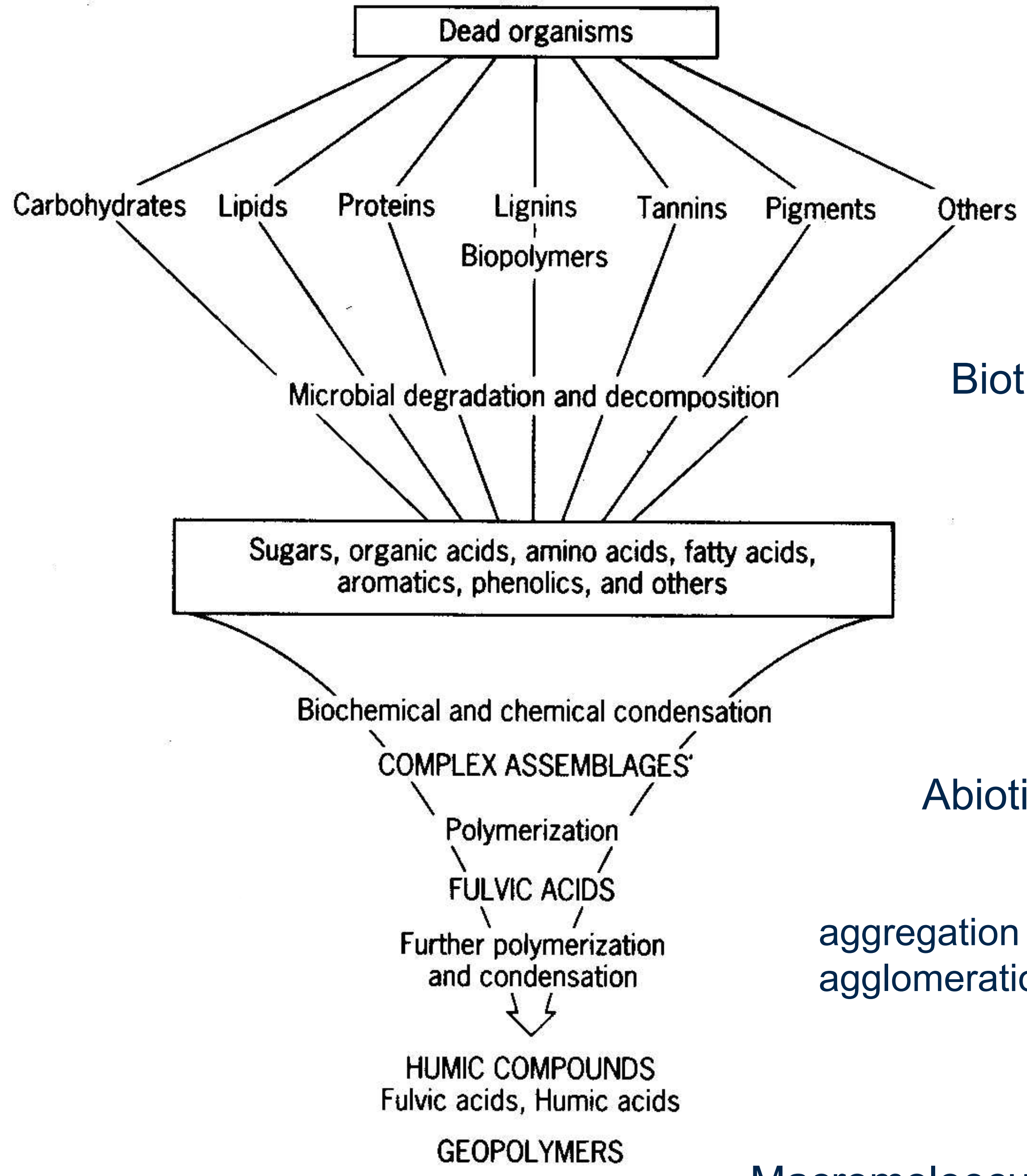
Chemical Oceanography
Organics IV

Dr. David K. Ryan
Department of Chemistry
University of Massachusetts Lowell
&
Intercampus Marine Science (IMS) Program

http://faculty.uml.edu/david_ryan/84.653



Biotic

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

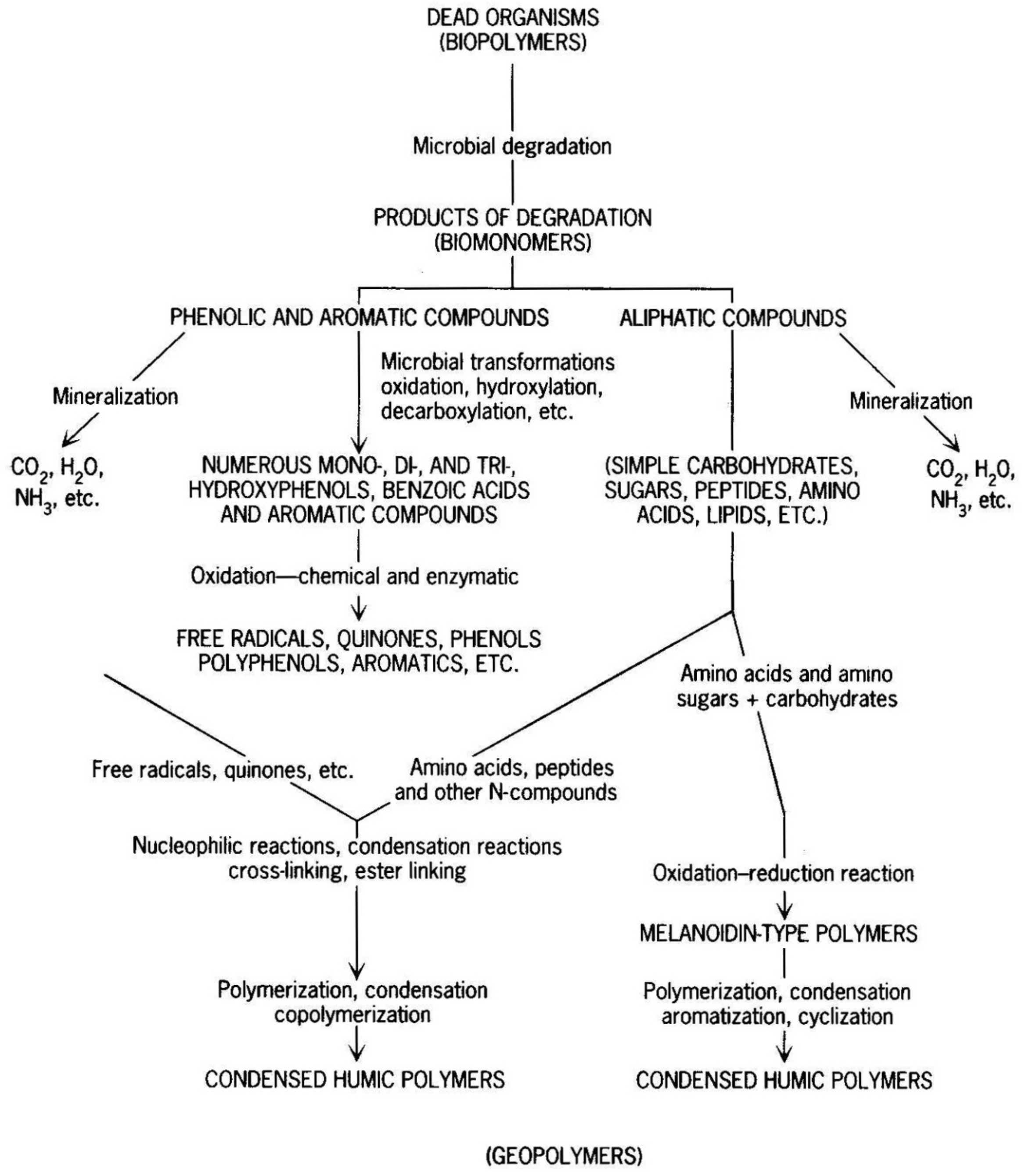
Humification of Organic Matter (possible scheme)

Abiotic

aggregation
agglomeration

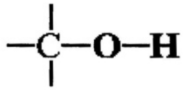
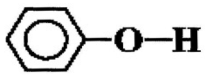
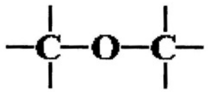
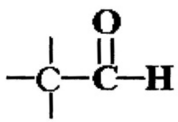
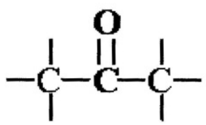
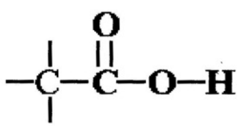
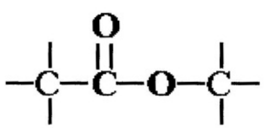
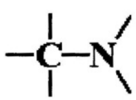
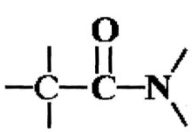
Libes, 1992

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

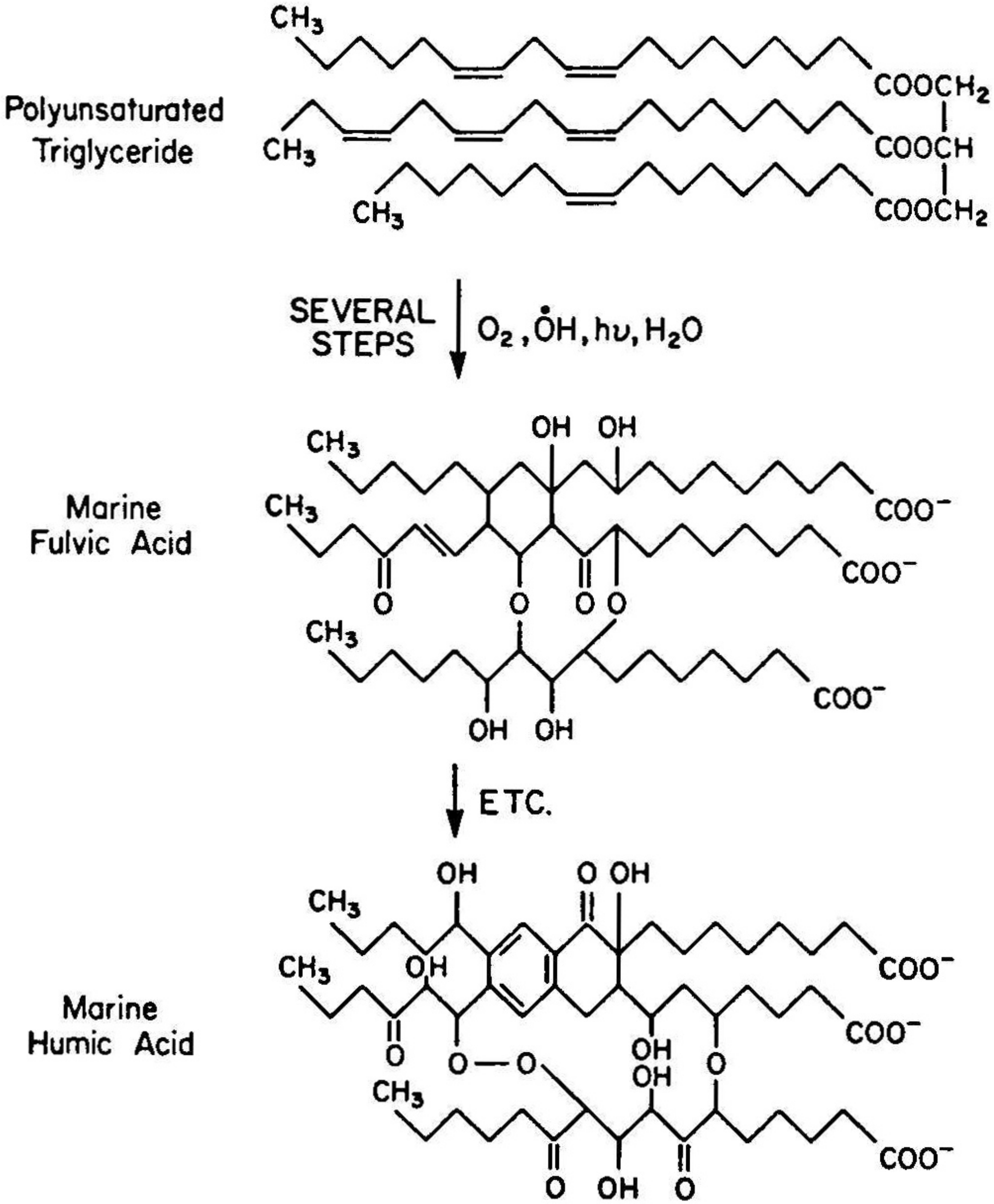
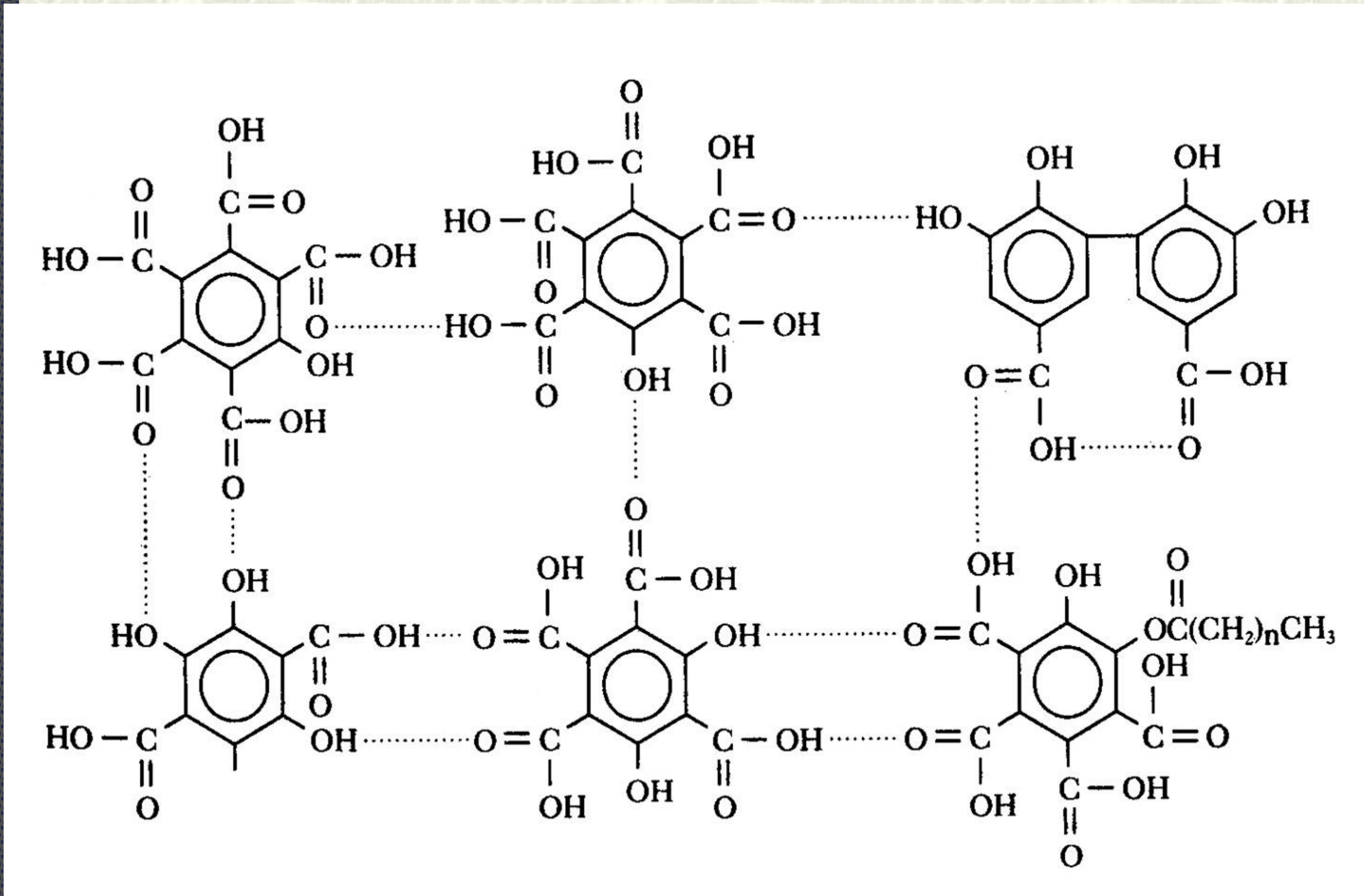
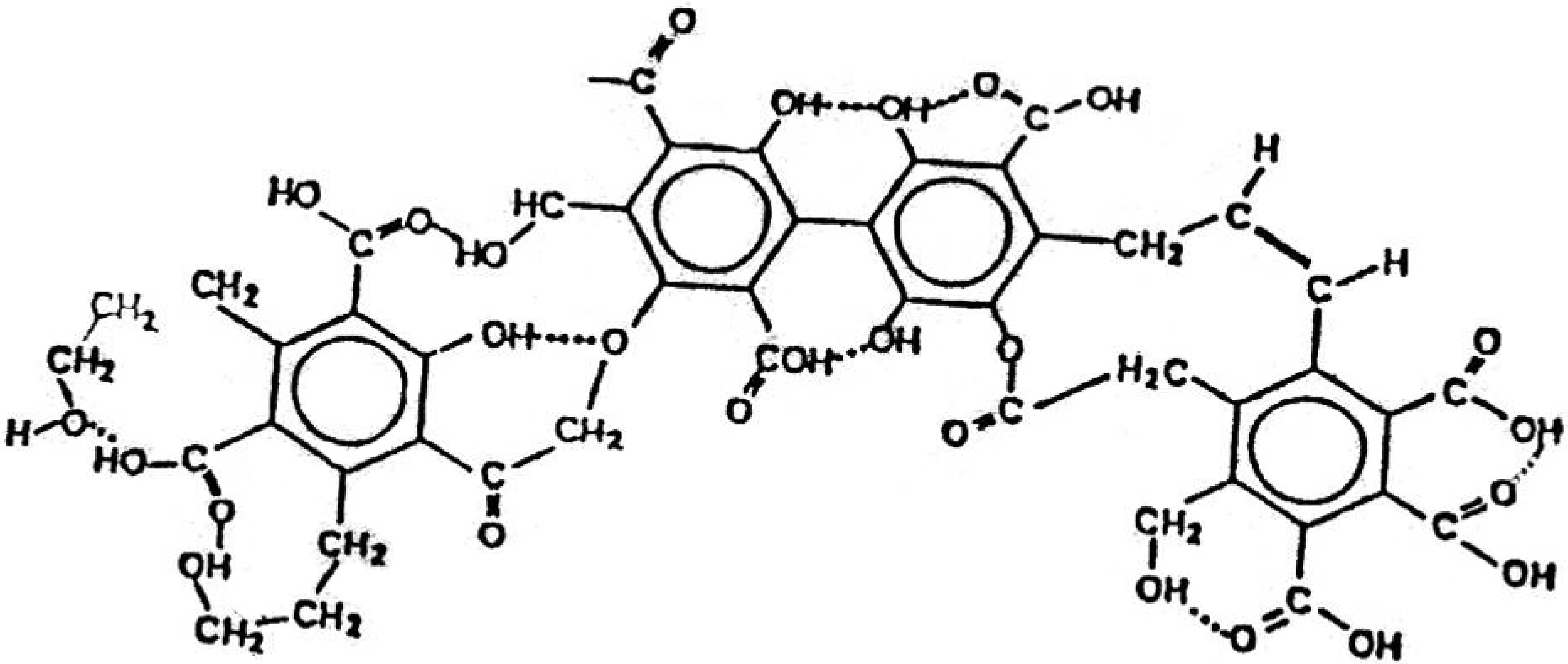


Figure 6.13 A possible pathway for the formation of marine humic acids from a triglyceride. From Harvey et al., 1983.

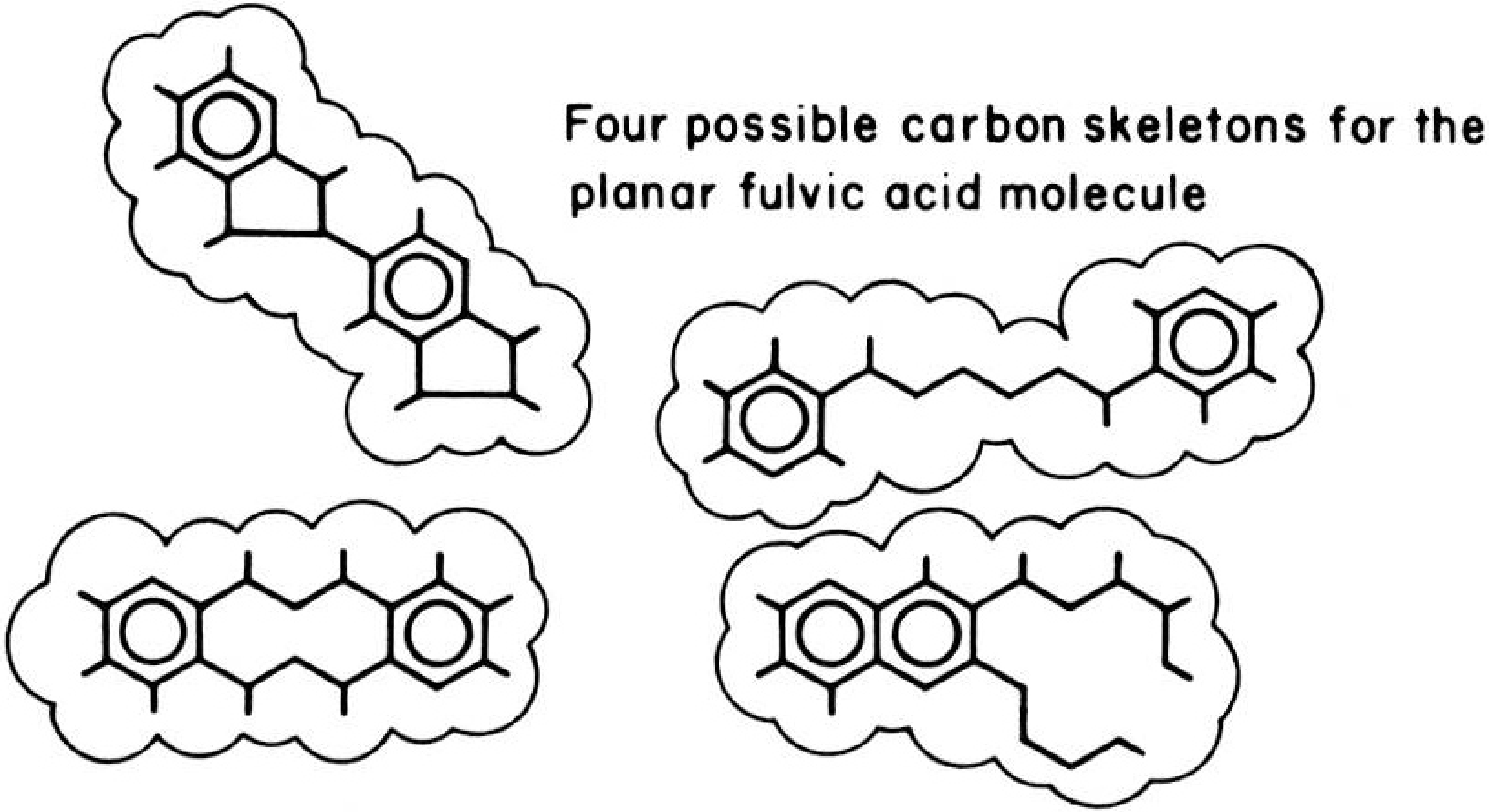
Morel & Hering, 1993
See also
Emerson & Hedges
Figure 8.11 & 8.12



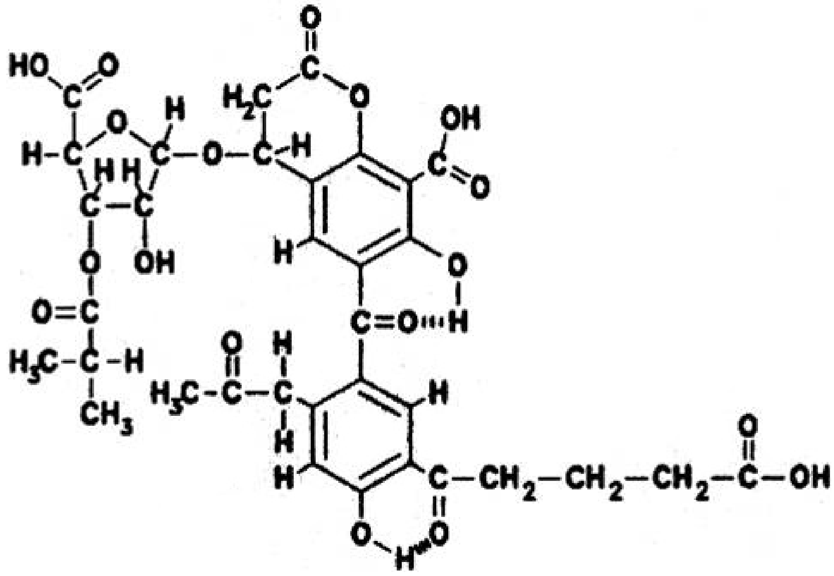
Humic Structure Proposed by Schnitzer (Rashid 1985)

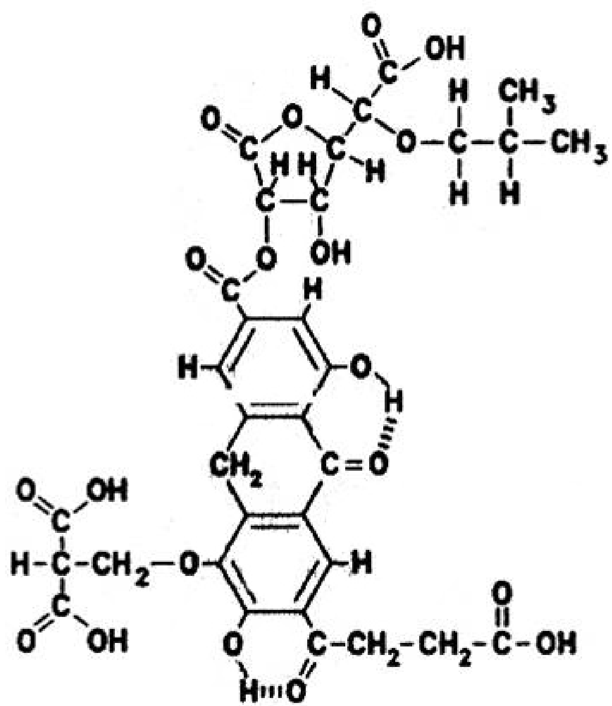


Structure Attributed to Gamble et al. (1985)

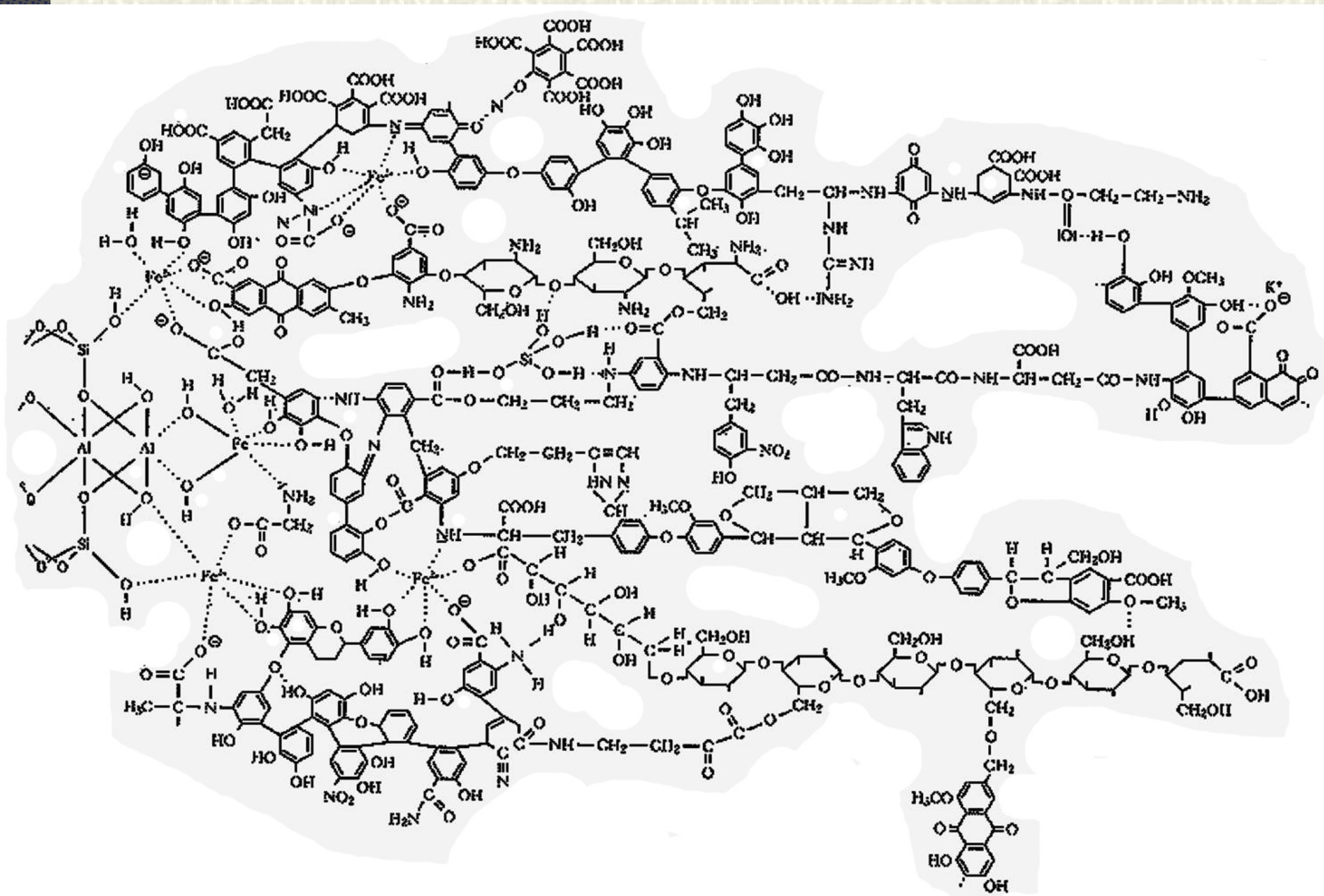


Morel & Hering (1993) Based on Aiken et al. (1985)

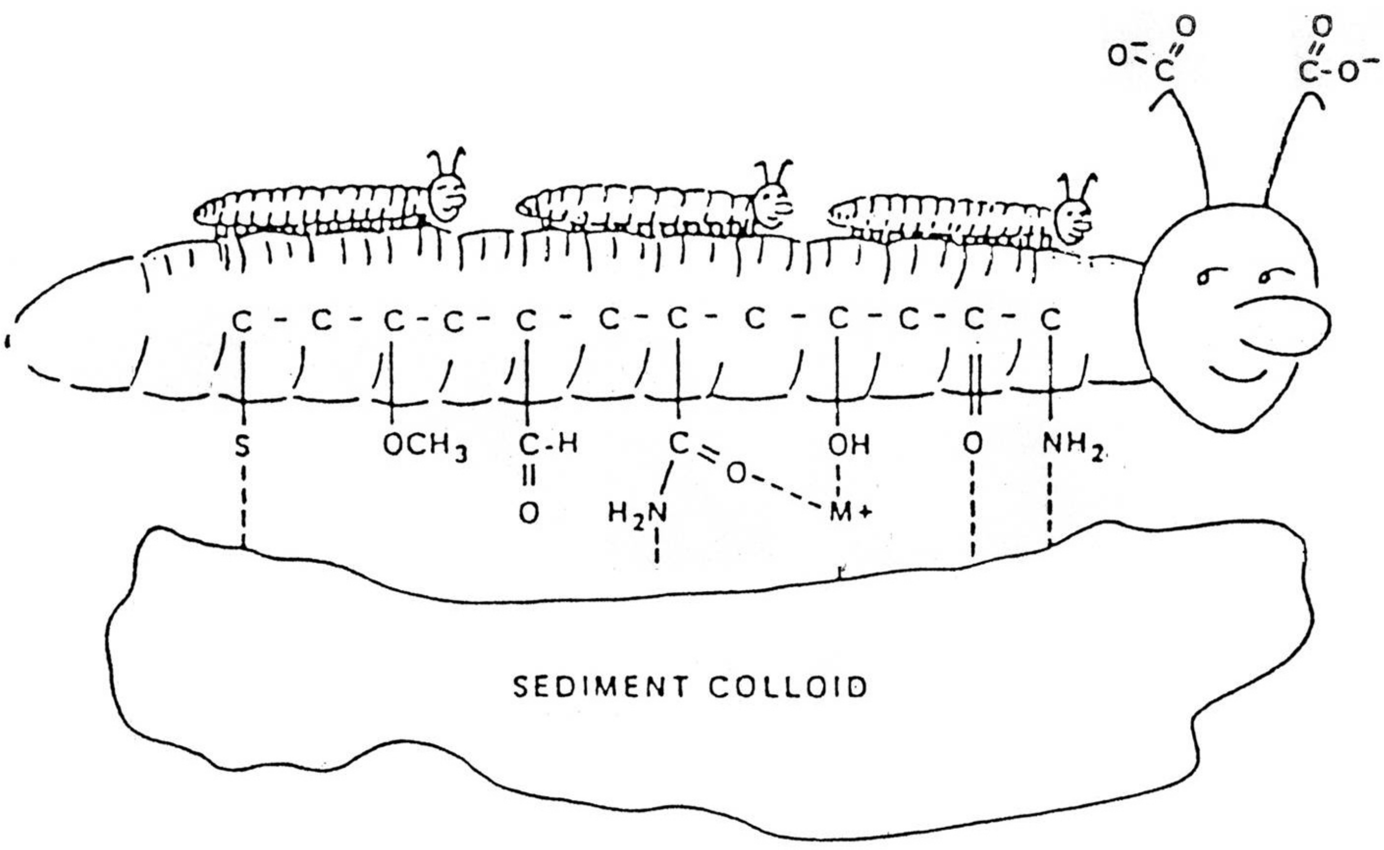




Possible Structural Units Set Forth by Averett, Leenheer, McKnight & Thorn (1989) From Morel & Hering, 1993

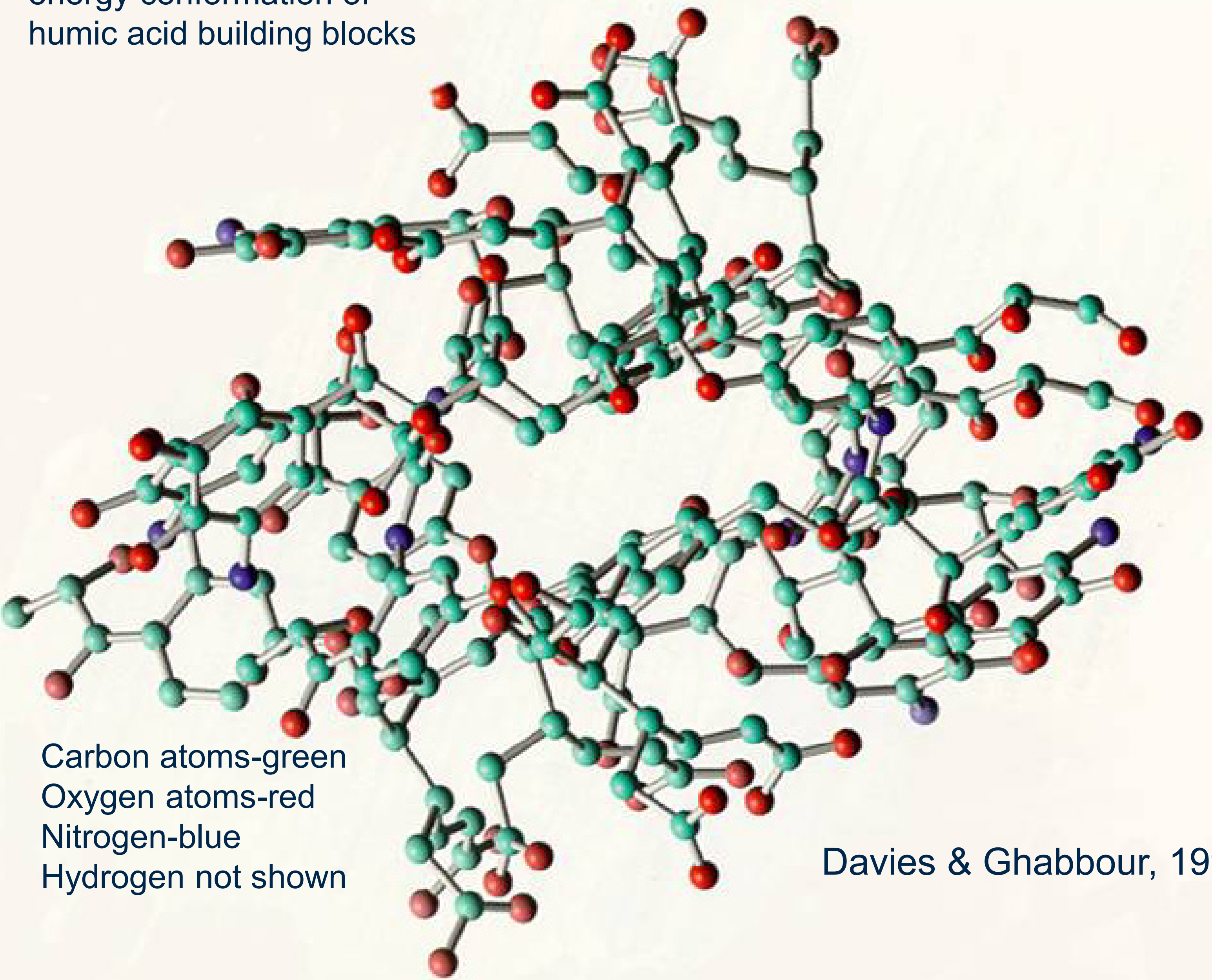


Kleinhempel reprinted from Albrecht Thaer Archiv (1970)



Organic Solute Macromolecule (ORSMAC) Leenheer 1985)

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

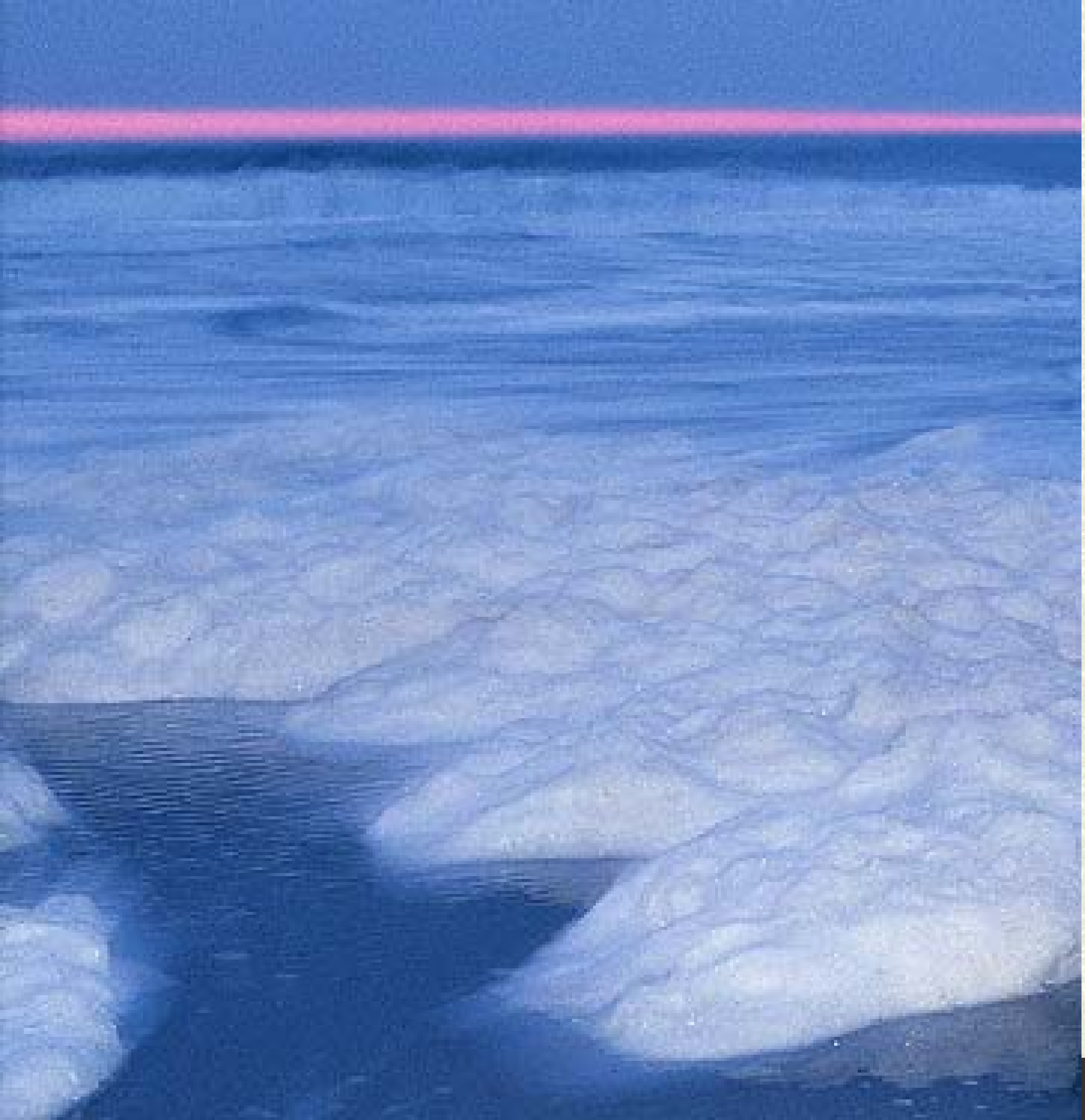


Carbon atoms-green
Oxygen atoms-red
Nitrogen-blue
Hydrogen not shown

Davies & Ghabbour, 1999

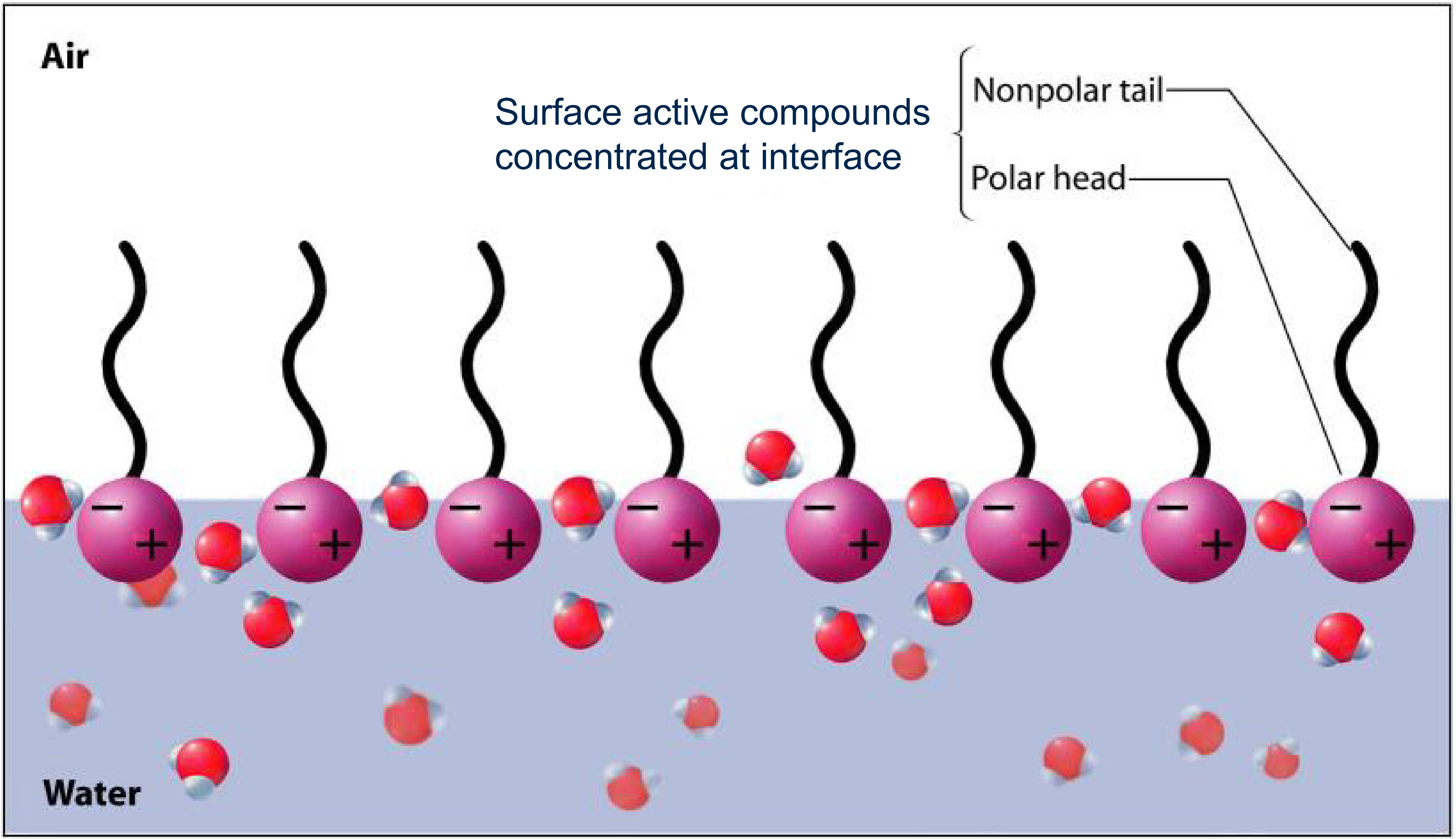
Importance of Humic Materials

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



Sea Foam caused by naturally occuring surface active agents

Air-Sea Interfacial Chemistry



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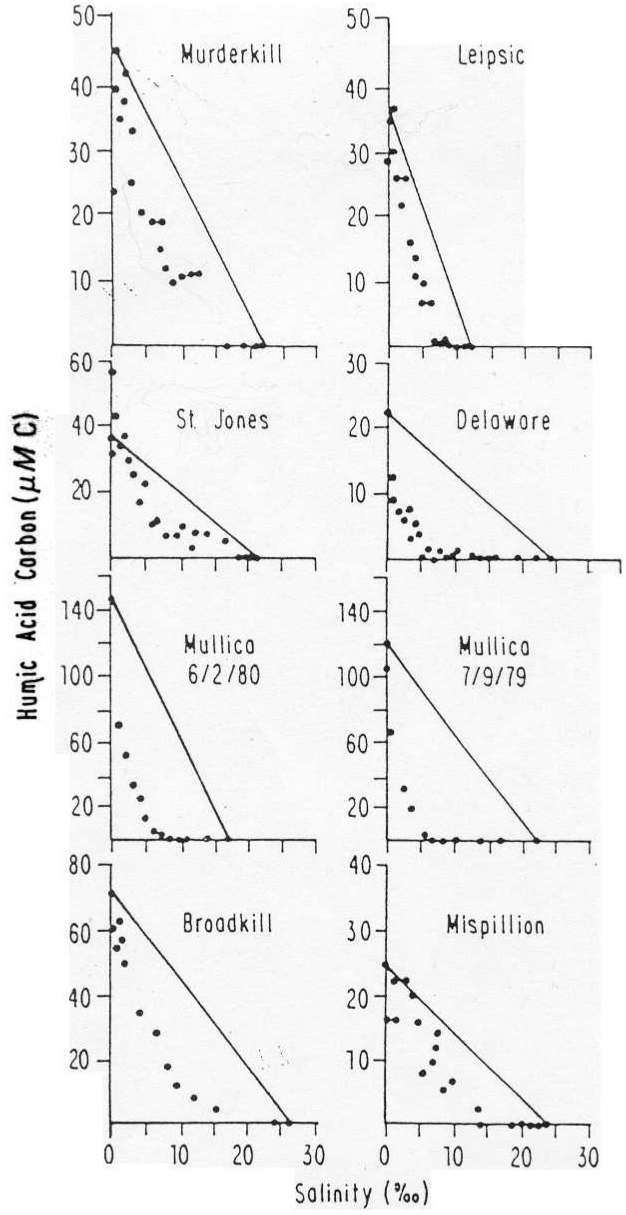

Figure 3. Humic acid carbon as a function of salinity. The standard error of the mean is 5%.

Fox, 1983

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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

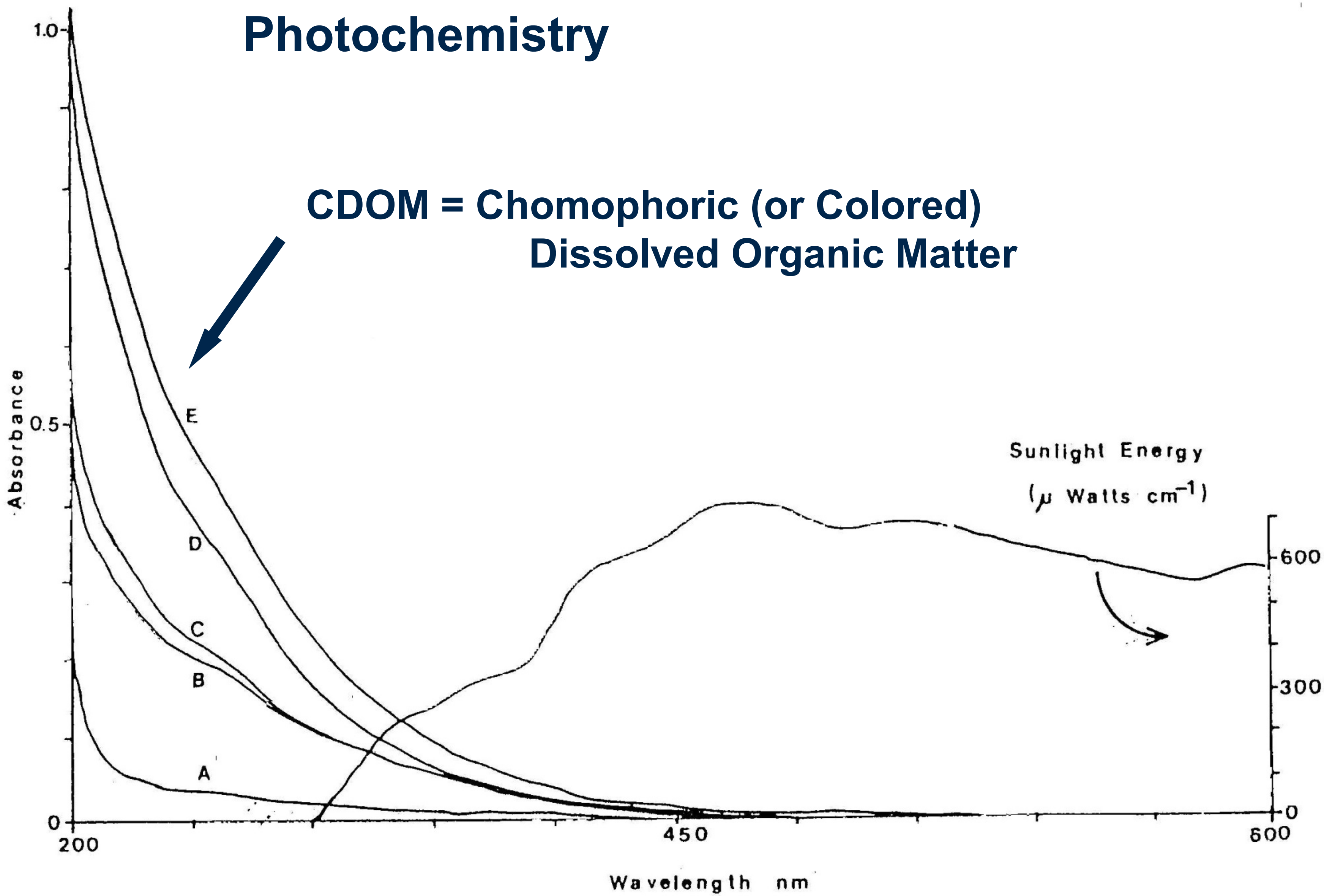

Figure 1. Absorption spectra (pathlength of 1 cm) of several waters and a generalized surface solar energy distribution (adapted from ref. 8). (DOC of waters: A = 3.0, B = 7.8, C = 13.4, D = 13.4, E = 15.4 mg L^{-1}).

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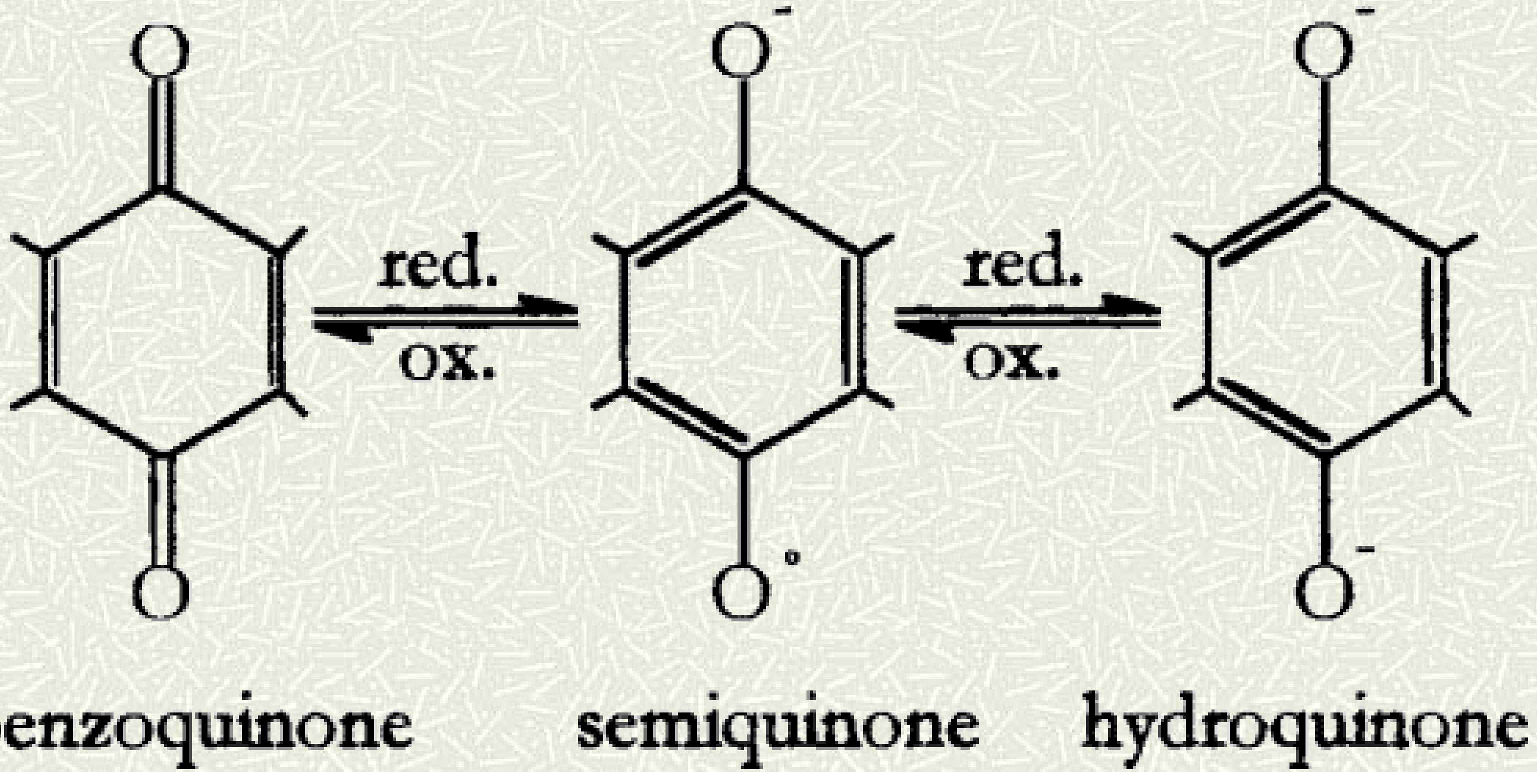
Quinone radical present in humic material



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

Importance of Humic Materials

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Humics involved in many reduction reactions

- Cr(IV) to Cr(III)
- Fe(III) to Fe(II)
- Hg(II) to Hg^o
- As, Se and V species

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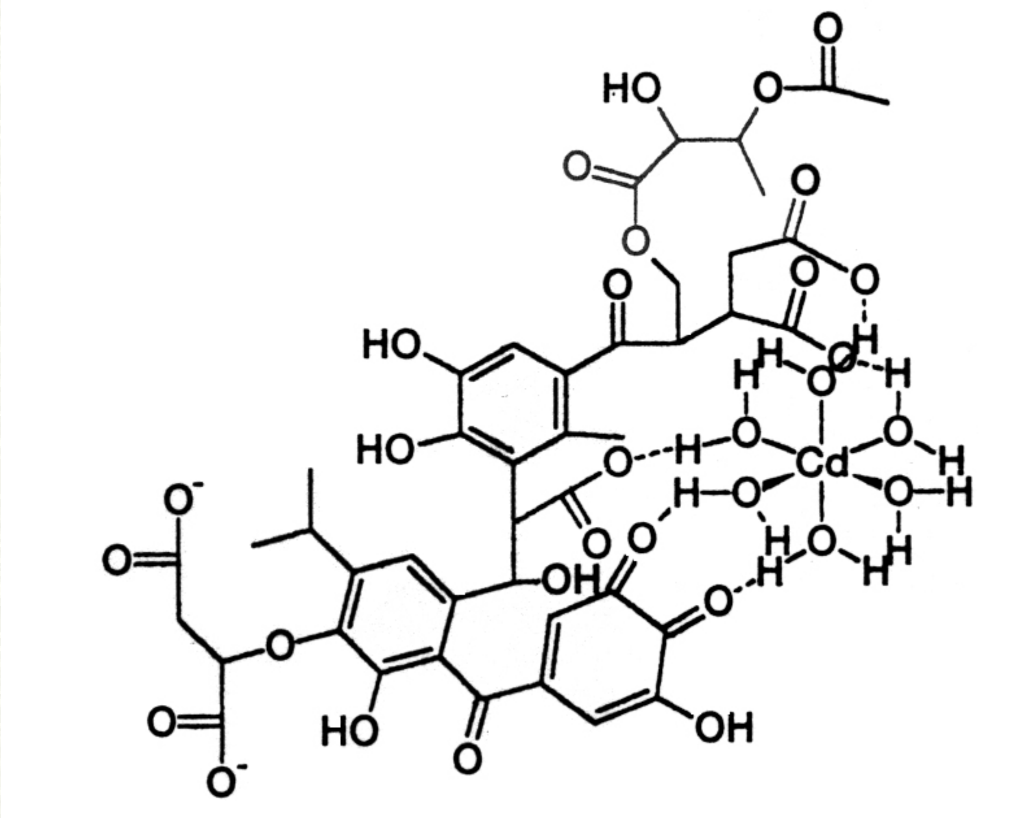
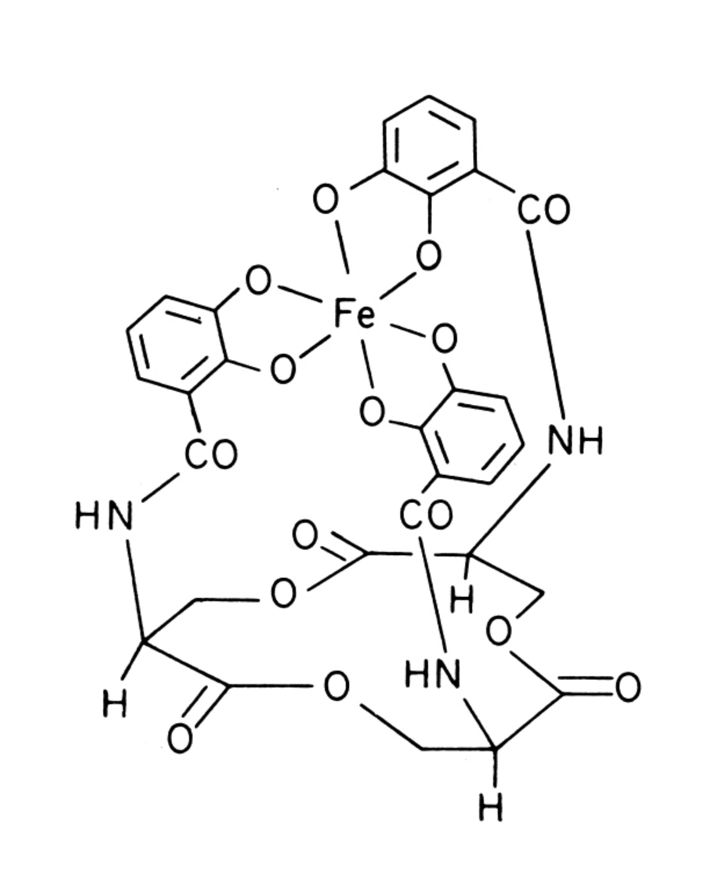
Metal Complexation by Humic Materials



Leenheer et al. (1998)



Morel (1983)

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Humic material will aggregate & may“salt out” when it binds a cation

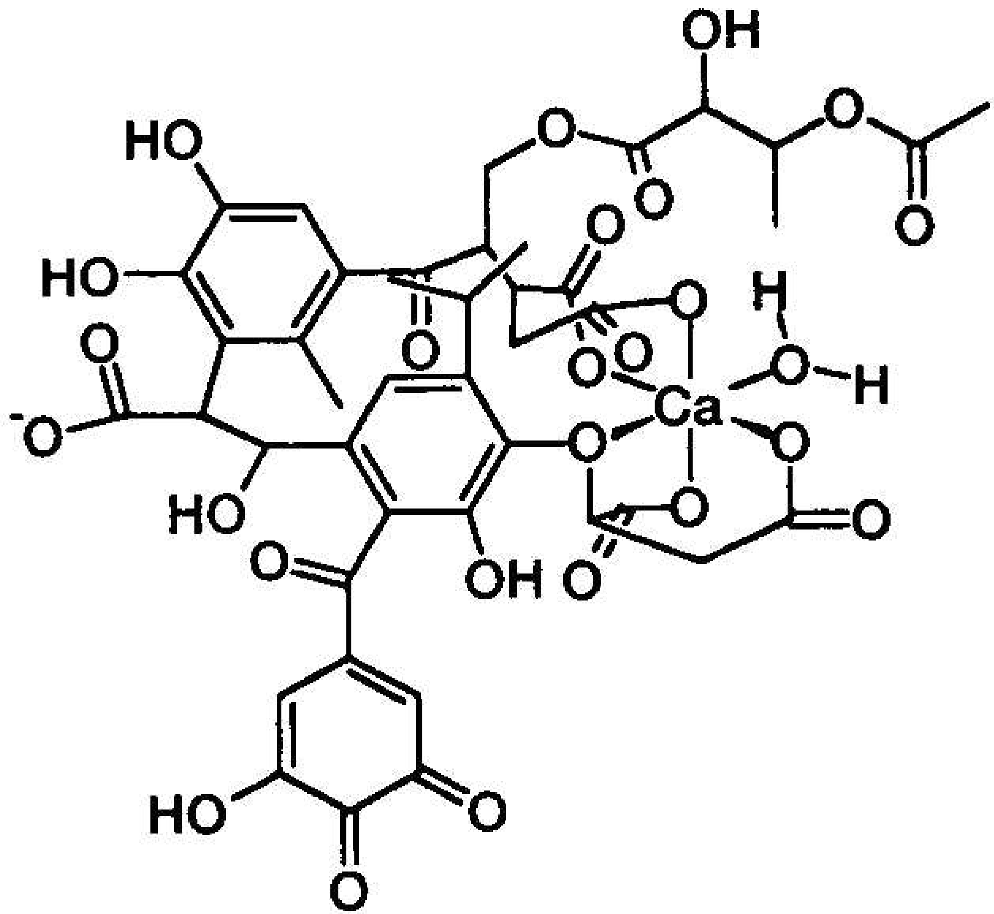

FIGURE 6. Structural model of a calcium inner-sphere complex

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

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Influence Transport
Bind Metals & Organic Pollutants
Terminal Electron Acceptor for Bacteria (TEA)

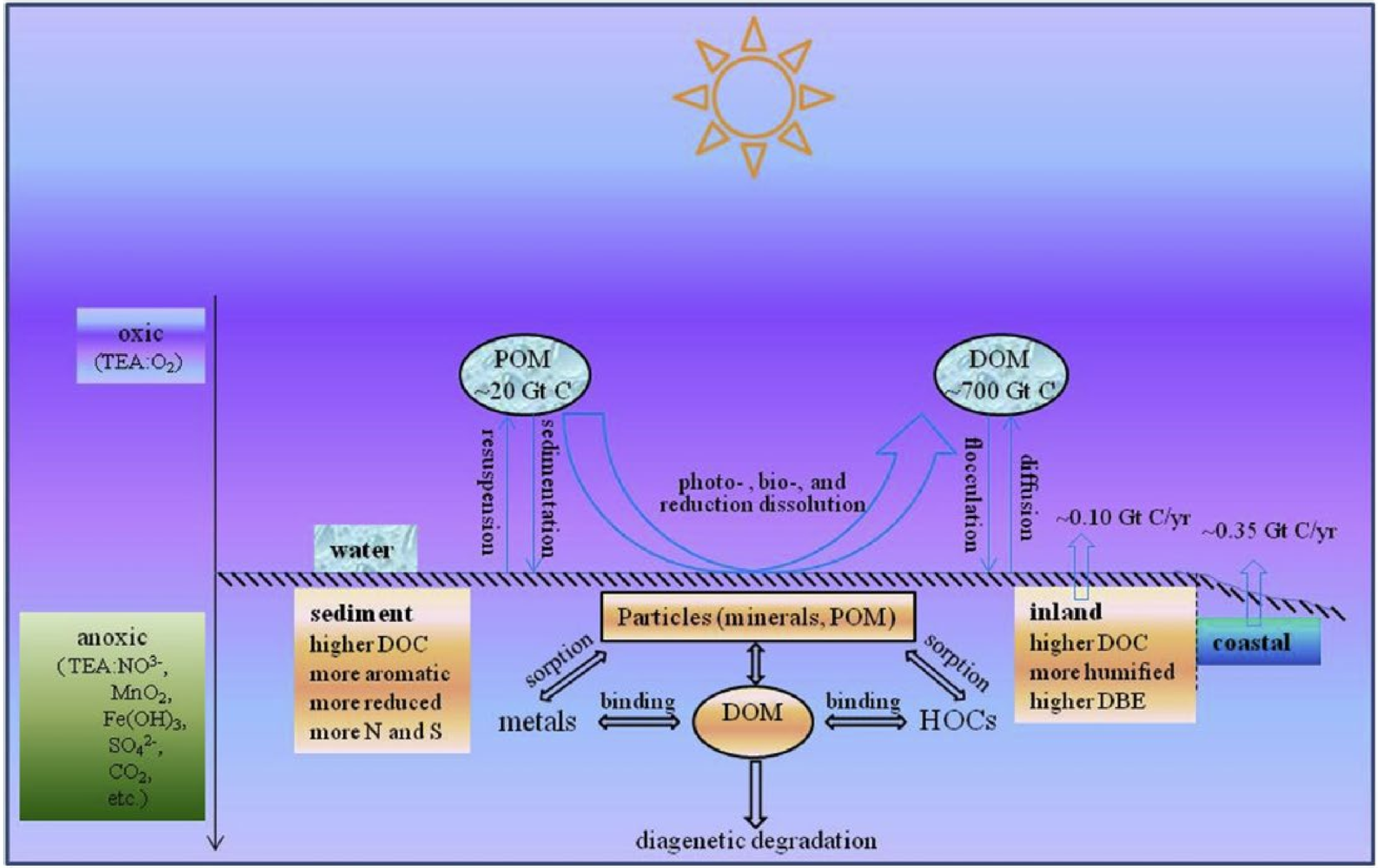


Fig. 1 – Conceptual sketch of DOM flux and biogeochemical interactions in sediments. Carbon stock data regarding particulate and dissolved organic matter (POM and DOM) are from Jiao et al. (2010). Benthic flux estimation data for inland and coastal environments from Yang et al. (2014) and Burdige et al. (1999), respectively. Anoxic status may be above or below sediment depending on different ecosystems' situation. TEA: terminal electron acceptor. (Chen & Hur 2015)

Maturation and Fossilization are terms that refer to the formation of fossil fuels (coal, petroleum) from plant and animal material (biomolecules)

The overall process can be split into two or three major parts:

Marine ➡ Diagenesis, Catagenesis, Metagenesis

Terrestrial ➡ Humification, Coalification

May 1981, Volume 212, Number 4496

SCIENCE

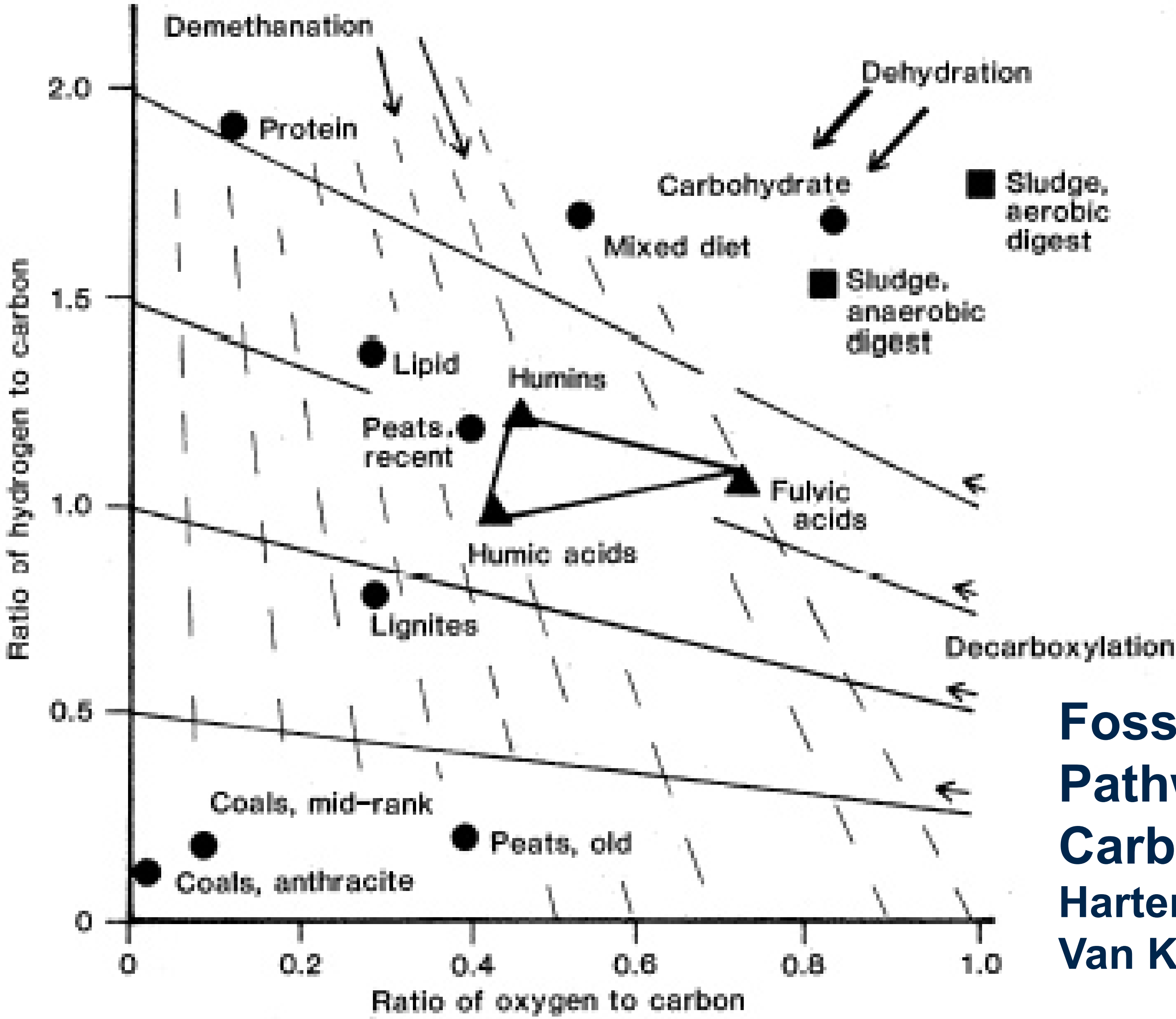
Sludge Decomposition and Stabilization

Roy Hartenstein

of sludge decomposition and stabilization can be enhanced, to discuss the highly probable consequences of sludge stabilization in light of the basic information, and to suggest procedures for evaluating the sludge stabilization process. As a starting point, it is necessary to describe the fossilization pathway of the carbon cycle.

The Fossilization Pathway of the Carbon Cycle

Kerogens, coals, and petroleum oils are the earth's major fossil fuels; they



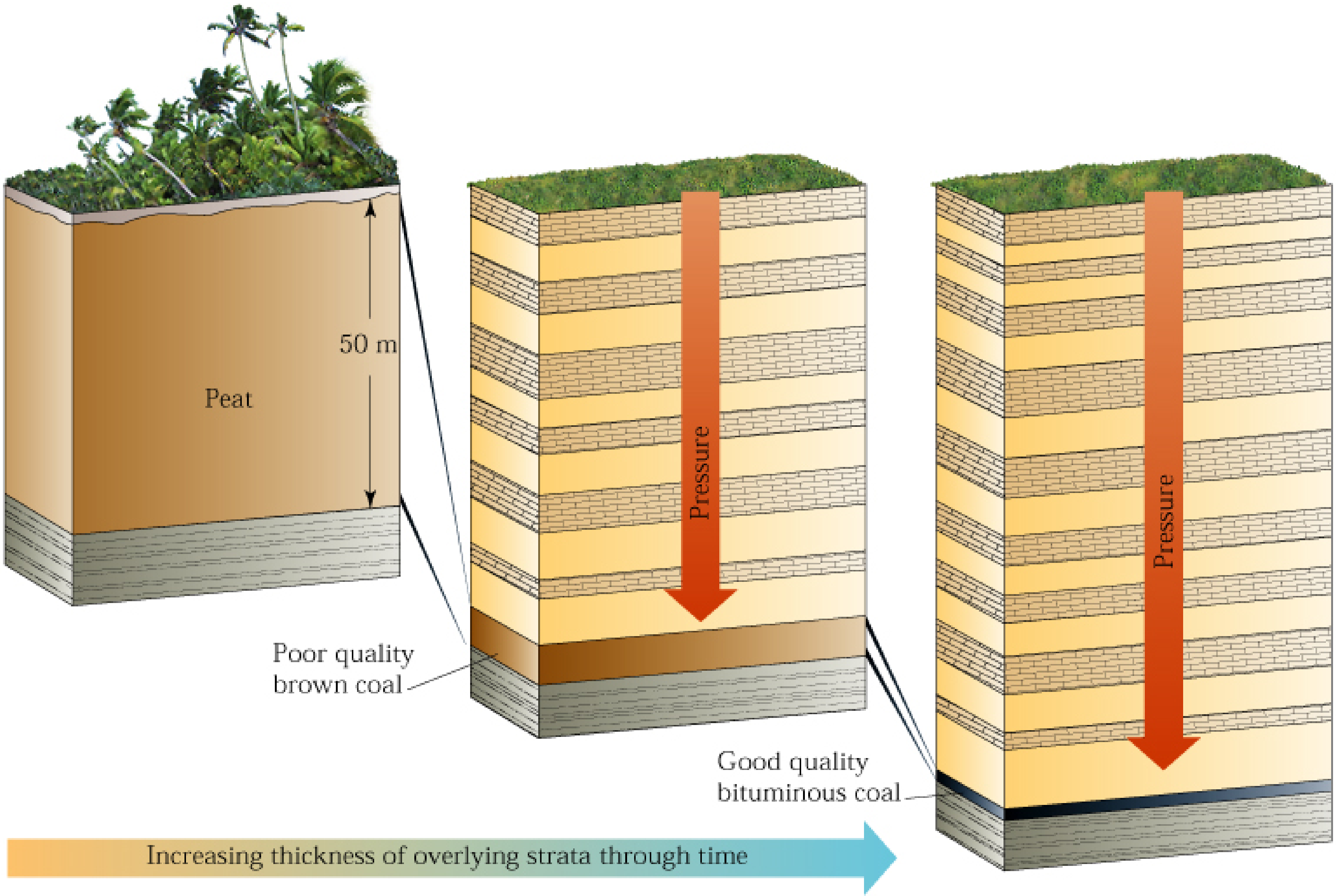
Fossilization Pathway of the Carbon Cycle

Hartenstein, 1981

Van Krevelen plot

Table1. Analysis of organic Materials in Fossilization pathway (Percent dry wt.)									
	Carbo-hydrate	Protein	Fat	Mixed Diet	Sludge (act.)	Fulvic Acid	Humic Acid	Peat (old)	Coal (mid.)
C	44	58	75	53	32	47	59	59	85
H	6	7	12	7	4	4.4	5	6	5
N		11		2		2	3	2	1.5
O	49	23	12	36	37	46	34	31	8

from Hartenstein, 1981


50 m
Peat
Pressure
Pressure
Poor quality
brown coal
Good quality
bituminous coal
Increasing thickness of overlying strata through time

Libes, 1992 "…diagenetic changes …occur under anoxic conditions at temperatures less than 50 ^{o}C."

Pergamon

Applied Geochemistry, Vol. 11, pp. 711–720, 1996

0883–2927/96 $15.00 + 0.00

Early diagenesis of organic matter in recent Black Sea sediments: characterization and source assessment

Abstract—The organic matter in 9 recent (not more than 250 years old) and 'organic-rich' sediments from the southern Black Sea shelf and upper slope have been characterized semi-quantitatively by Pyrolysis/Gas Chromatography/Mass Spectrometry (PY/GC/MS) and ^{13}C Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (CPMAS-NMR) spectrometry. The organic matter of 7 of the studied sediments was found to be ligno-carbohydrate with a proteinaceous component, one sediment appeared to contain oxidized coal dust and one contained thiophenes in association with pyrite. The ligno component is derived from grasses and soft wood lignin. Material entrapped in an anoxic environment contained the highest proportions of carbohydrate and protein. All the samples had suffered diagenesis as is generally shown by the attachment of carboxyl groups and the removal of methoxyl groups. The evidence suggests that diagenesis occurred whilst the particles traversed the oxic water column.

Sediment Diagenesis includes more than Organic Matter Transformations – Many redox processes occur

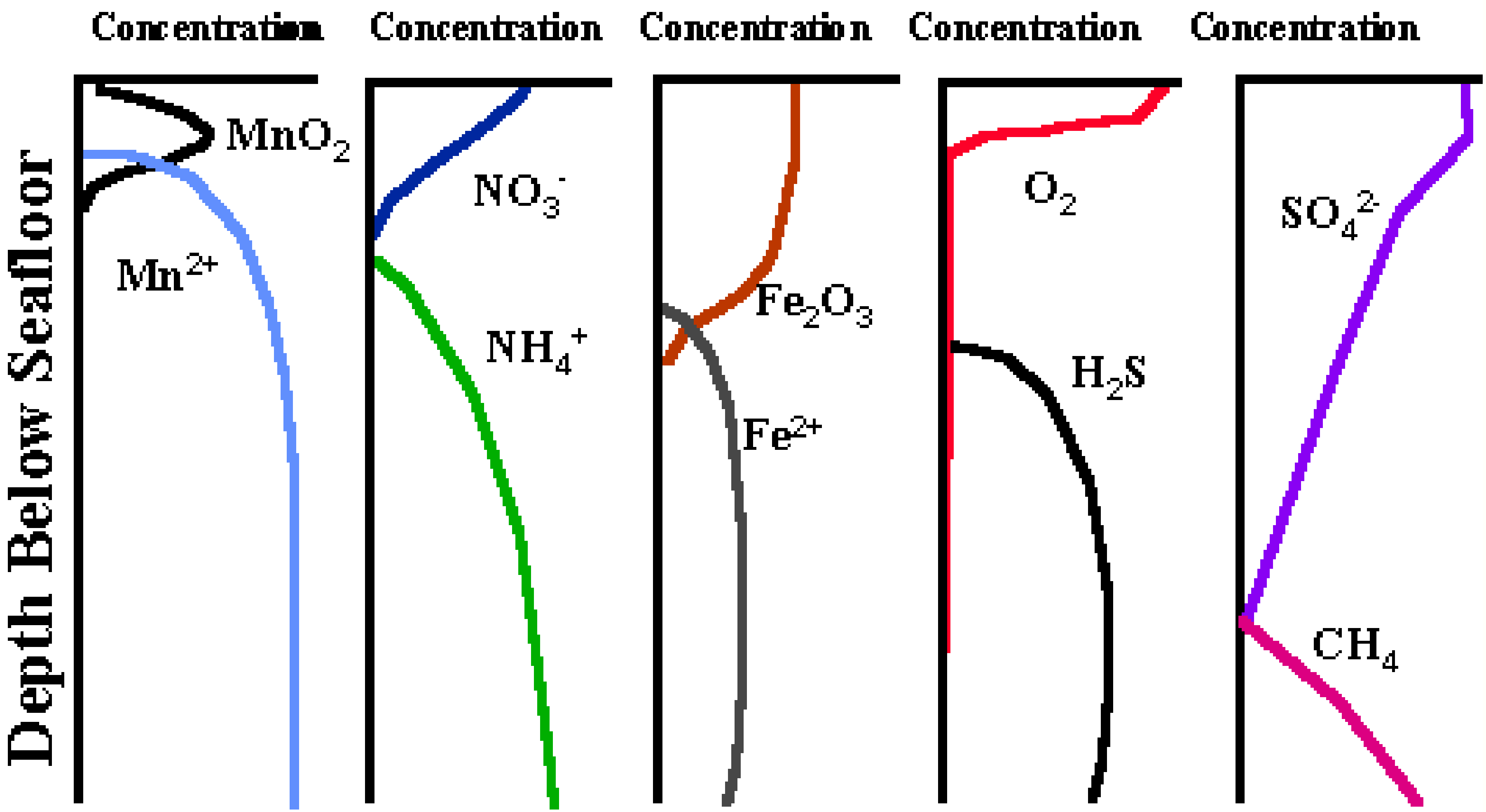
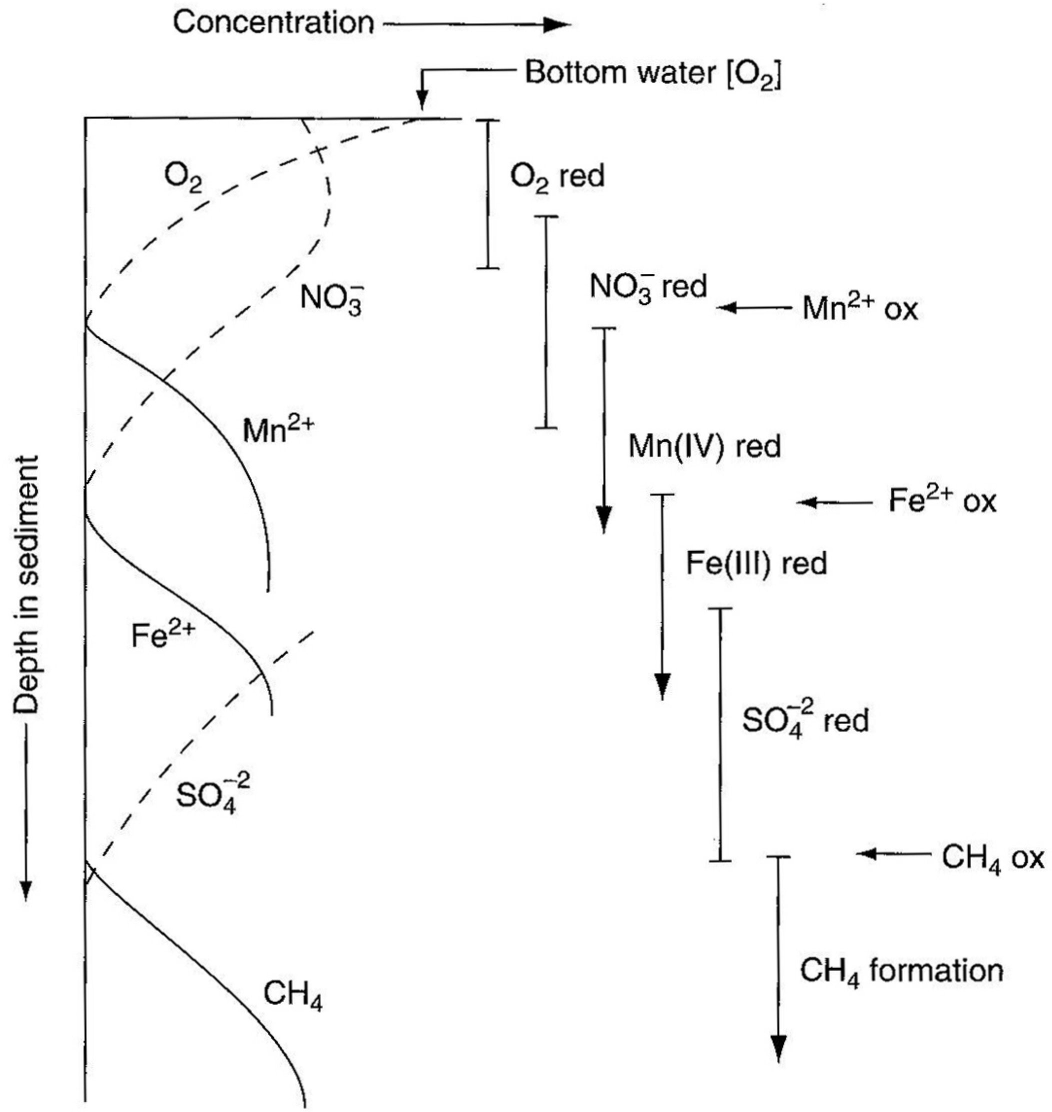


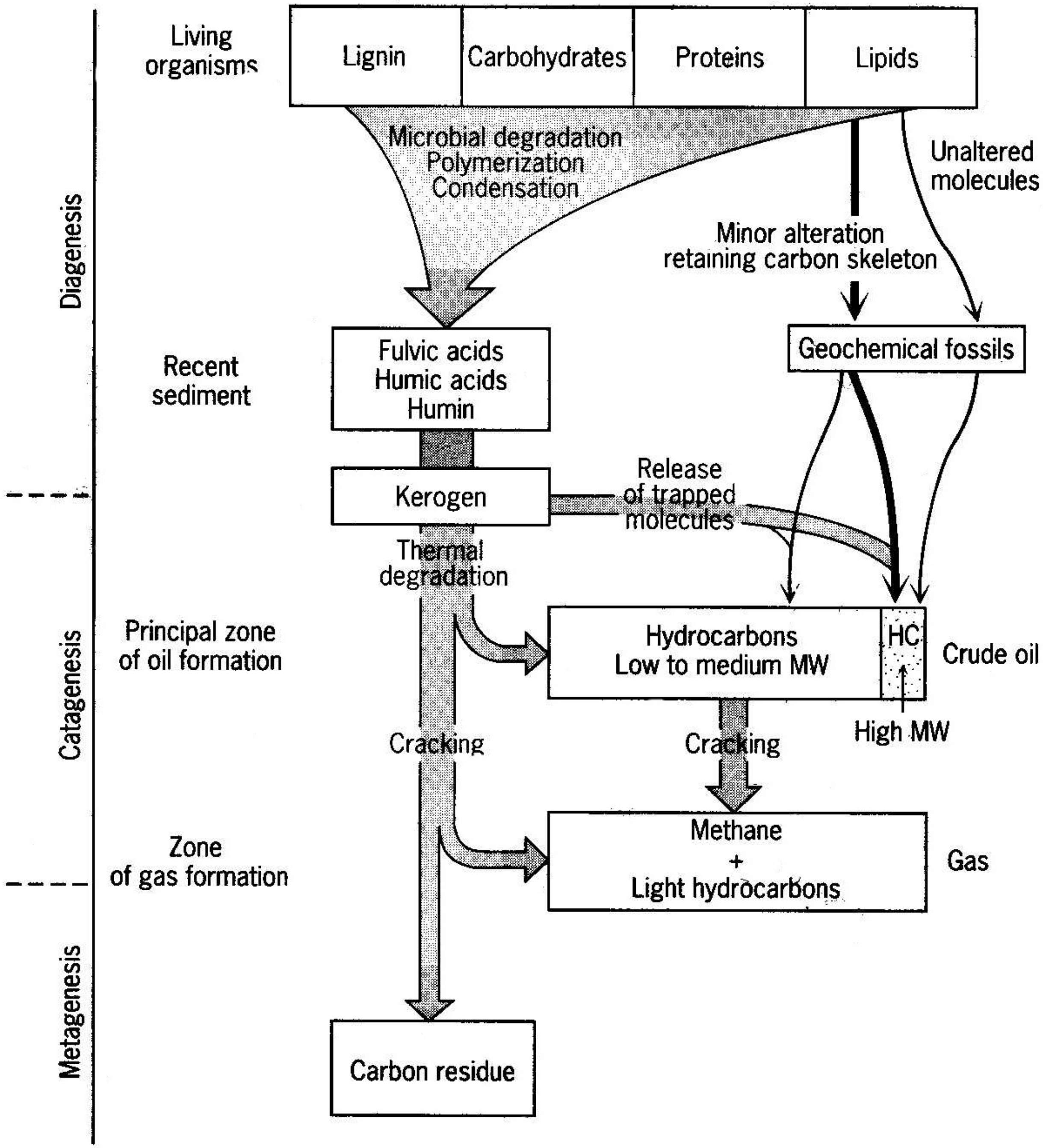
Table 12.2. *Stoichiometry of organic matter oxidation reactions*

Redfield ratios for *x*, *y* and *z* are 106, 16, 1.

Redox process	Reaction
Aerobic respiration	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + (x+2y)O_2 \rightarrow$ $xCO_2 + (x+y)H_2O + yHNO_3 + zH_3PO_4$
Nitrate reduction	$5(CH_2O)_x(NH_3)_y(H_3PO_4)_z + 4xNO_3^- \rightarrow$ $xCO_2 + 3xH_2O + 4xHCO_3^- + 2xN_2 + 5yNH_3 + 5zH_3PO_4$
Manganese reduction	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + 2xMnO_2(s) + 3xCO_2 + xH_2O \rightarrow$ $2xMn^{2+} + 4xHCO_3^- + yNH_3 + zH_3PO_4$
Iron reduction	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z + 4xFe(OH)_3(s) + 7xCO_2 \rightarrow$ $4xFe^{2+} + 8xHCO_3^- + 3xH_2O + yNH_3 + zH_3PO_4$
Sulfate reduction	$2(CH_2O)_x(NH_3)_y(H_3PO_4)_z + xSO_4^{2-} \rightarrow$ $xH_2S + 2xHCO_3^- + 2yNH_3 + 2zH_3PO_4$
Methane production	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z \rightarrow$ $xCH_4 + xCO_2 + 2yNH_3 + 2zH_3PO_4$

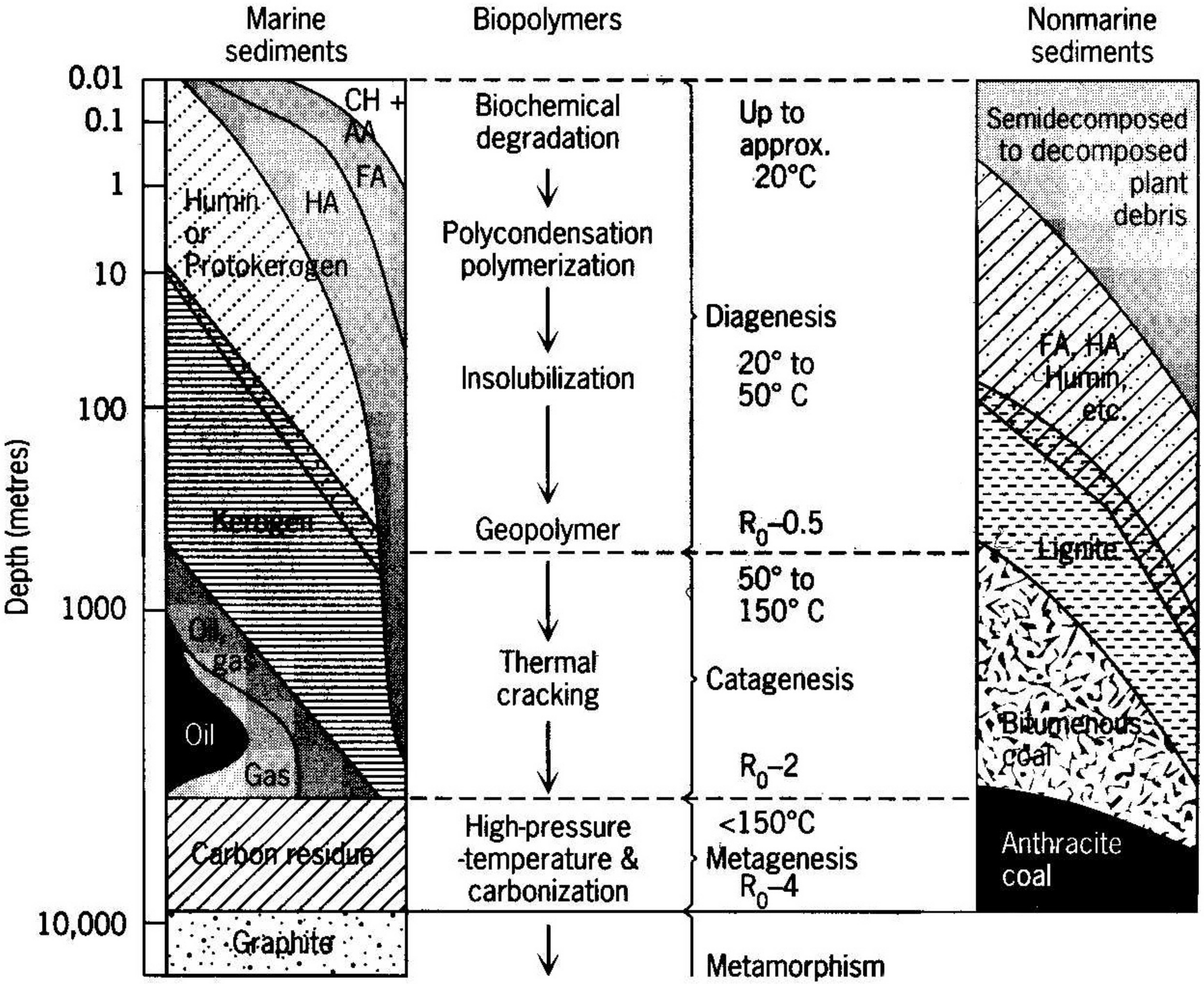
Figure 12.1. A schematic representation of the porewater profiles that have been observed to show the sequential use of electron acceptors during organic matter degradation. Modified from Froelich *et al.* (1979).





Petroleum Maturation Process

Libes, 1992



Evolution of Fossil Fuels

Libes, 1992

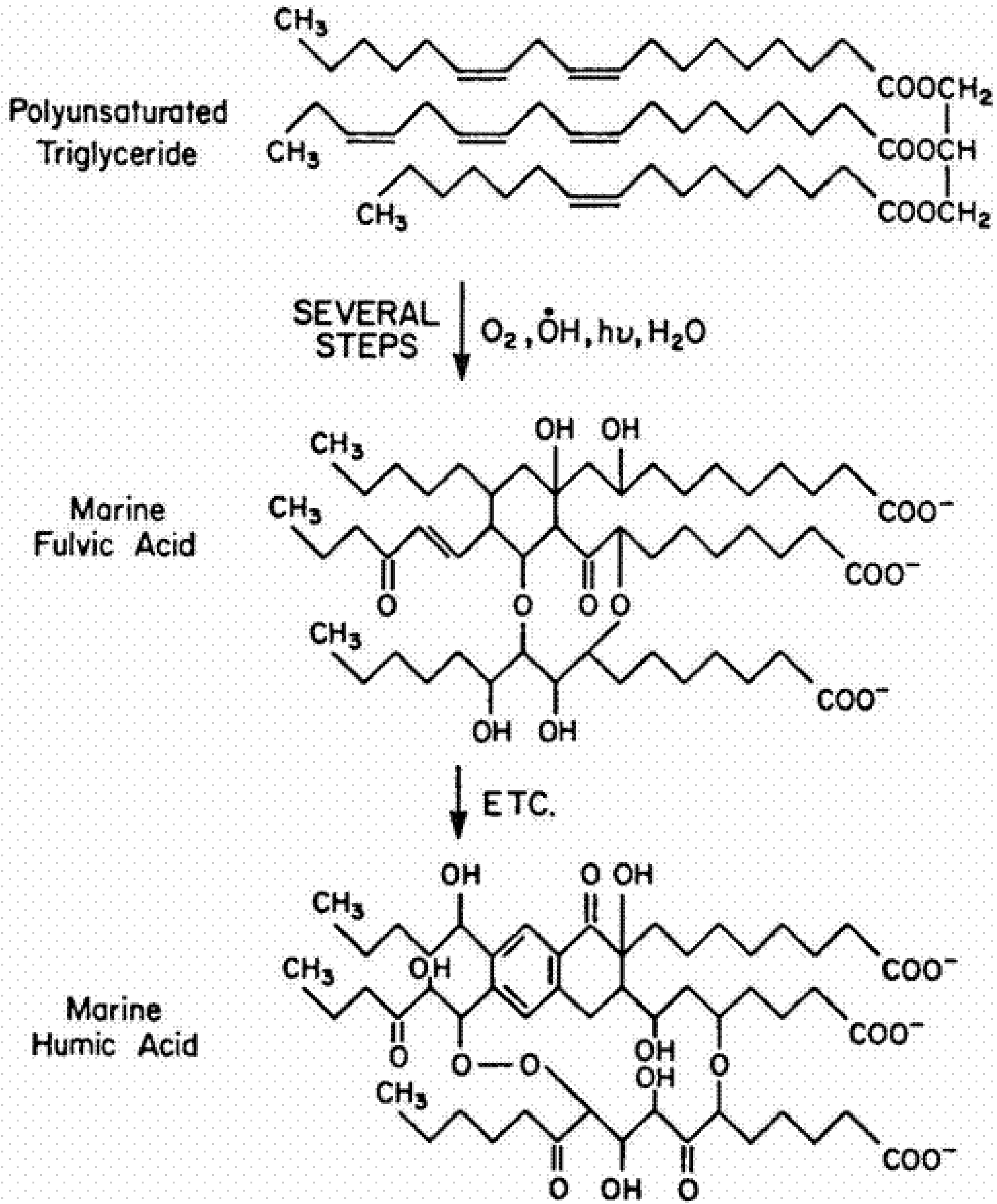


Figure 6.13 A possible pathway for the formation of marine humic acids from a triglyceride. From Harvey et al., 1983.

Morel & Hering, 1993