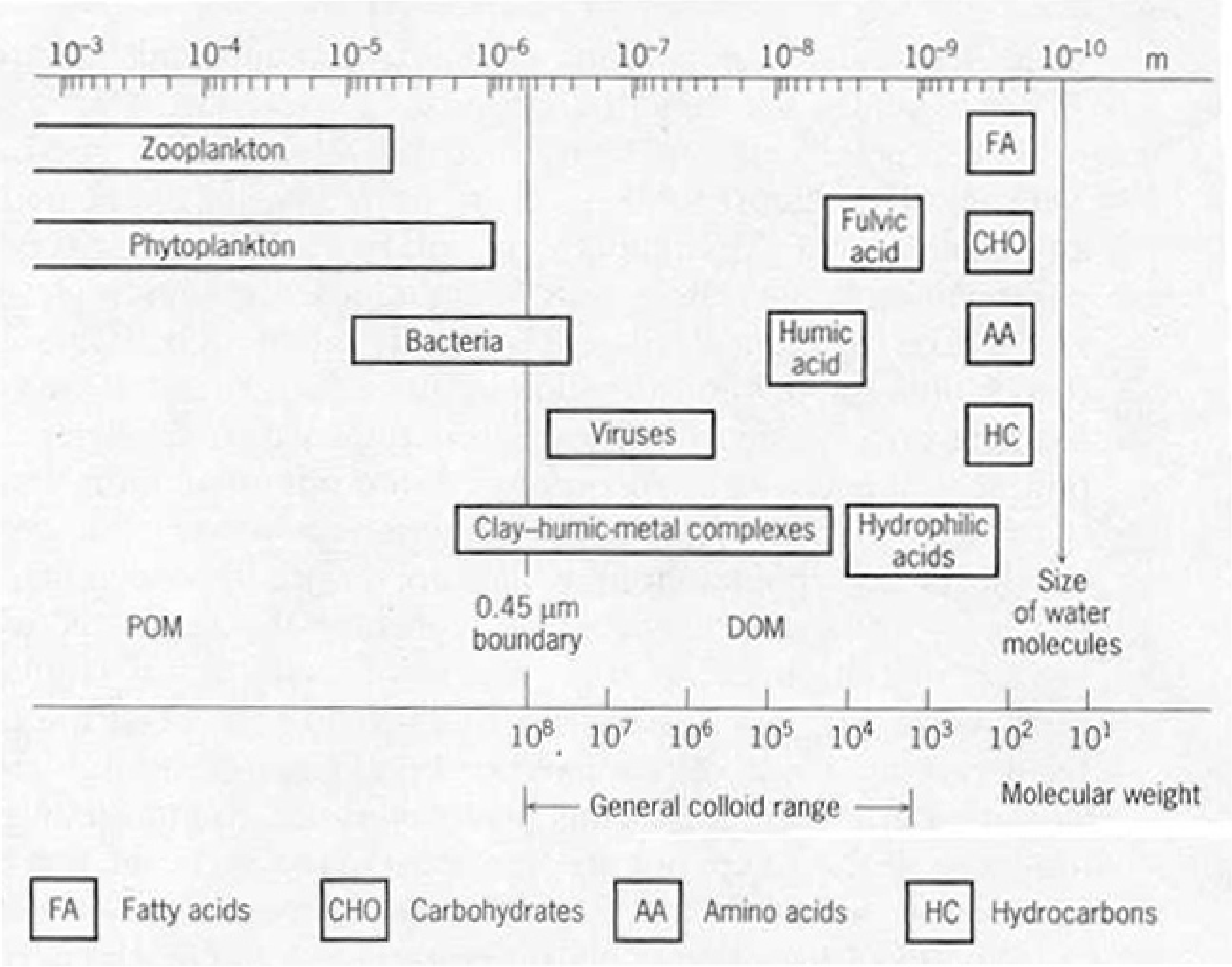
Libes, 1992

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

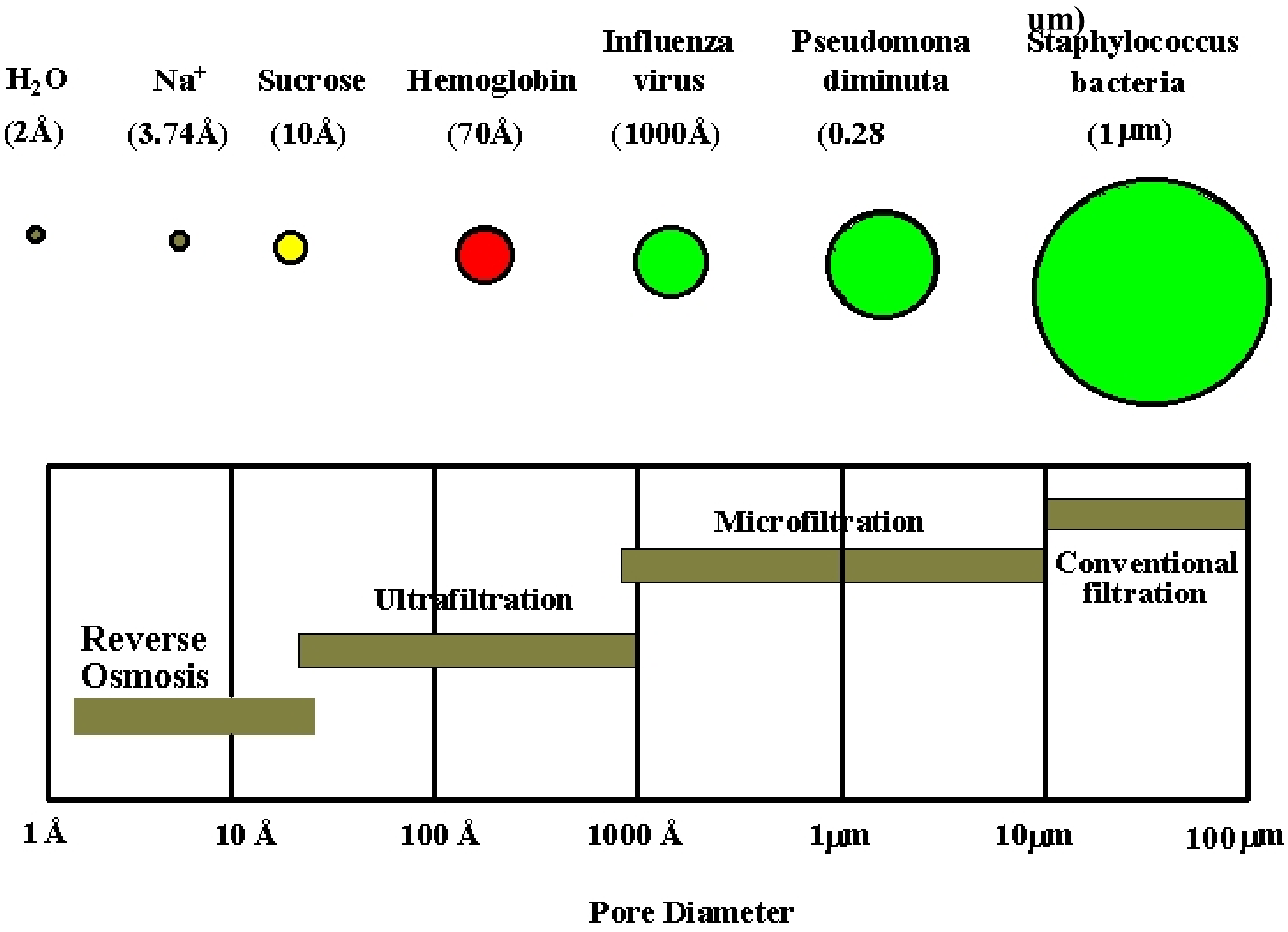
- Complex natural organic molecules
- Properties & importance understood
- Some structural components known
- Exact chemical nature or exact structure unknown because:
  - Complexity
  - Heterogeneity
  - Concentrations
  - Deficiencies in analytical techniques
  - Interfering species

Organic Carbon Continuum

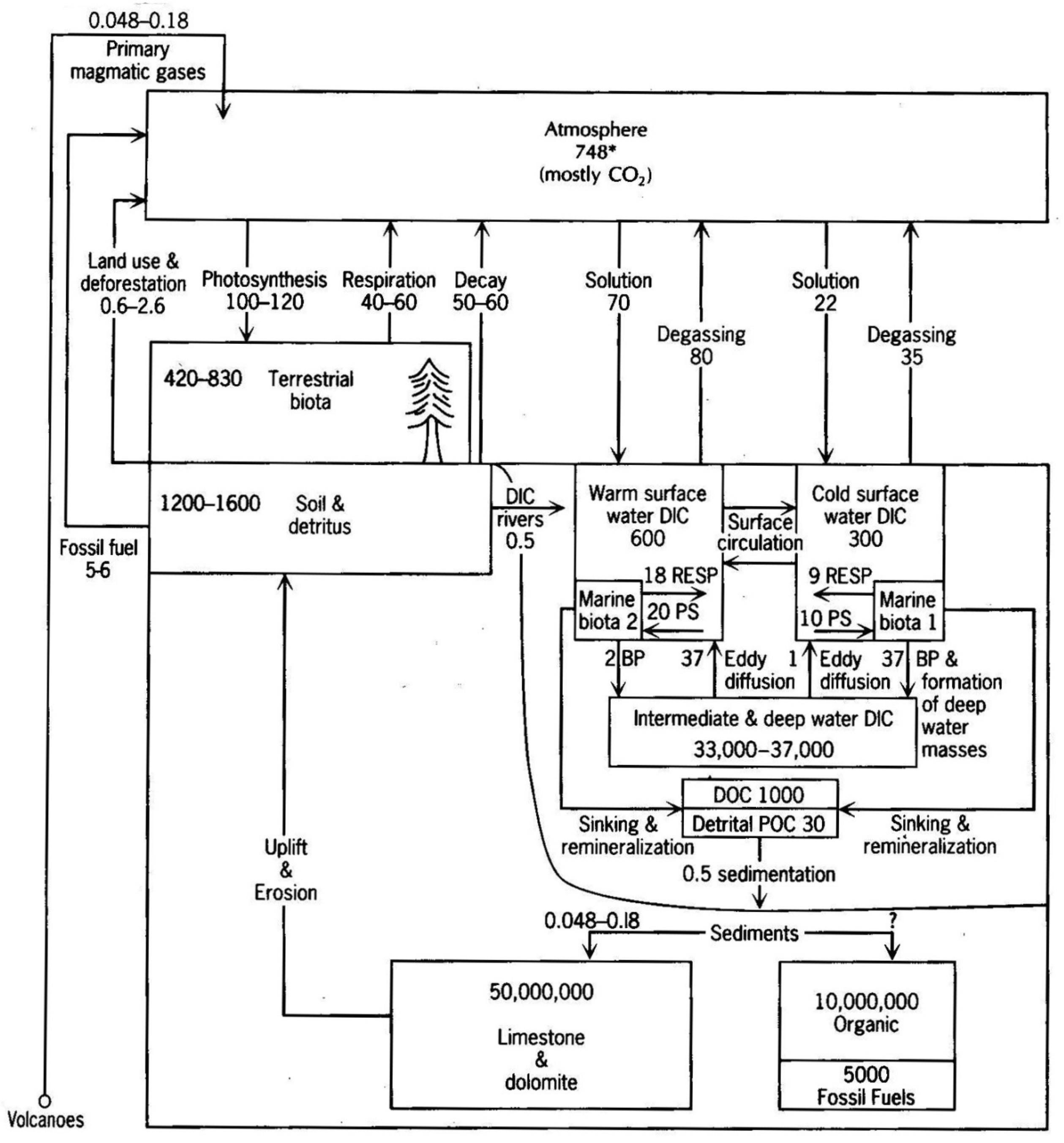


Libes, 1992

PORE SIZE OF FILTRATION PROCESSES



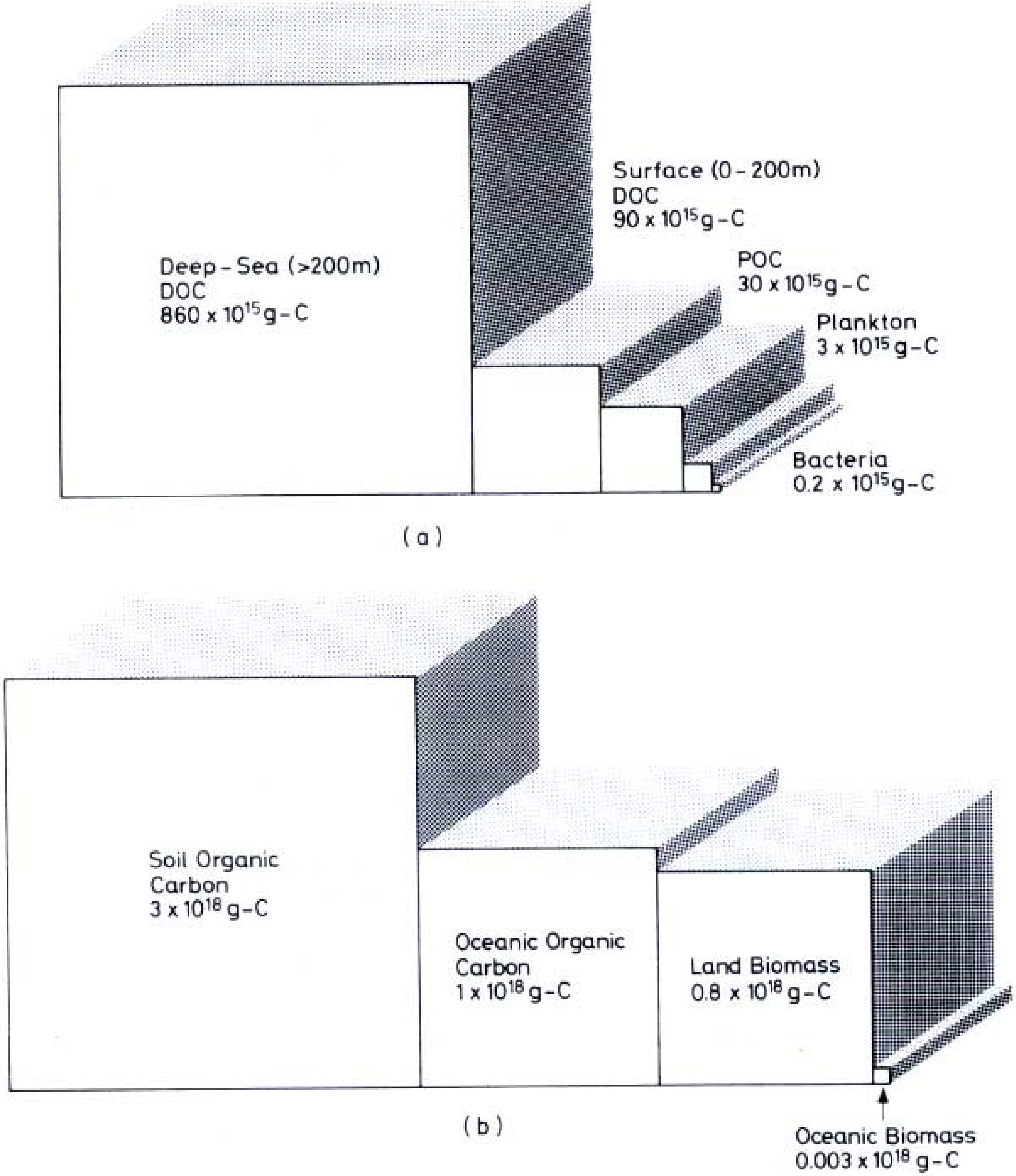
Millero, 2007



Carbon Cycle
Libes, 1992

Inventories in
10^{15} g C = BMT

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



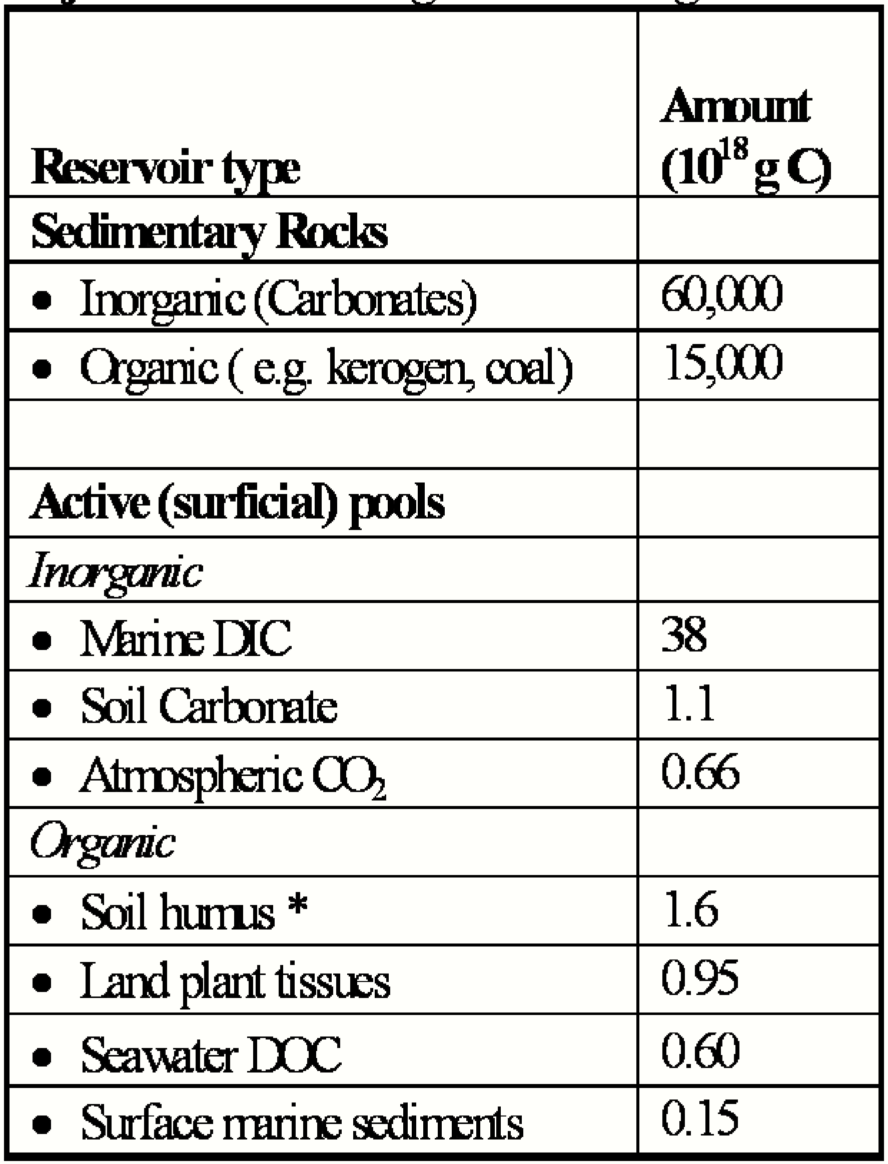
Distribution of Organic Carbon

(a) Major compartments in the global ocean

(b) Major compartments for the planet

Cauwet, 1978

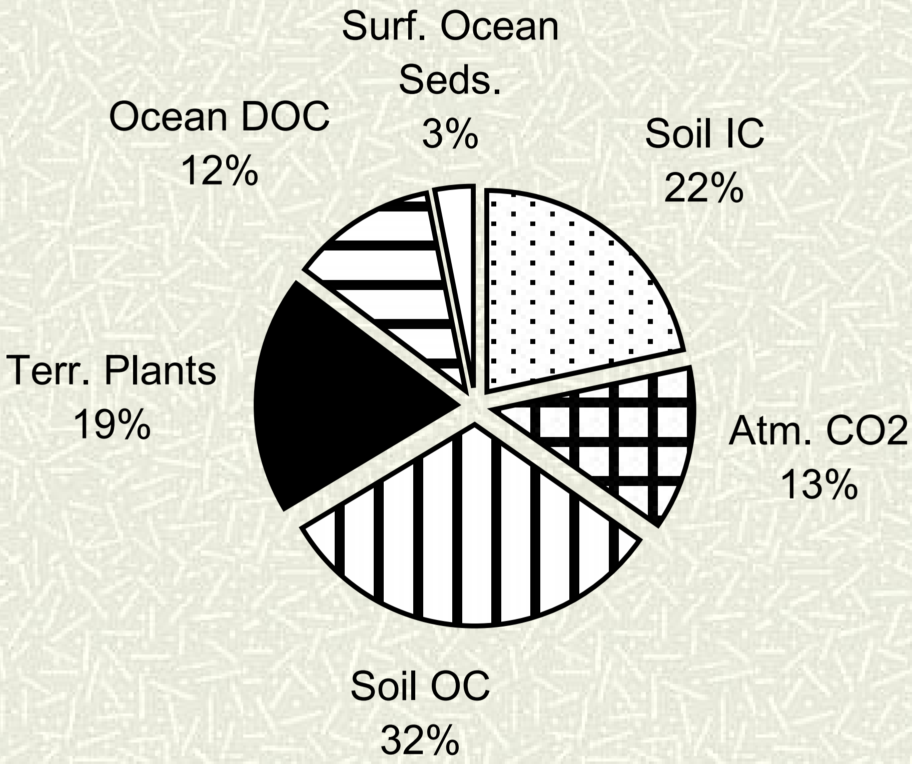
Major reservoirs of organic and inorganic carbon



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 Marine Environment

- 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

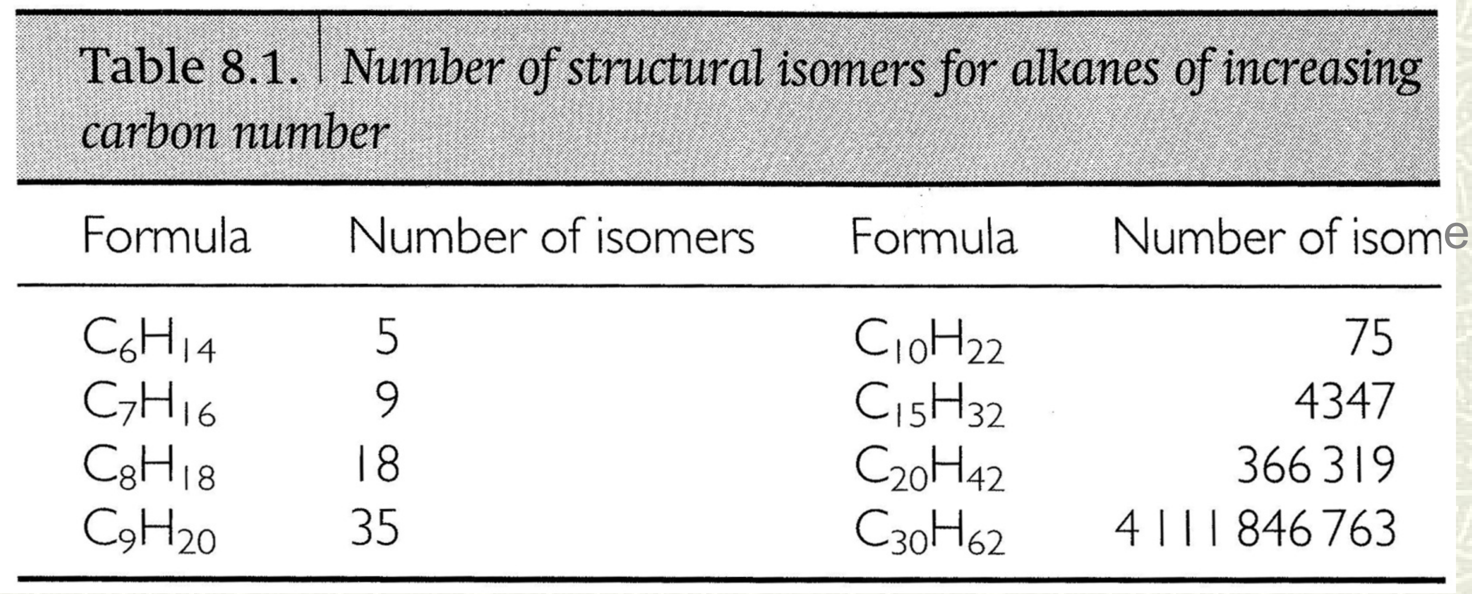


Table 8.1. *Number of structural isomers for alkanes of increasing carbon number*

Formula	Number of isomers	Formula	Number of isomers
C_6H_{14}	5	$C_{10}H_{22}$	75
C_7H_{16}	9	$C_{15}H_{32}$	4347
C_8H_{18}	18	$C_{20}H_{42}$	366 319
C_9H_{20}	35	$C_{30}H_{62}$	4 111 846 763

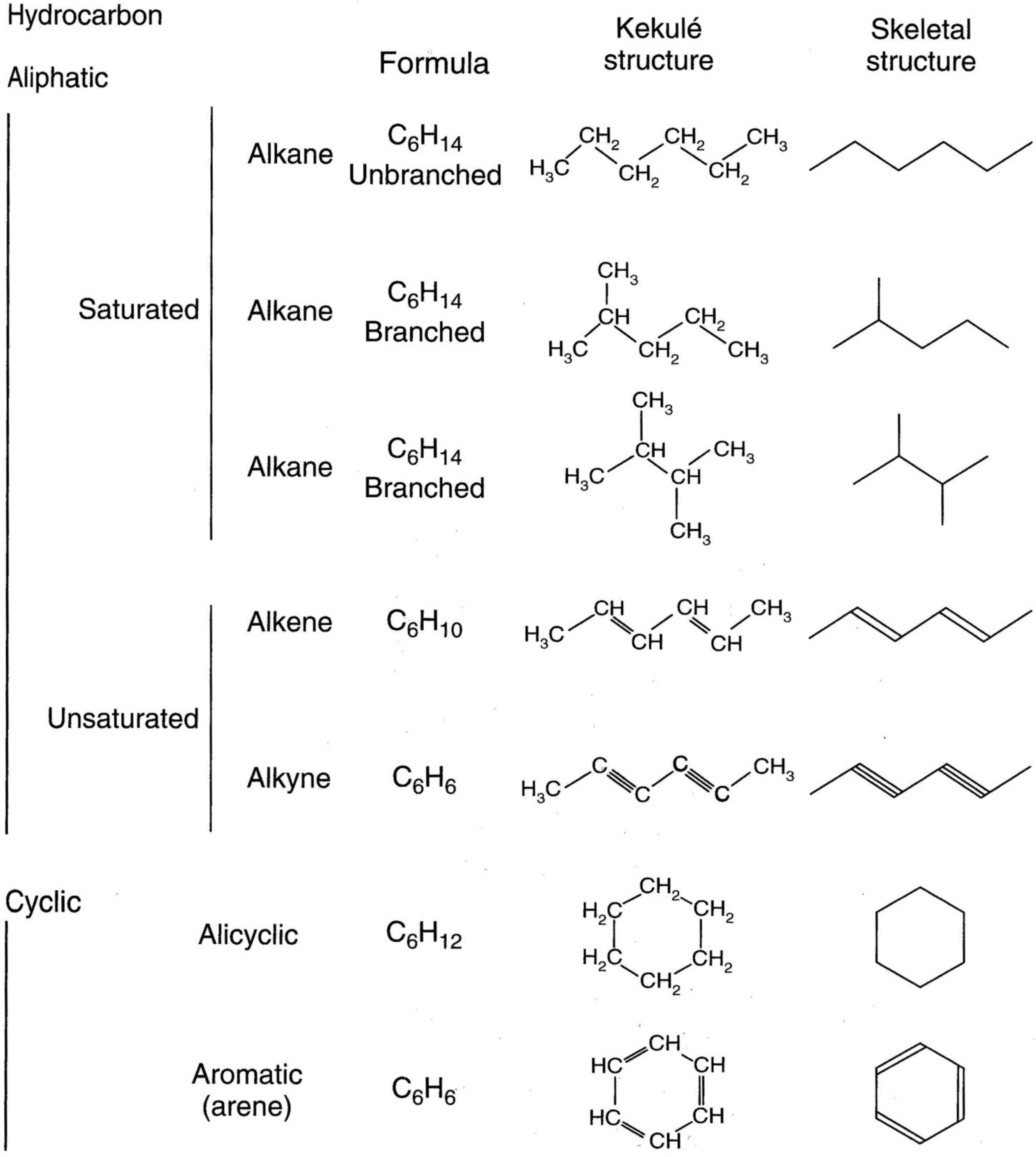


Figure 8.1. Hydrocarbons are classified by whether their carbon structure includes rings, multiple bonds, or branches. Classification of hydrocarbon structural families is shown here with the chemical formula. Structures are shown as Kekulé (also called line-bond) and skeletal structures.

Organic Compounds in Marine Environment

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- 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 the Ocean

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

Most Marine Humic Material is formed *in situ* through both biotic & abiotic processes

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

Transformation of DOC

- Biological molecules are

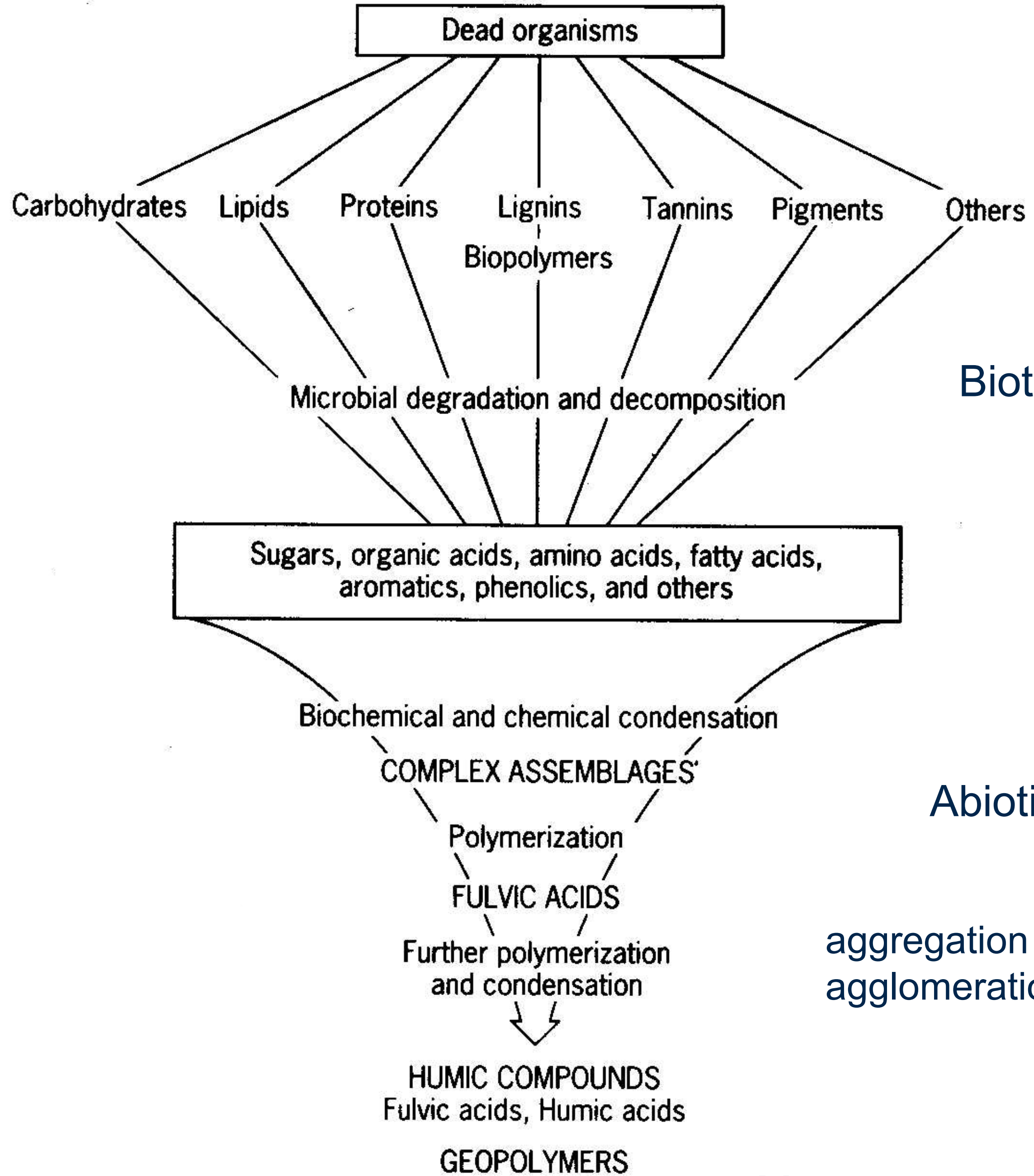
  labile = readily broken down

  or degraded quickly
- 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 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

  the water column, in sediments, & 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

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

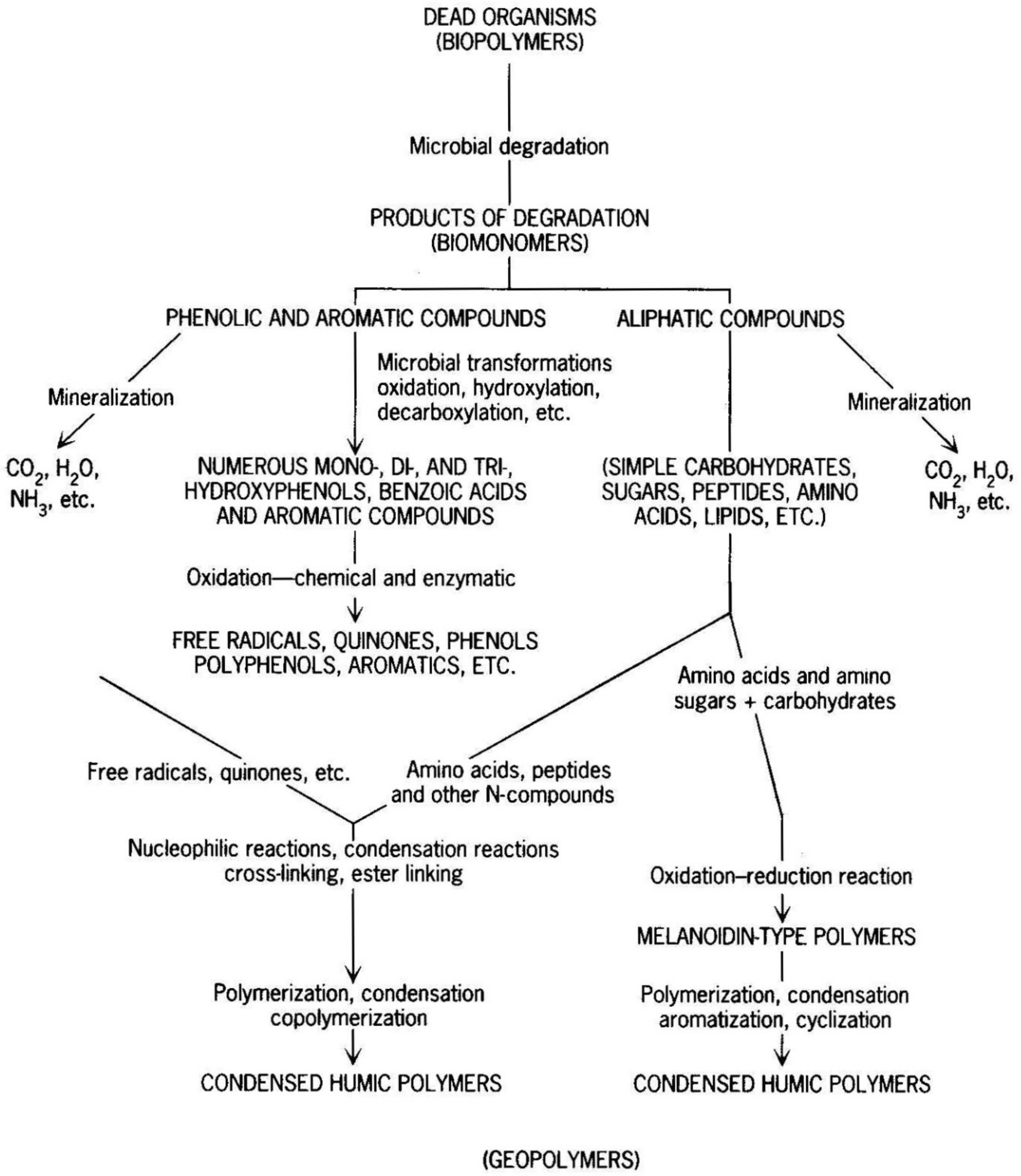
Humification of
Organic Matter
(possible scheme)

Abiotic

aggregation
agglomeration

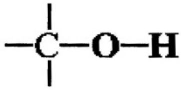
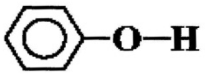
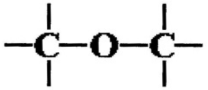
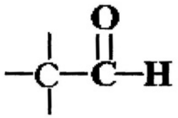
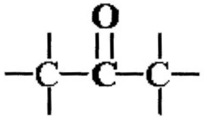
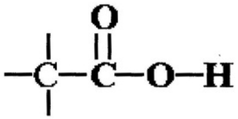
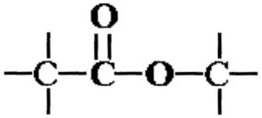
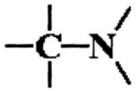
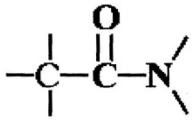
Libes, 1992

Macromoloecules



Humification of Organic Matter (another scheme)

Libes, 1992

Group	Structure	pK_a	Hydrolysis Products	Exchange H ?
Alcohol		12	None	Yes
Phenol		10	None	Yes
Ether			None	
Aldehyde			None	No
Ketone			None	
Carboxyl		5	None	Yes
Ester			Carboxyl + Alcohol	
Amine		10	None	Yes
Amide			Carboxyl + Amine	Yes

Emerson & Hedges
Figure 8.2

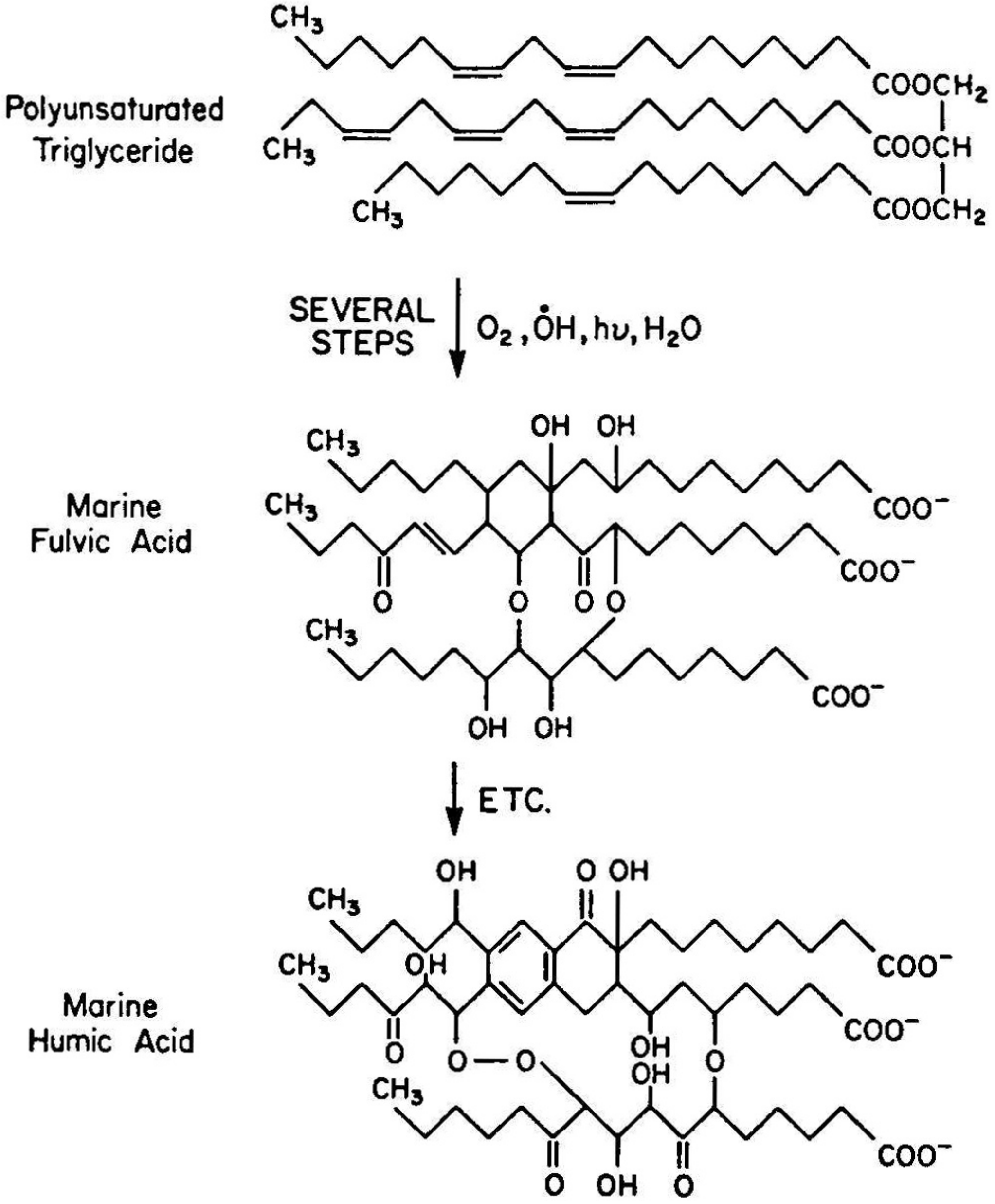
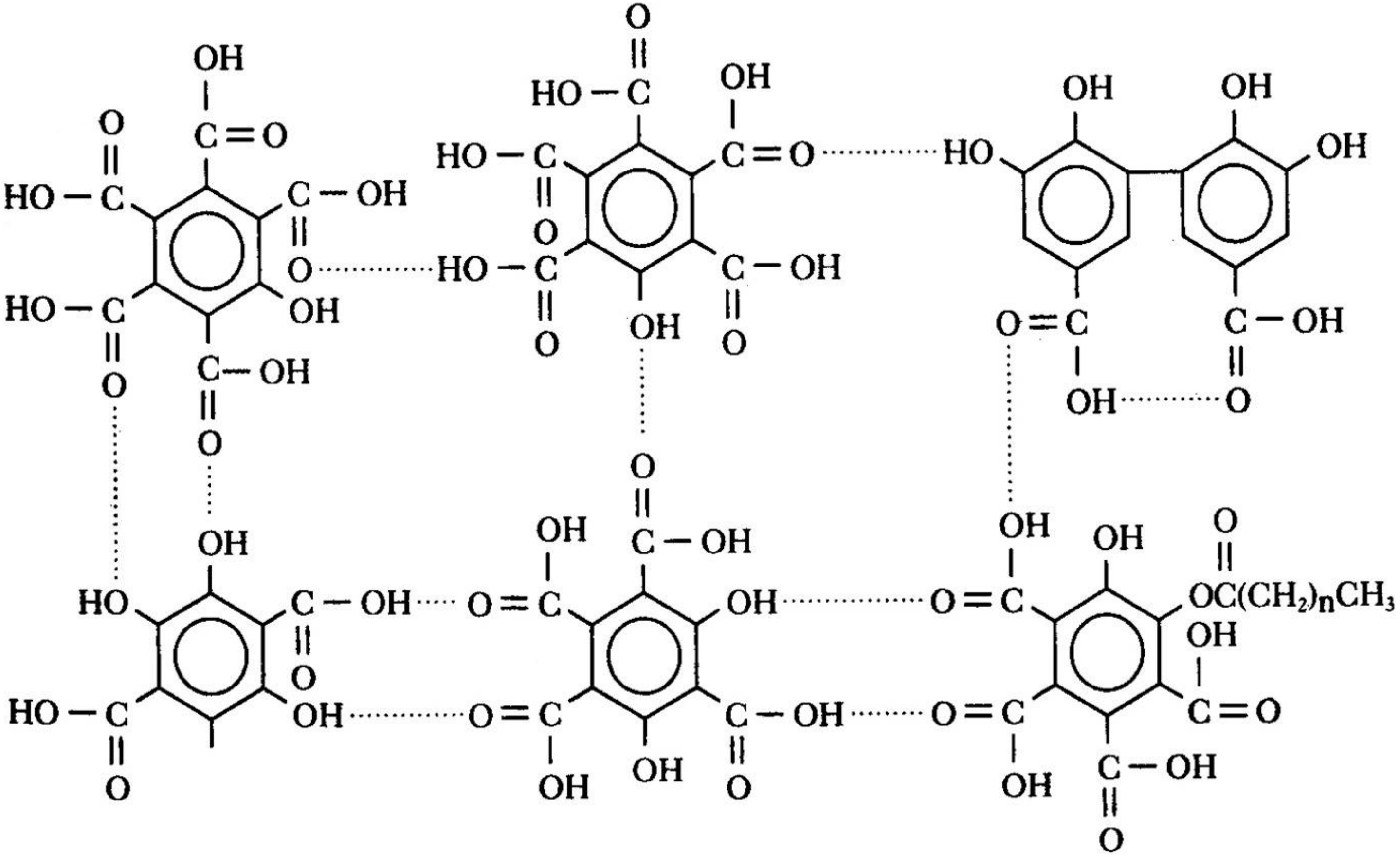
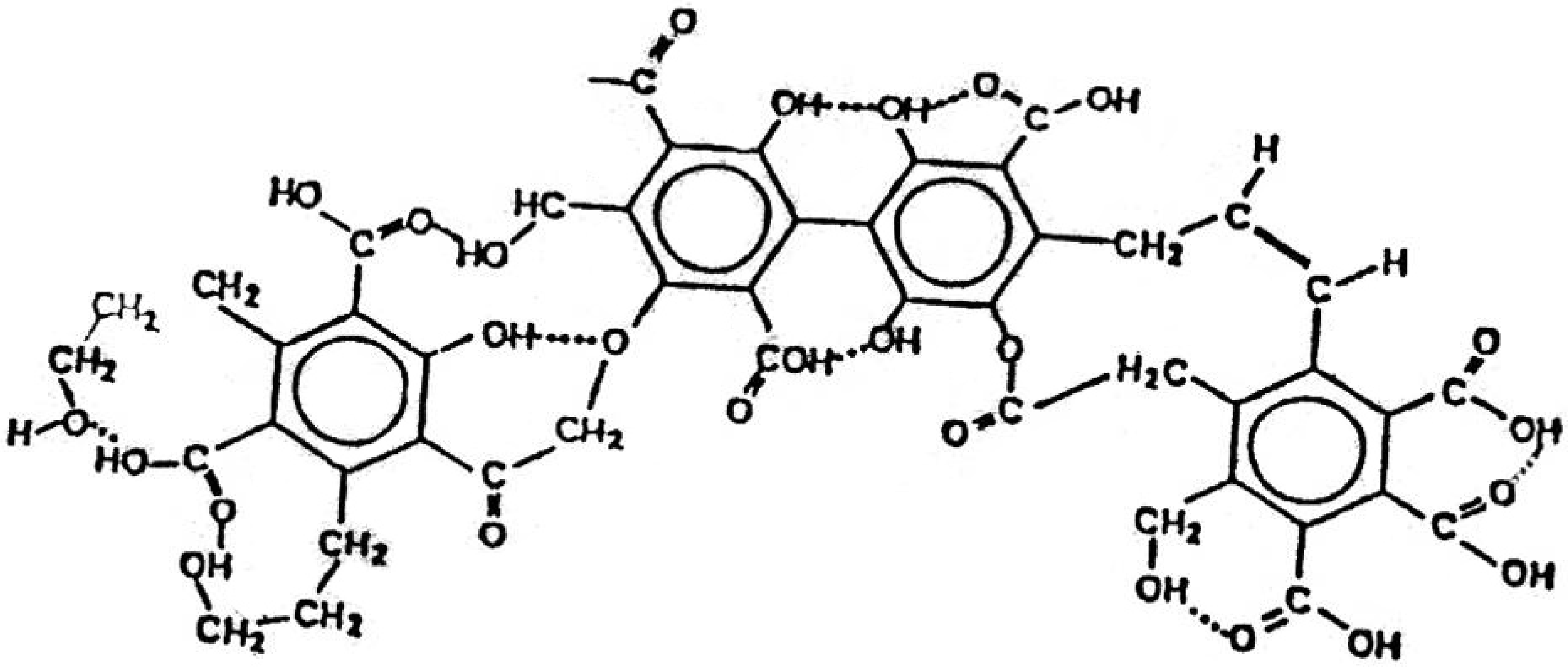


Figure 6.13 A possible pathway for the formation of marine humic acids from a triglyceride. From Harvey et al., 1983.

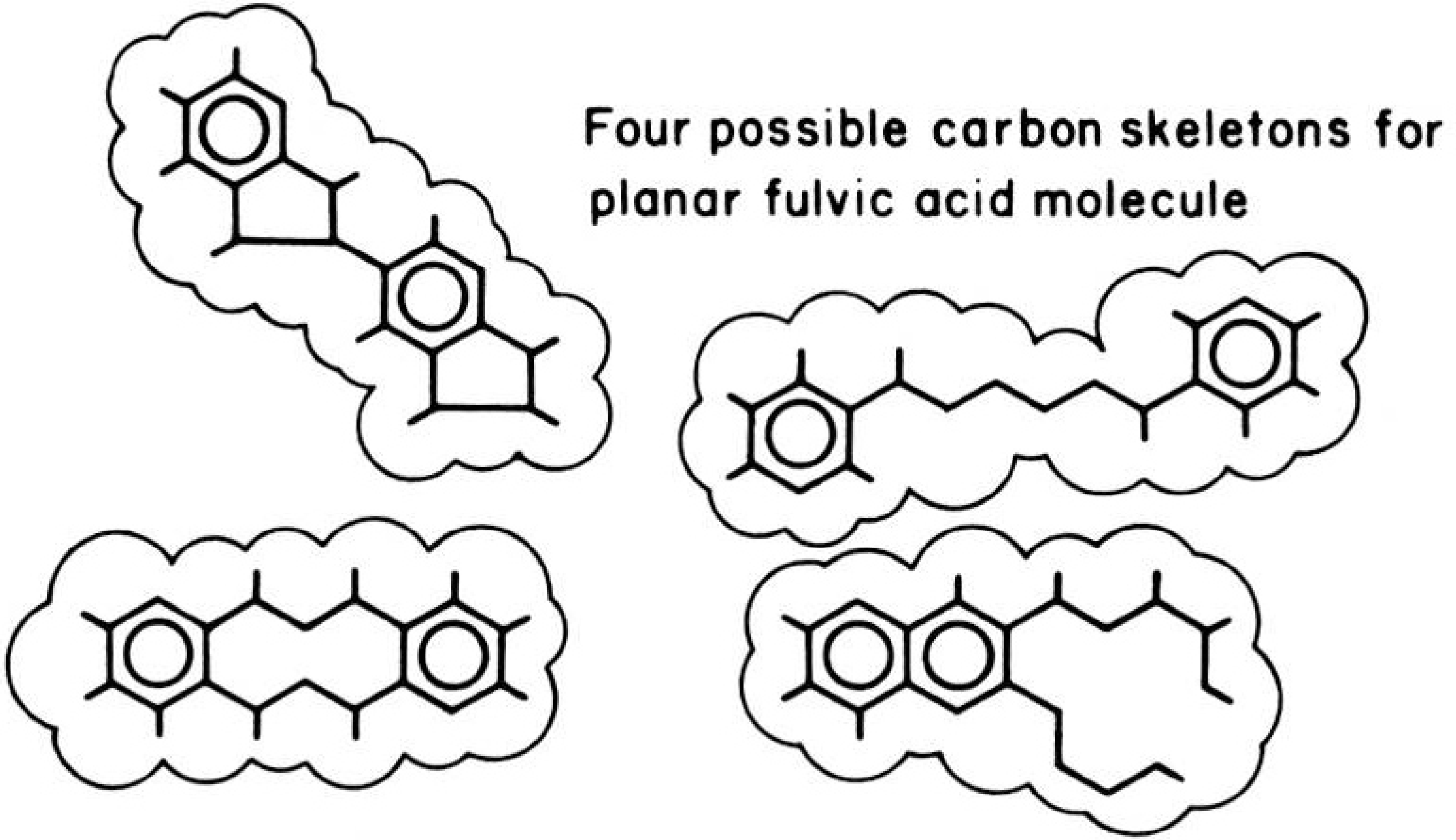
Morel & Hering, 1993
See also
Emerson & Hedges
Figure 8.11 & 8.12



Humic Structure Proposed by Schnitzer (Rashid 1985)

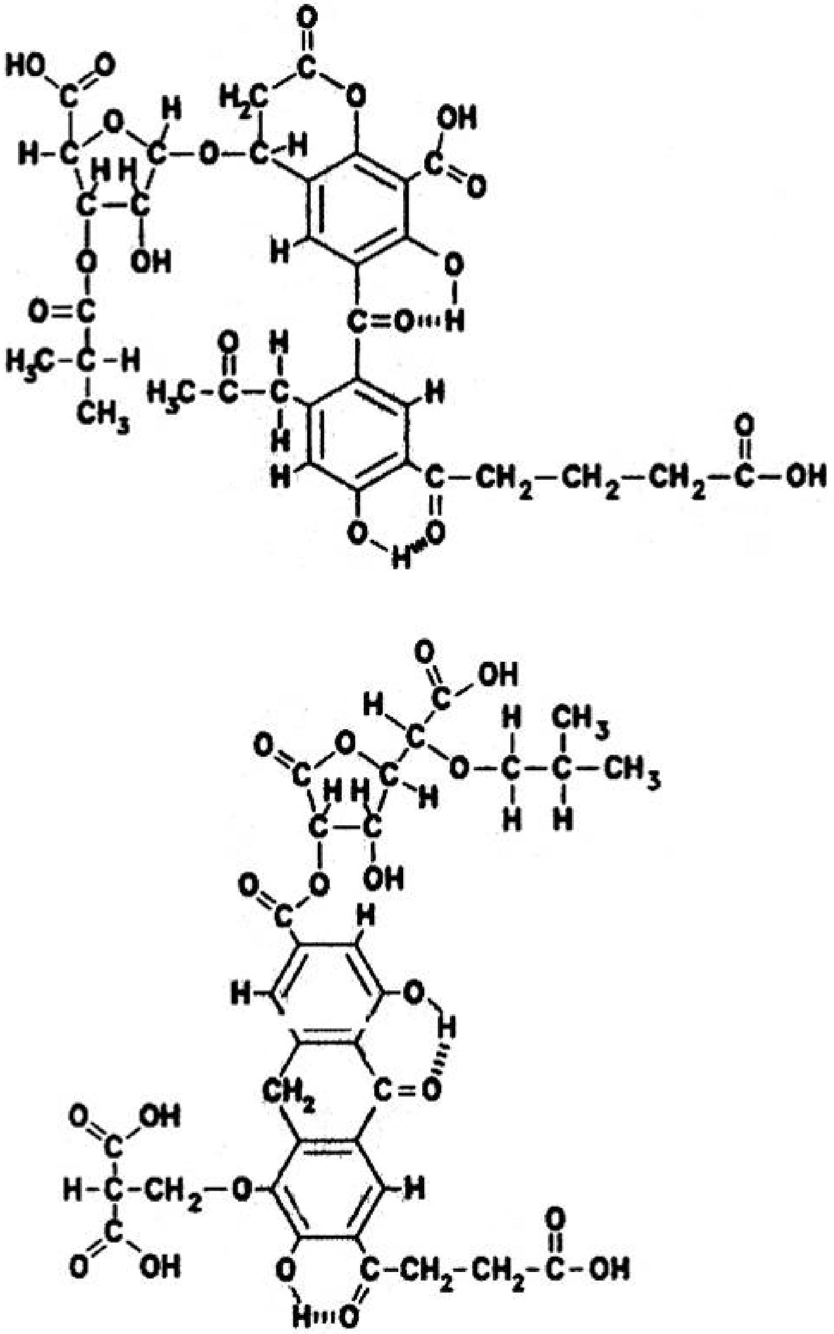


Structure Attributed to Gamble et al. (1985)

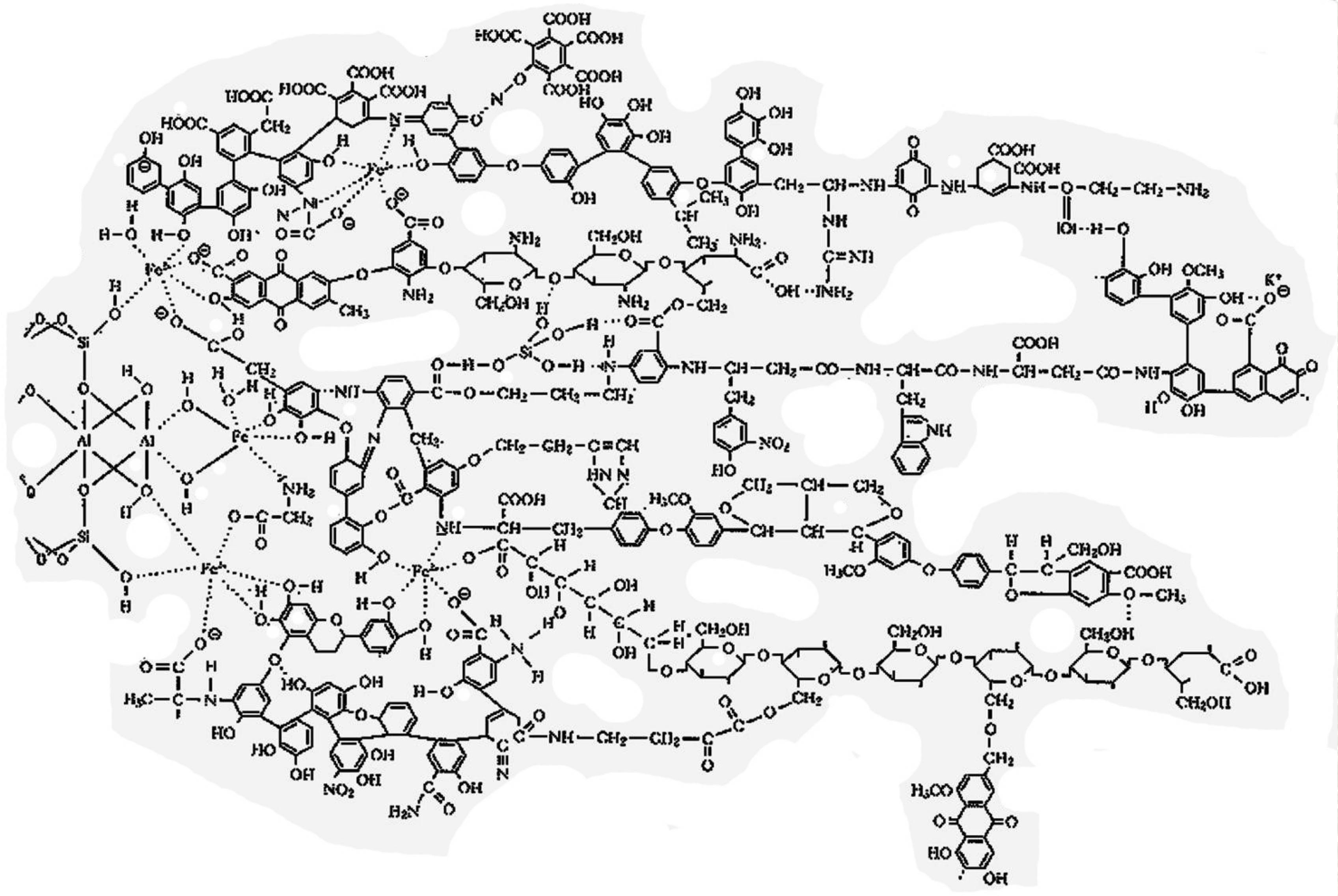


Four possible carbon skeletons for the planar fulvic acid molecule

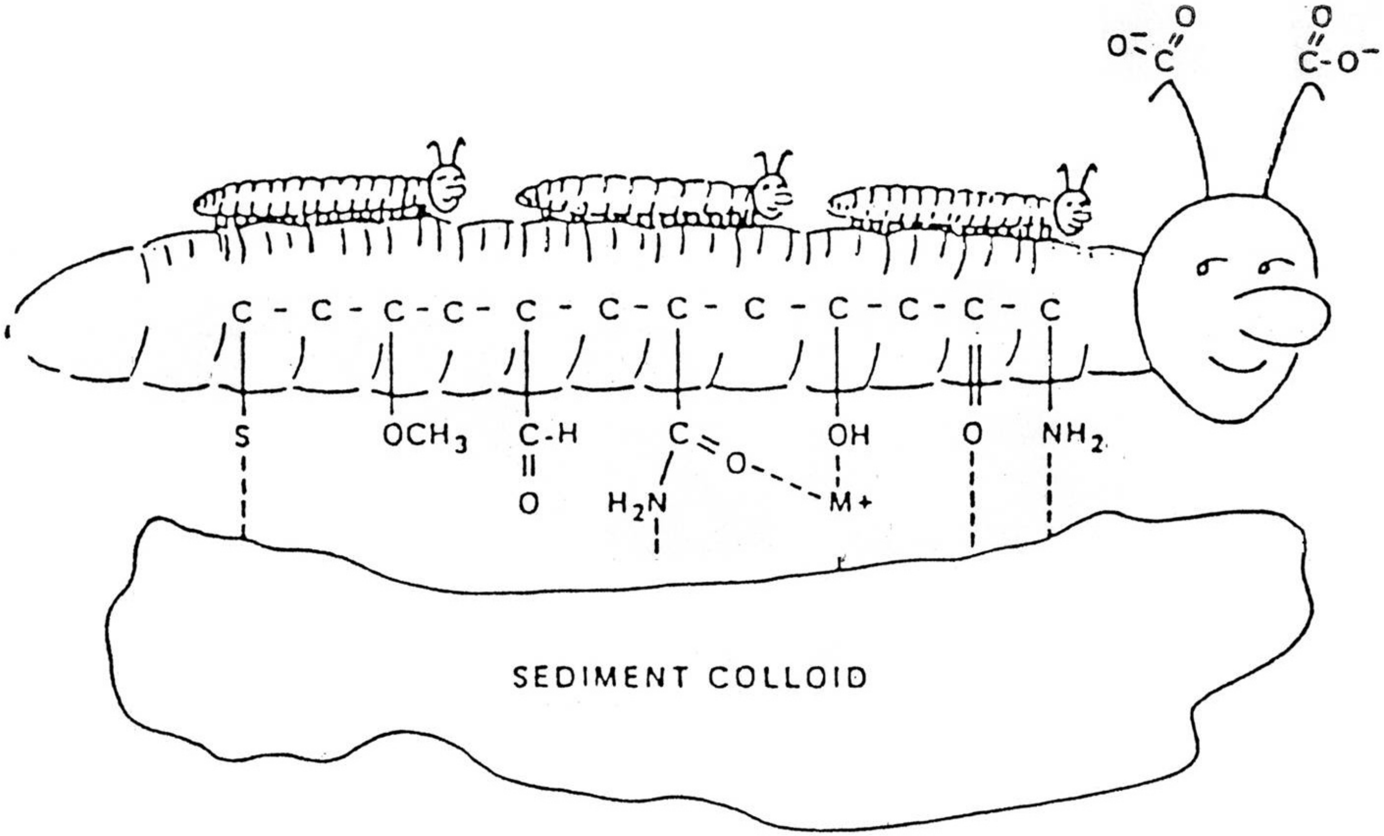
Morel & Hering (1993) Based on Aiken et al. (1985)



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

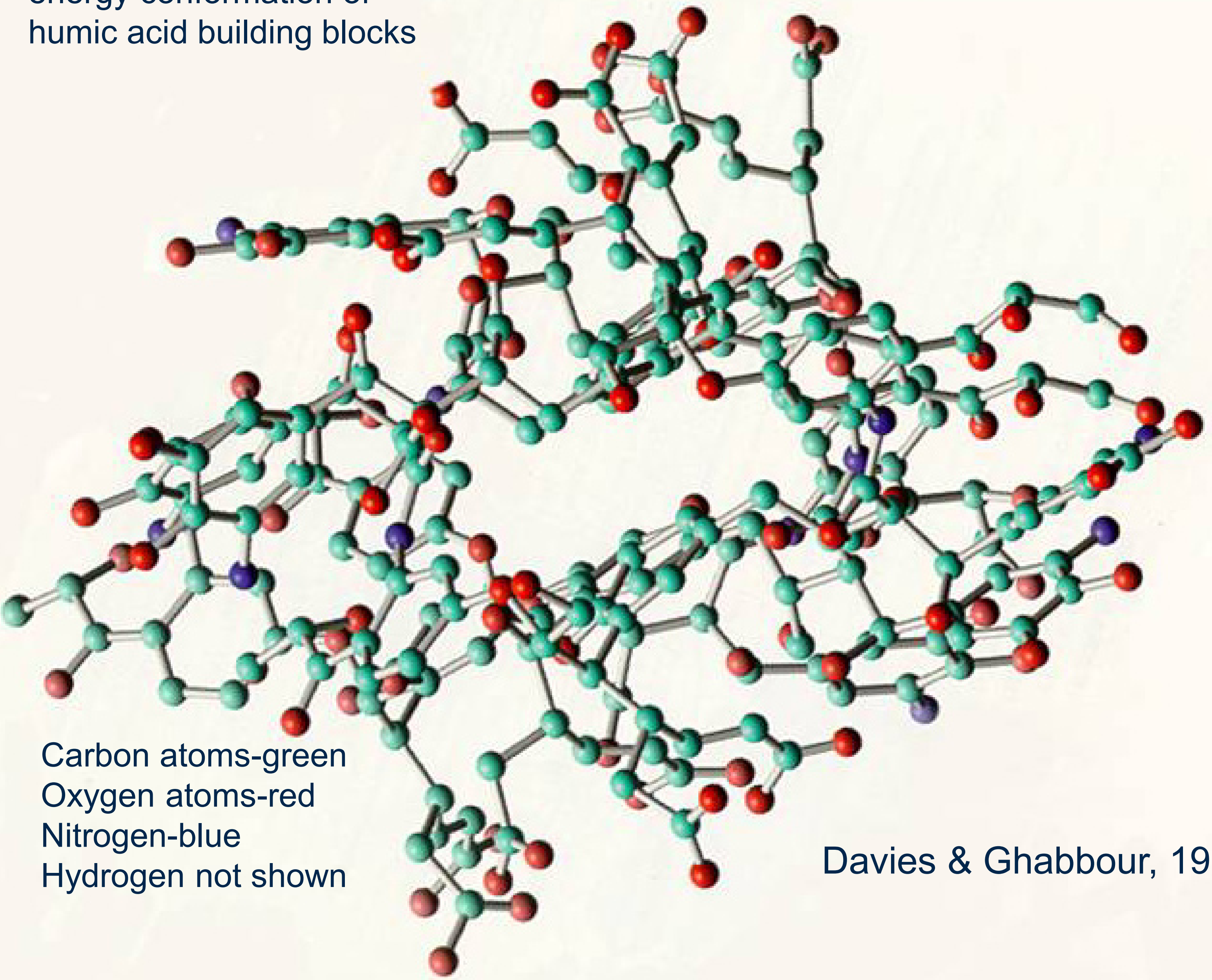


Kleinhempel reprinted from Albrecht Thaer Archiv (1970)



Organic Solute
Macromolecule
(ORSMAC)
Leenheer 1985)

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

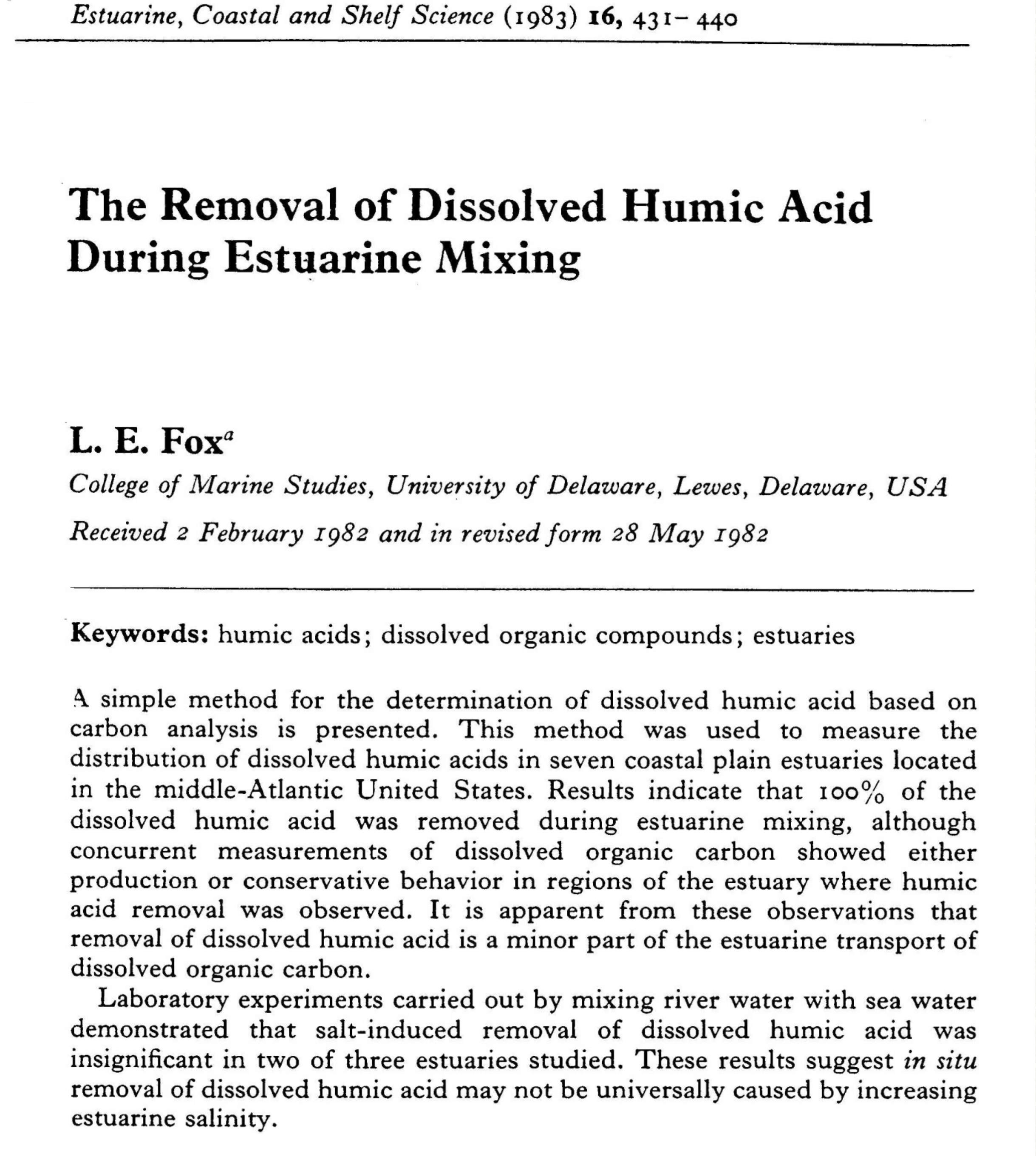


Carbon atoms-green
Oxygen atoms-red
Nitrogen-blue
Hydrogen not shown

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

L. E. Fox[a]

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.

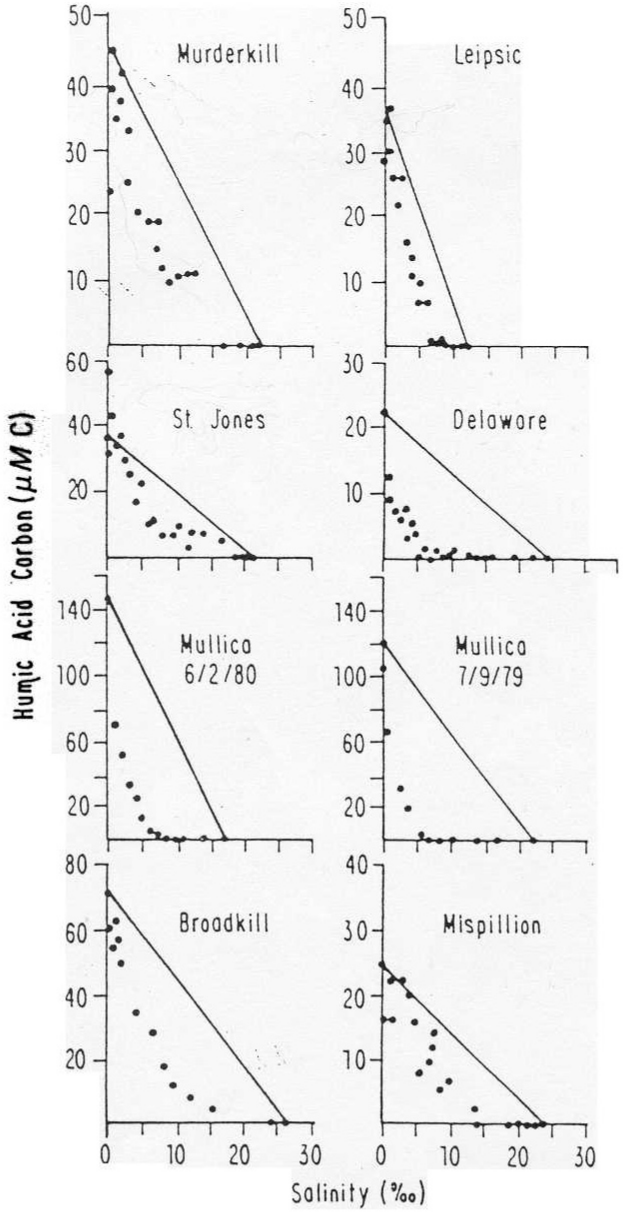
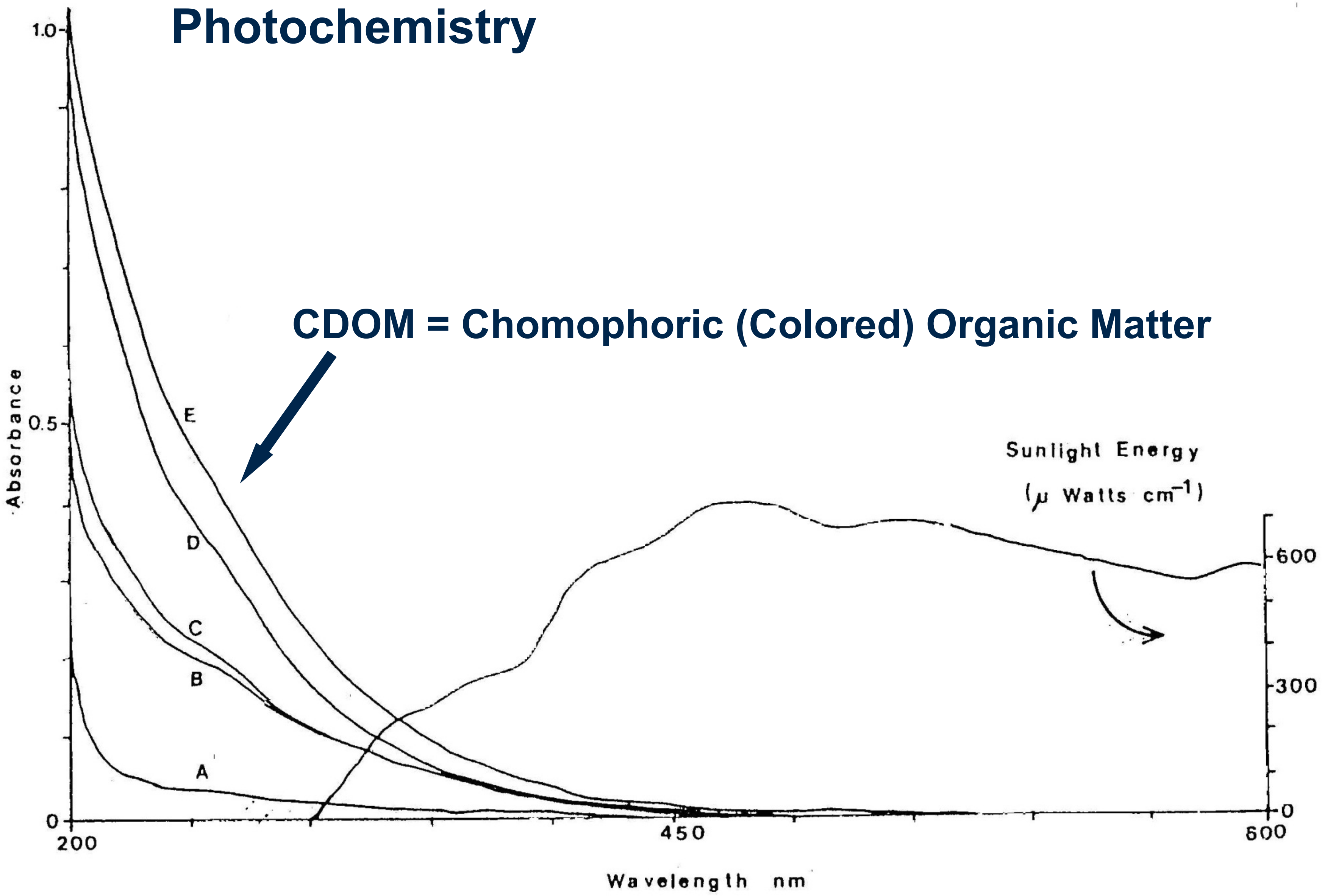


Figure 3. Humic acid carbon as a function of salinity. The standard error of the mean is 5%.

Fox, 1983

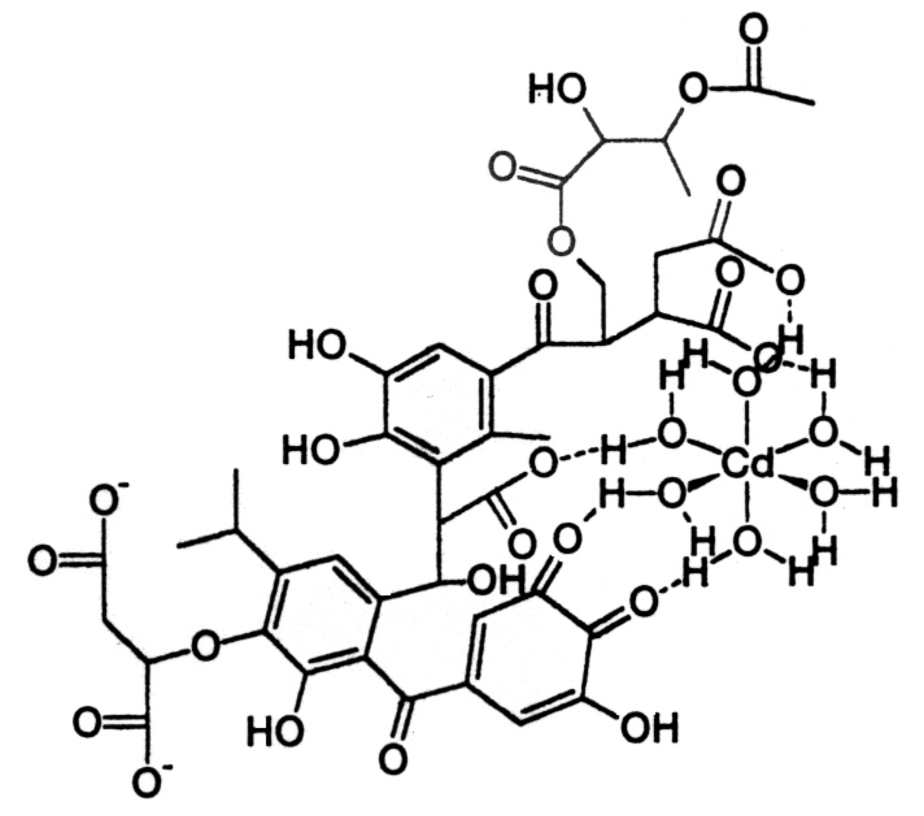
Photochemistry



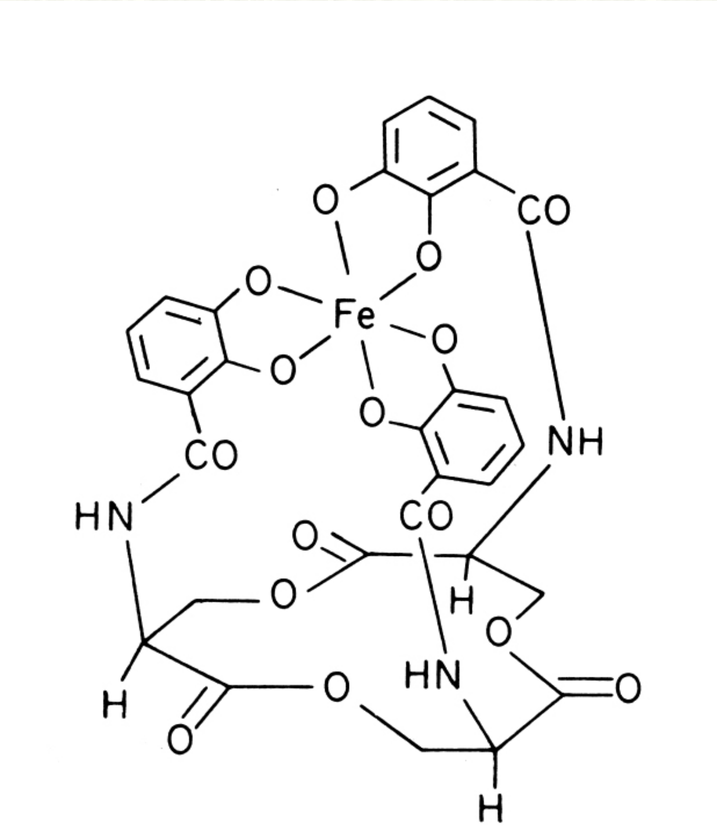
CDOM = Chomophoric (Colored) Organic Matter

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 Humic Materials



Leenheer et al. (1998)



Morel (1983)

References

Cauwet, G. (1978) Oceanologica Acta 1, 99

Davies & Ghabbour (1999) Chemistry & Industry 7, 426

Fox, L. (1983) Estuarine Coastal Shelf Sci. 16, 431

Hedges, J.I. (1992) Global Biogeochemical Cycles: Progress and Problems, Mar. Chem. 39, 67

Leenheer, J.A. (1985) in Humic Substances in Soil Sediment and Water: Geochemistry, Isolation and Characterization, Wiley, NY, pp. 409-429

Lenheer, J.A. et al. (1998) Environ. Sci. Technol. 32, 2410

Rashid, M.A. (1985) Geochemistry of Marine Humic Compounds, Springer-Verlag, NY, NY, 300 pages

Chemical Oceanography

Organics III

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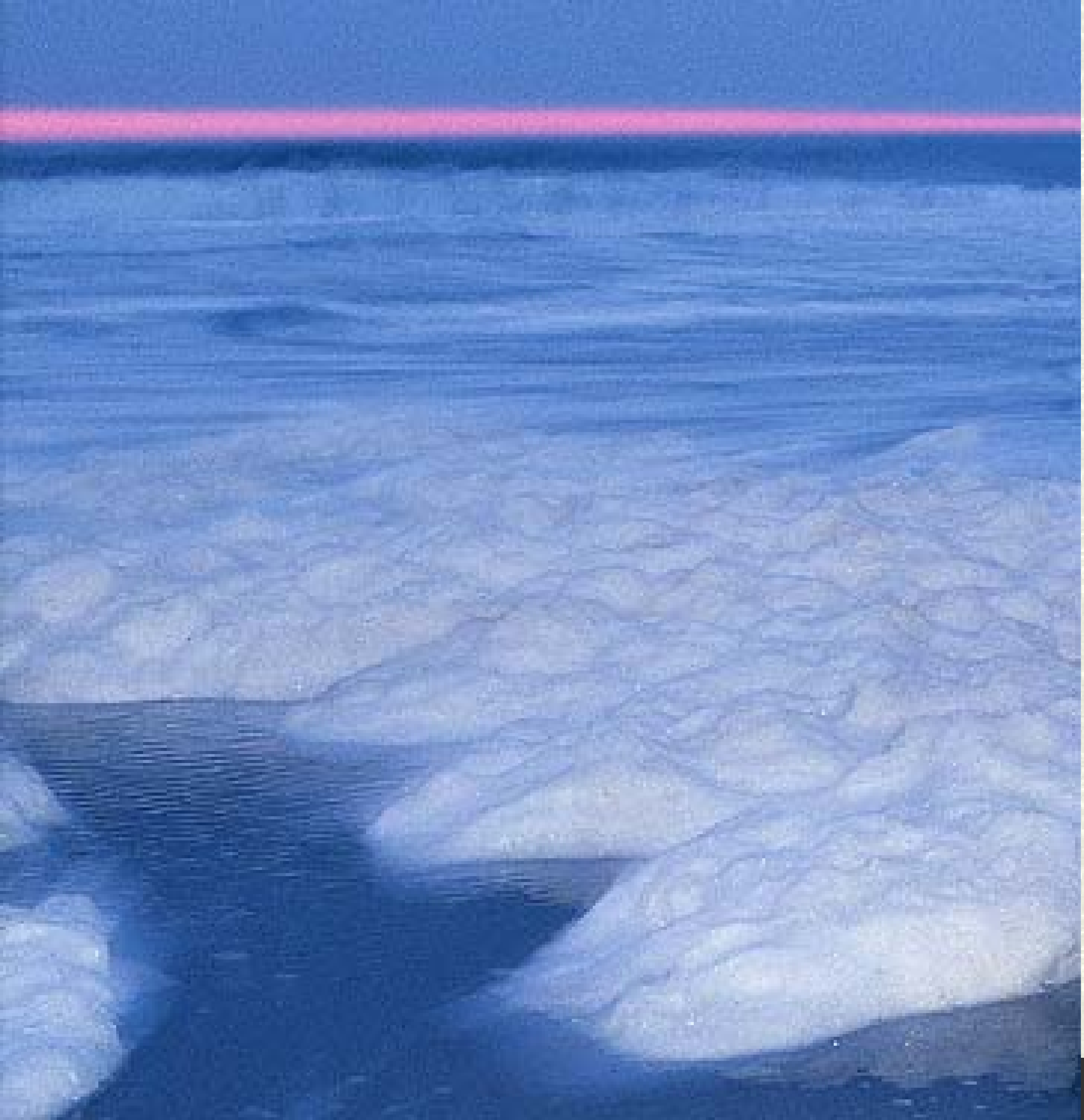
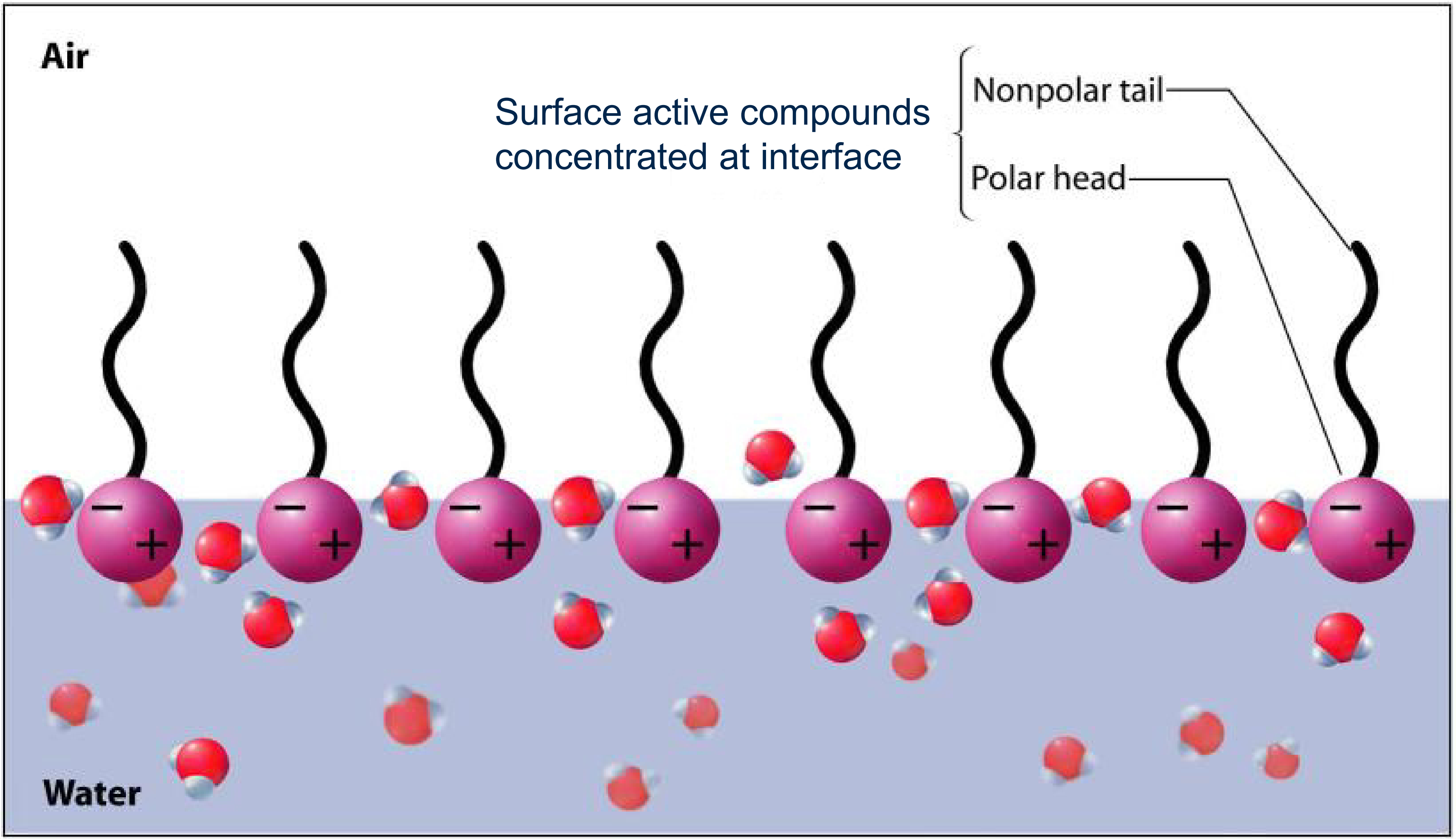


Sea Foam caused by naturally occuring surface active agents

Air-Sea Interfacial Chemistry



Surface active compounds concentrated at interface

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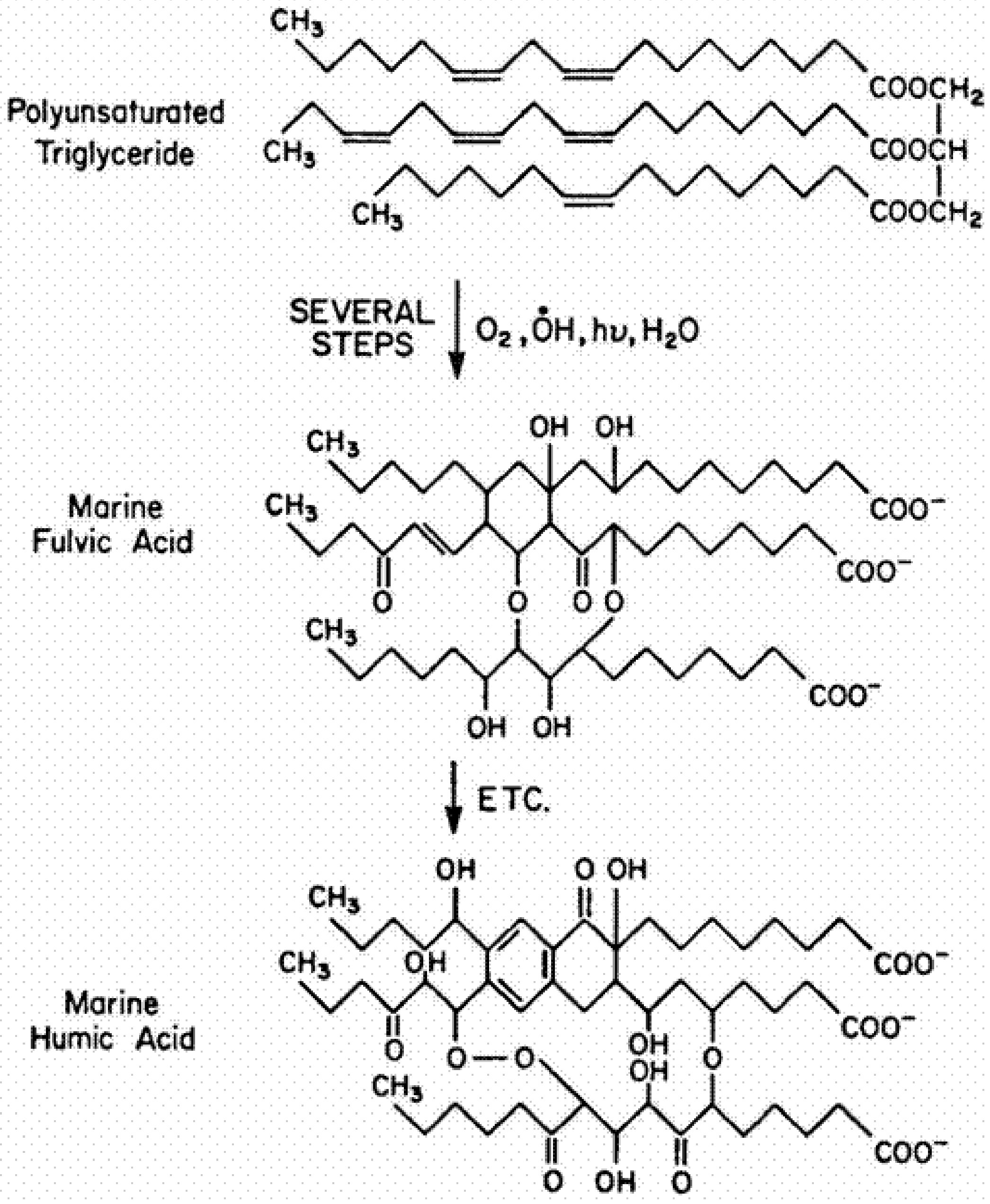

Morel & Hering, 1993

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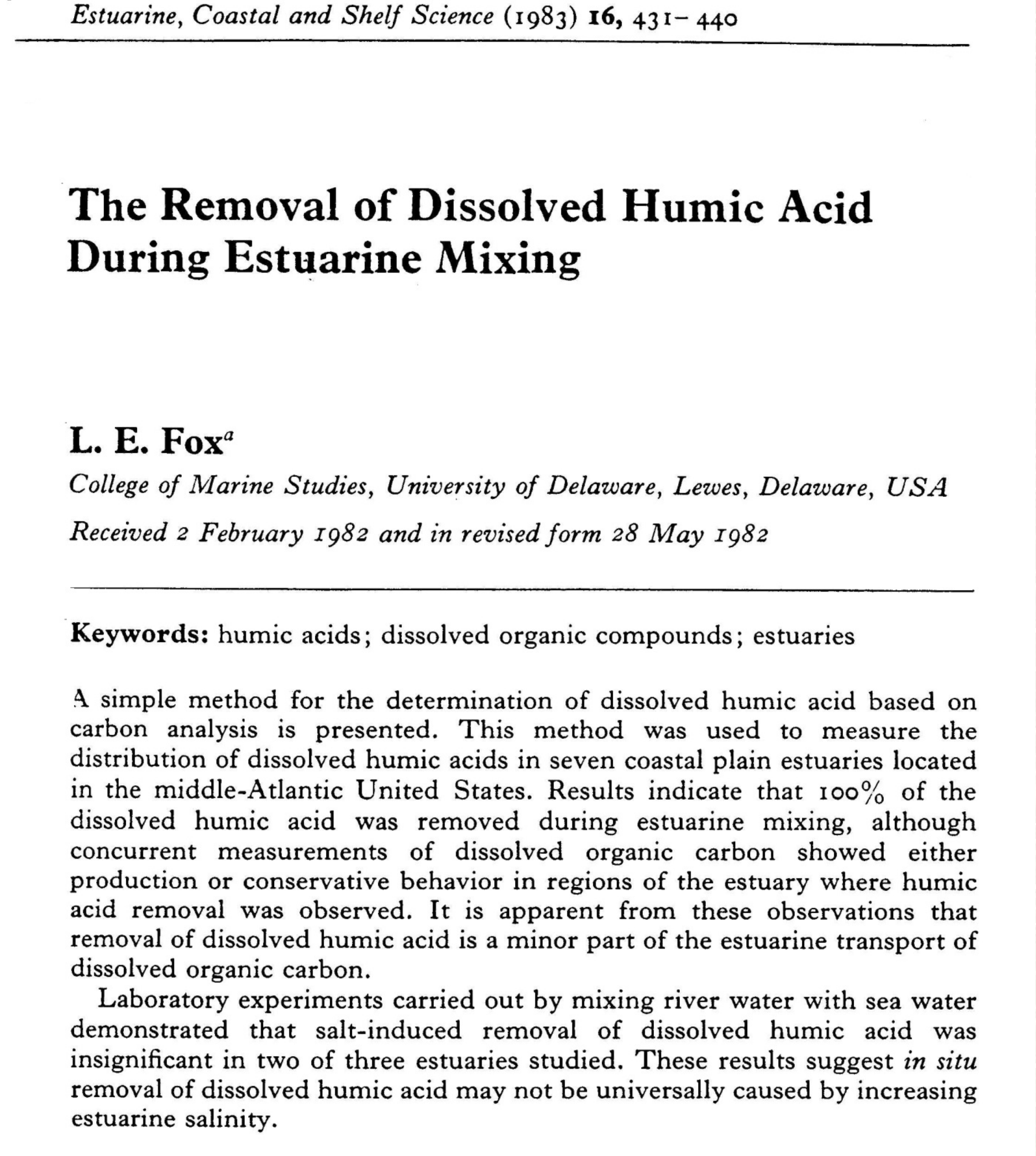

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Keywords: humic acids; dissolved organic compounds; estuaries

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.

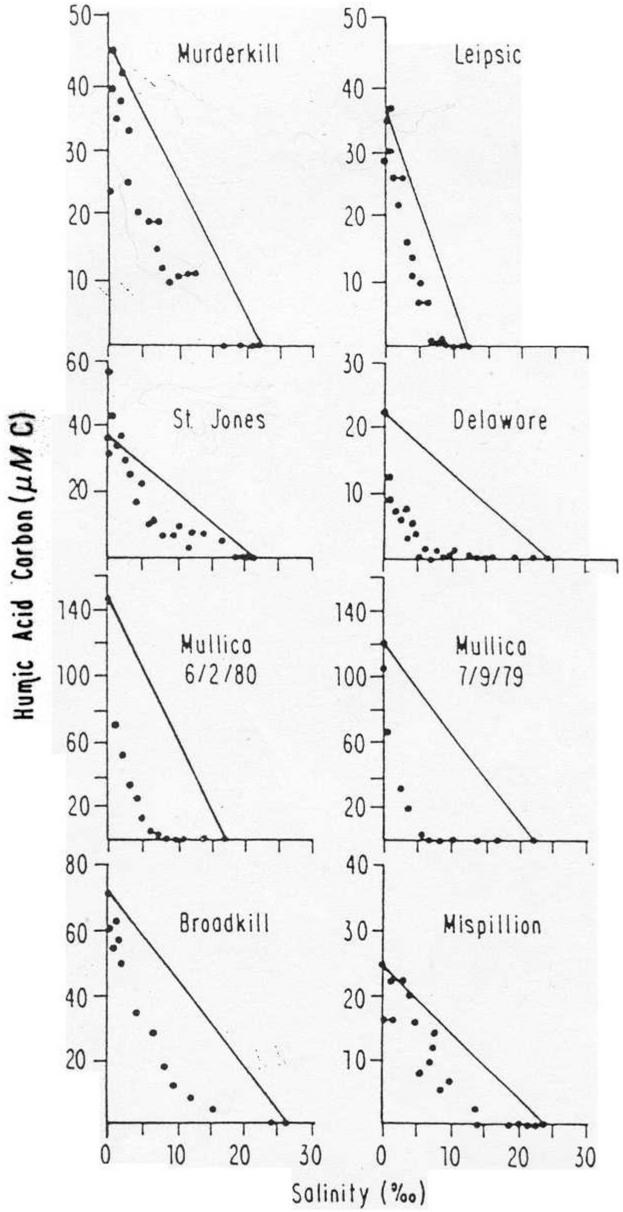


Figure 3. Humic acid carbon as a function of salinity. The standard error of the mean is 5%.

Fox, 1983

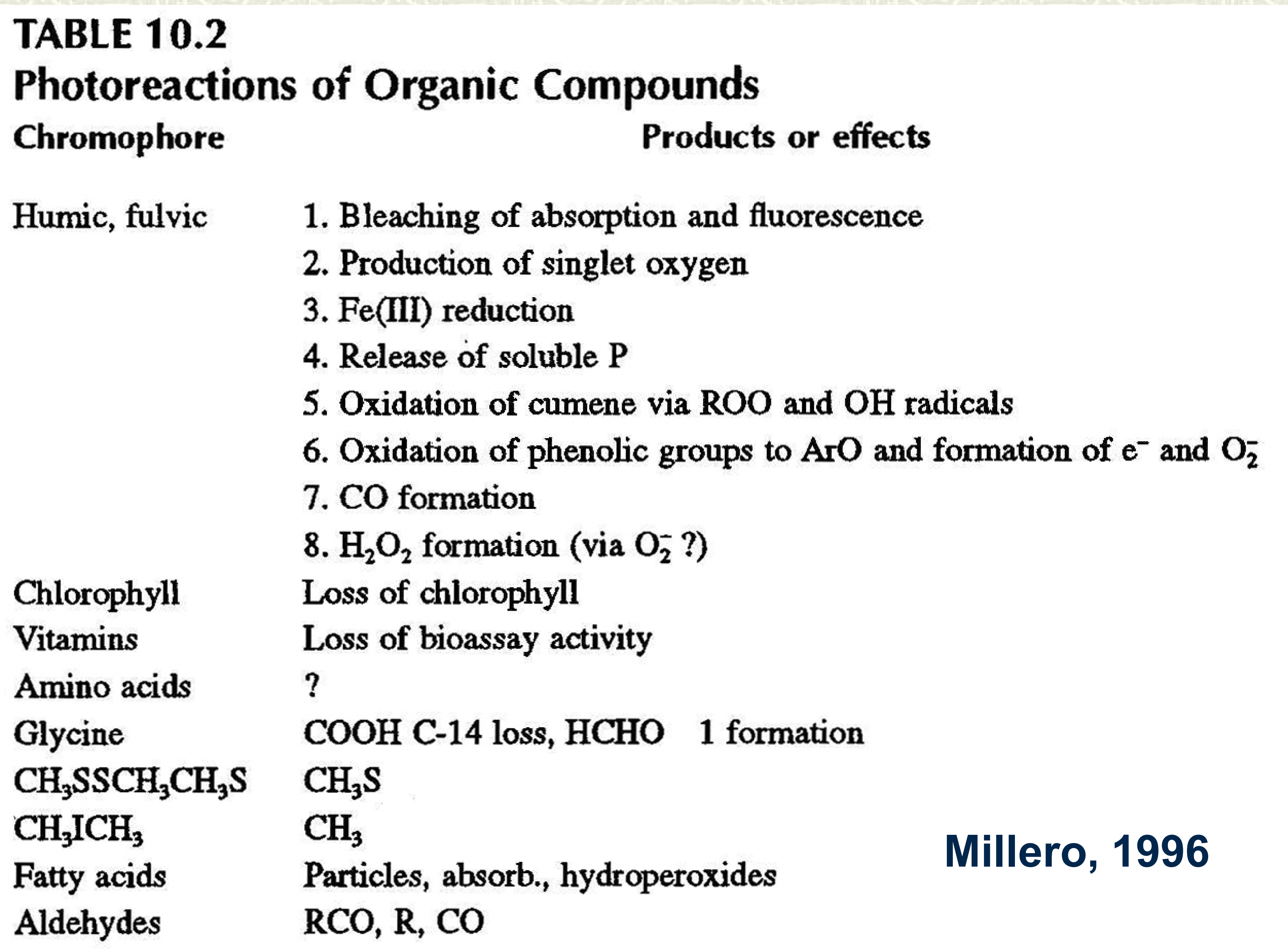
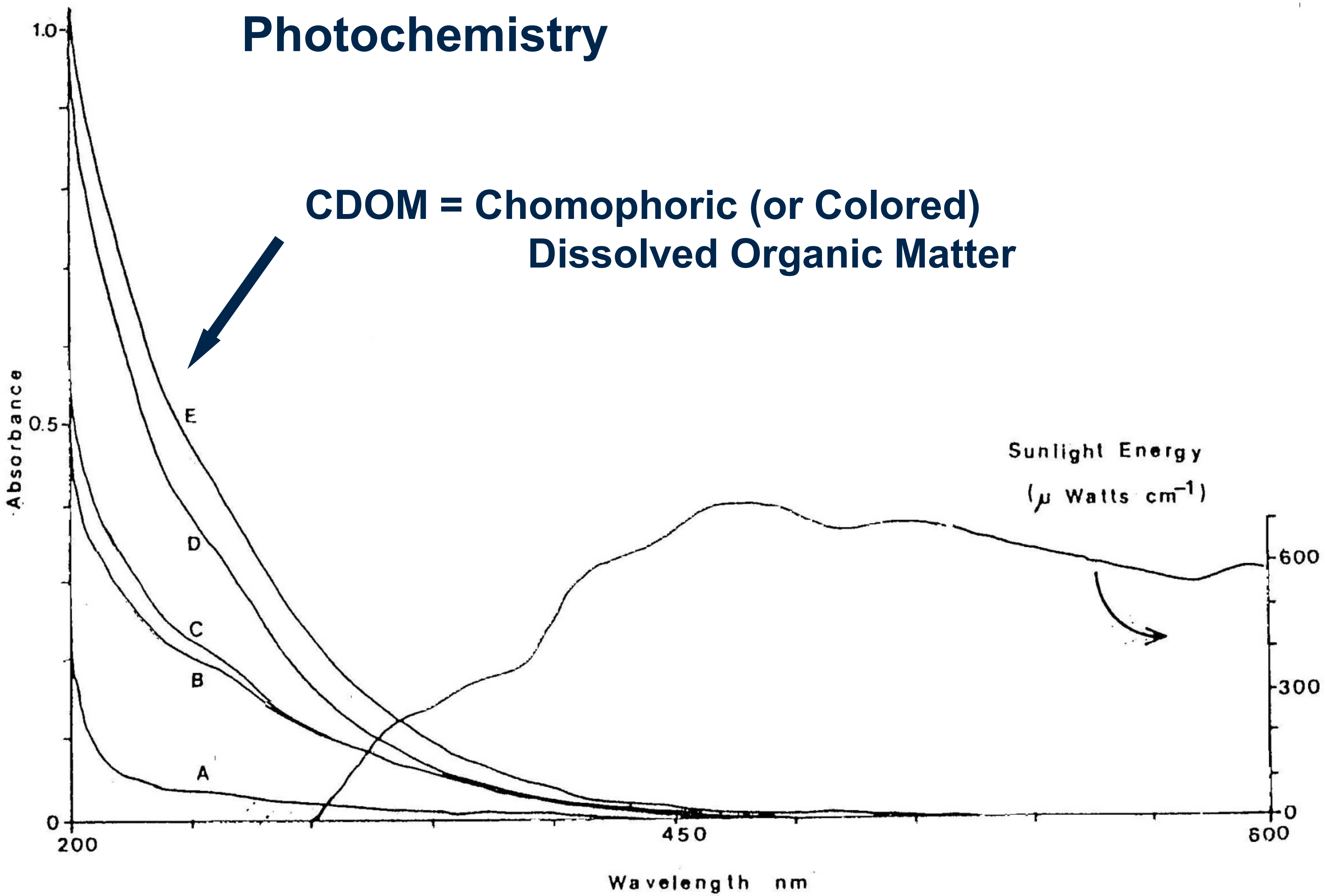


TABLE 10.2
Photoreactions of Organic Compounds

Chromophore	Products or effects
Humic, fulvic	1. Bleaching of absorption and fluorescence 2. Production of singlet oxygen 3. Fe(III) reduction 4. Release of soluble P 5. Oxidation of cumene via ROO and OH radicals 6. Oxidation of phenolic groups to ArO and formation of e^- and O_2^- 7. CO formation 8. H_2O_2 formation (via O_2^- ?)
Chlorophyll	Loss of chlorophyll
Vitamins	Loss of bioassay activity
Amino acids	?
Glycine	COOH C-14 loss, HCHO 1 formation
$CH_3SSCH_3CH_3S$	CH_3S
CH_3ICH_3	CH_3
Fatty acids	Particles, absorb., hydroperoxides
Aldehydes	RCO, R, CO

Millero, 1996

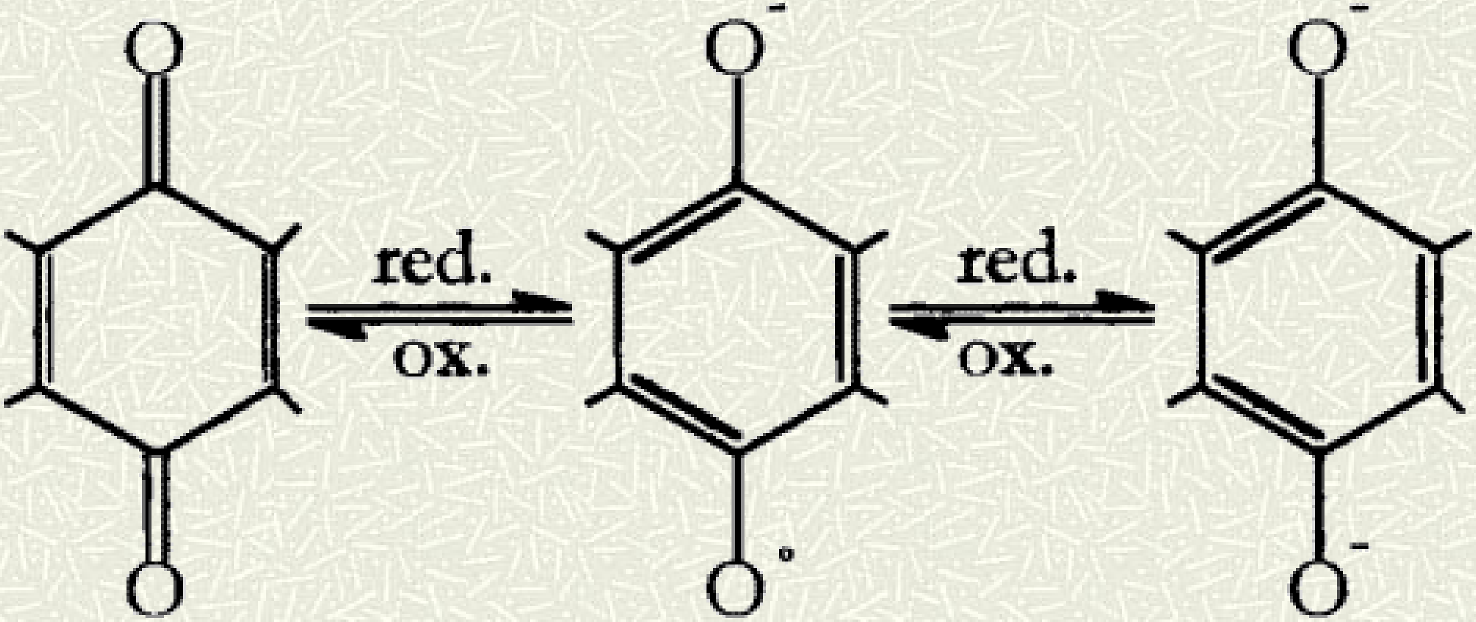
Photochemistry



CDOM = Chomophoric (or Colored) Dissolved 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}).

Quinone radical present in humic material



benzoquinone semiquinone hydroquinone

Scott, McKnight, Blunt-Harris, Kolesar & Lovely (1998) Environ. Sci. Technol. 32, 19

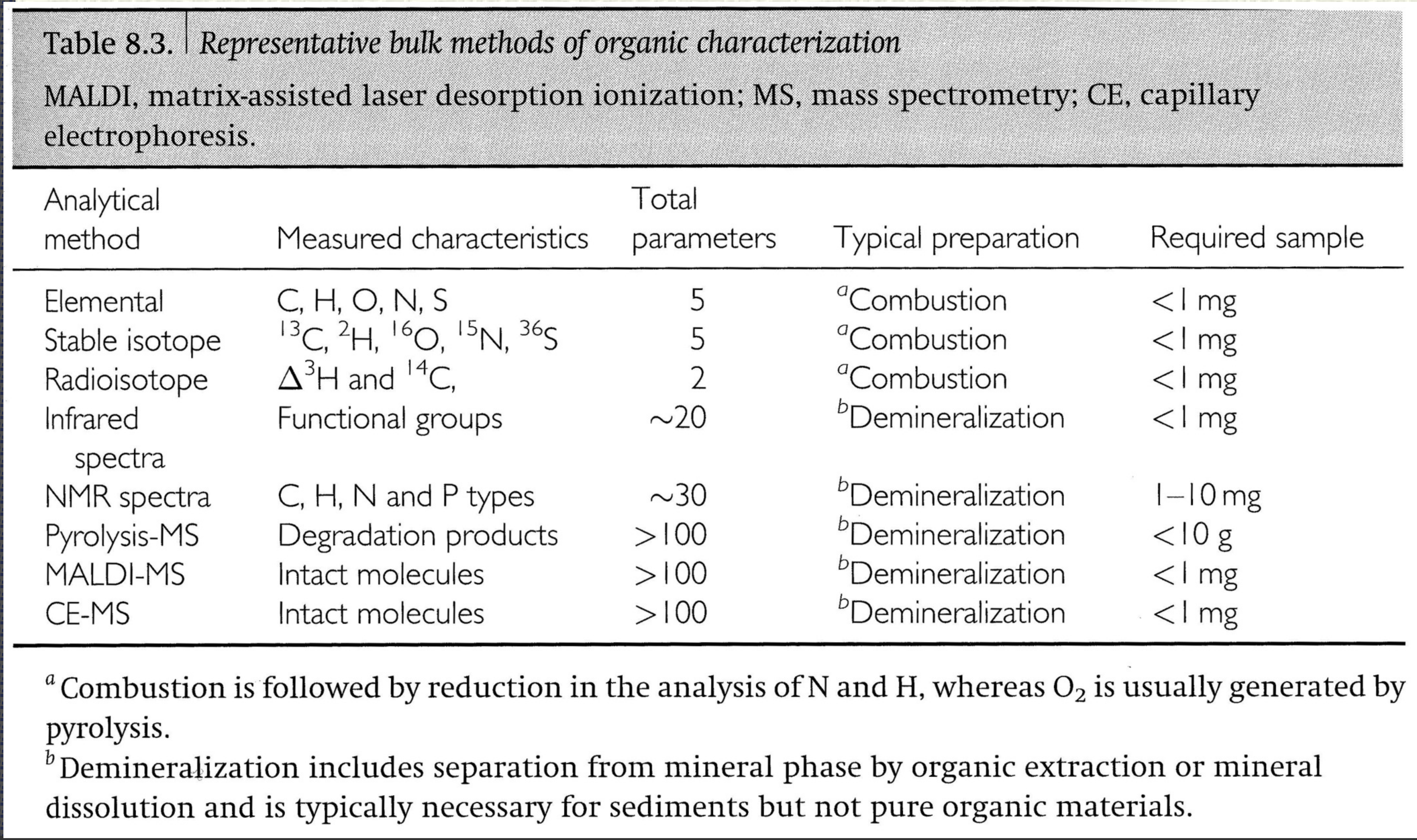


Table 8.3. *Representative bulk methods of organic characterization*

MALDI, matrix-assisted laser desorption ionization; MS, mass spectrometry; CE, capillary electrophoresis.

Analytical method	Measured characteristics	Total parameters	Typical preparation	Required sample
Elemental	C, H, O, N, S	5	[a]Combustion	<1 mg
Stable isotope	^{13}C, ^{2}H, ^{16}O, ^{15}N, ^{36}S	5	[a]Combustion	<1 mg
Radioisotope	Δ^{3}H and ^{14}C,	2	[a]Combustion	<1 mg
Infrared spectra	Functional groups	~20	[b]Demineralization	<1 mg
NMR spectra	C, H, N and P types	~30	[b]Demineralization	1–10 mg
Pyrolysis-MS	Degradation products	>100	[b]Demineralization	<10 g
MALDI-MS	Intact molecules	>100	[b]Demineralization	<1 mg
CE-MS	Intact molecules	>100	[b]Demineralization	<1 mg

[a] Combustion is followed by reduction in the analysis of N and H, whereas O_2 is usually generated by pyrolysis.

[b] Demineralization includes separation from mineral phase by organic extraction or mineral dissolution and is typically necessary for sediments but not pure organic materials.