Chemical Oceanography

Ryan Lecture 10 - April 14, 2005

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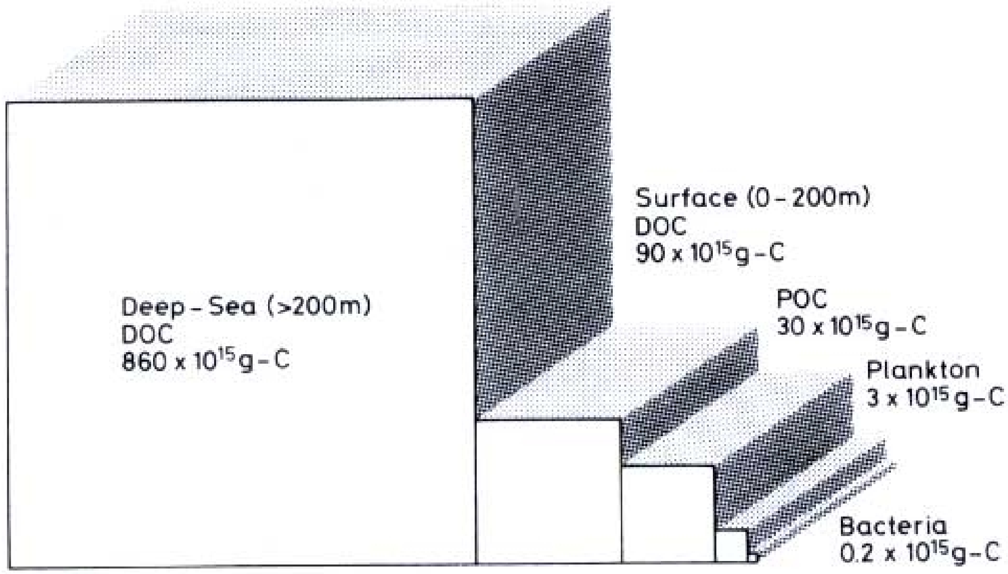
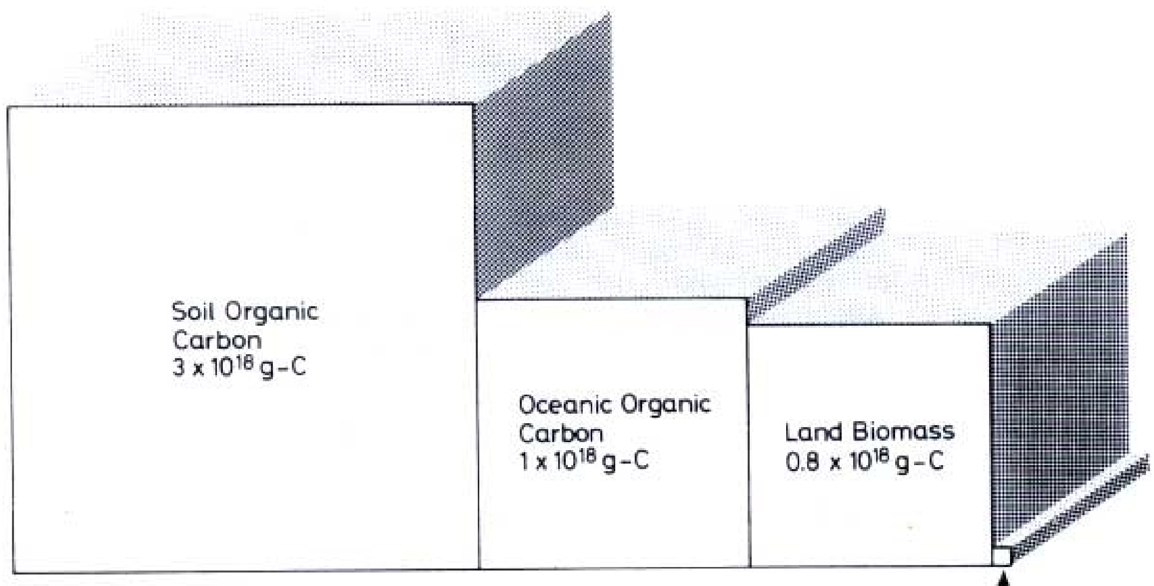
Importance of Humic Materials

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 Transport
Bind Metals & Organic Pollutants
Terminal Electron Acceptor for Bacteria



(a)



(b)

Distribution of Organic Carbon

(a) Major compartments in the global ocean

(b) Major compartments for the planet

Cauwet, 1978

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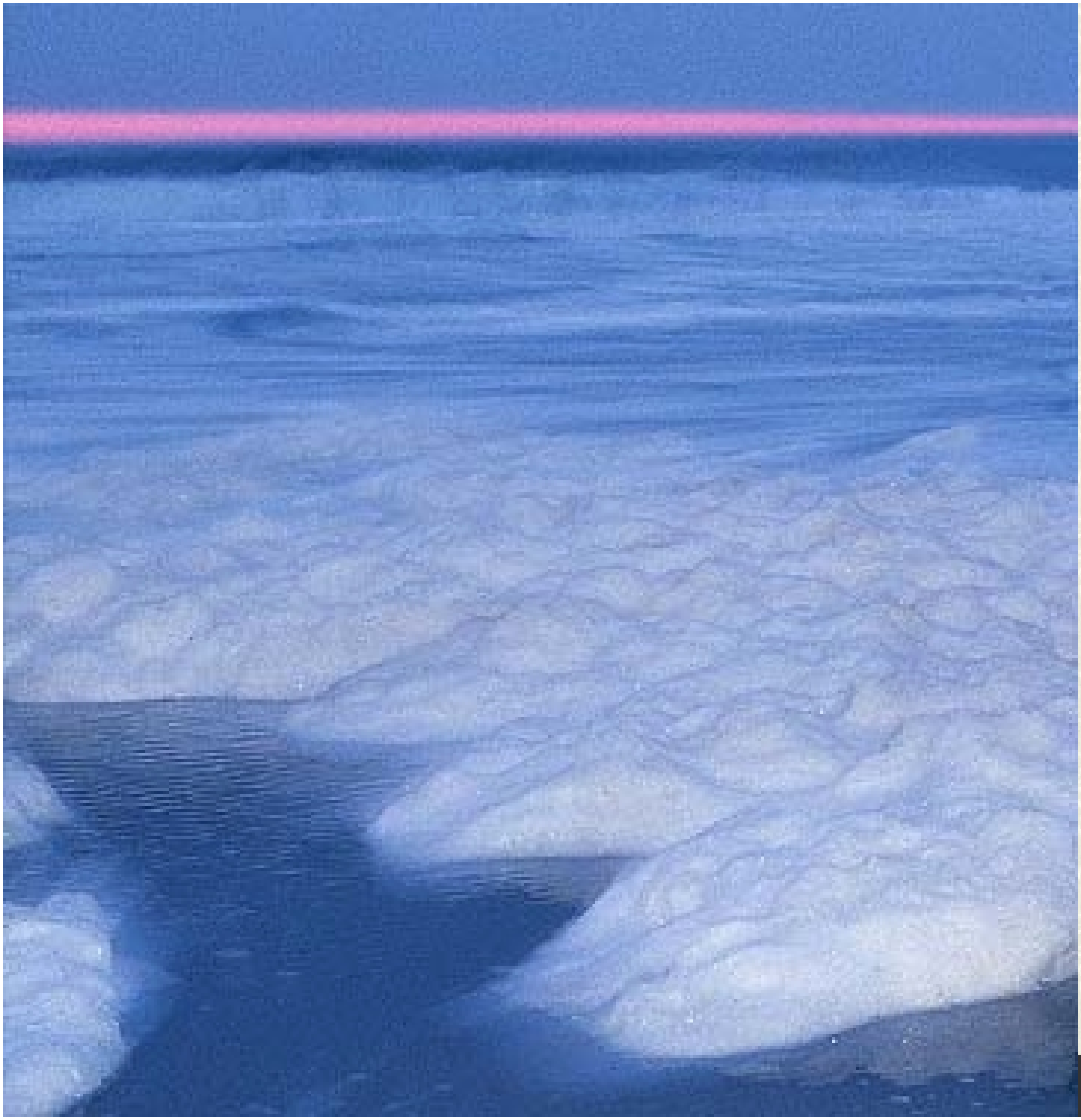
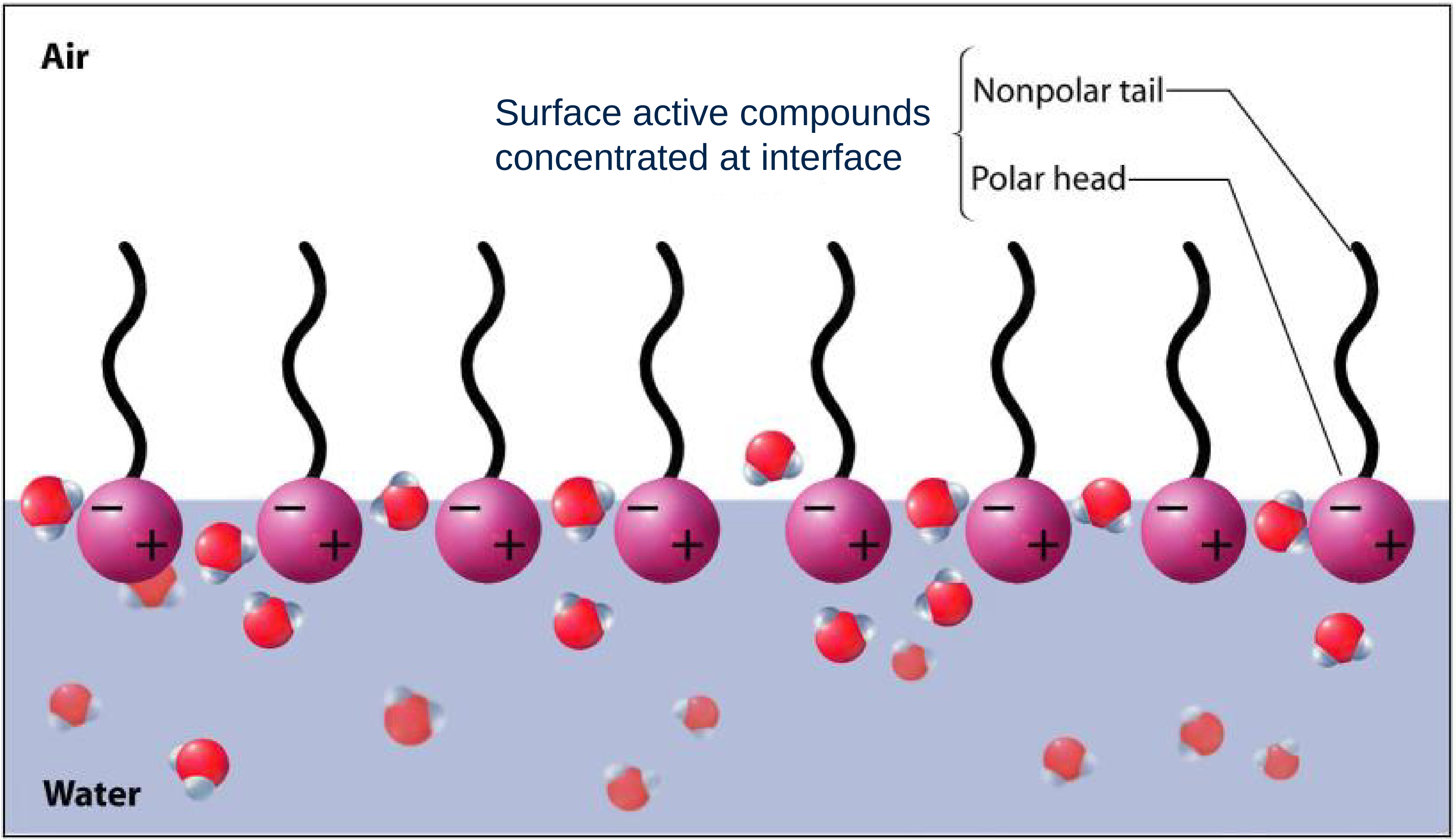
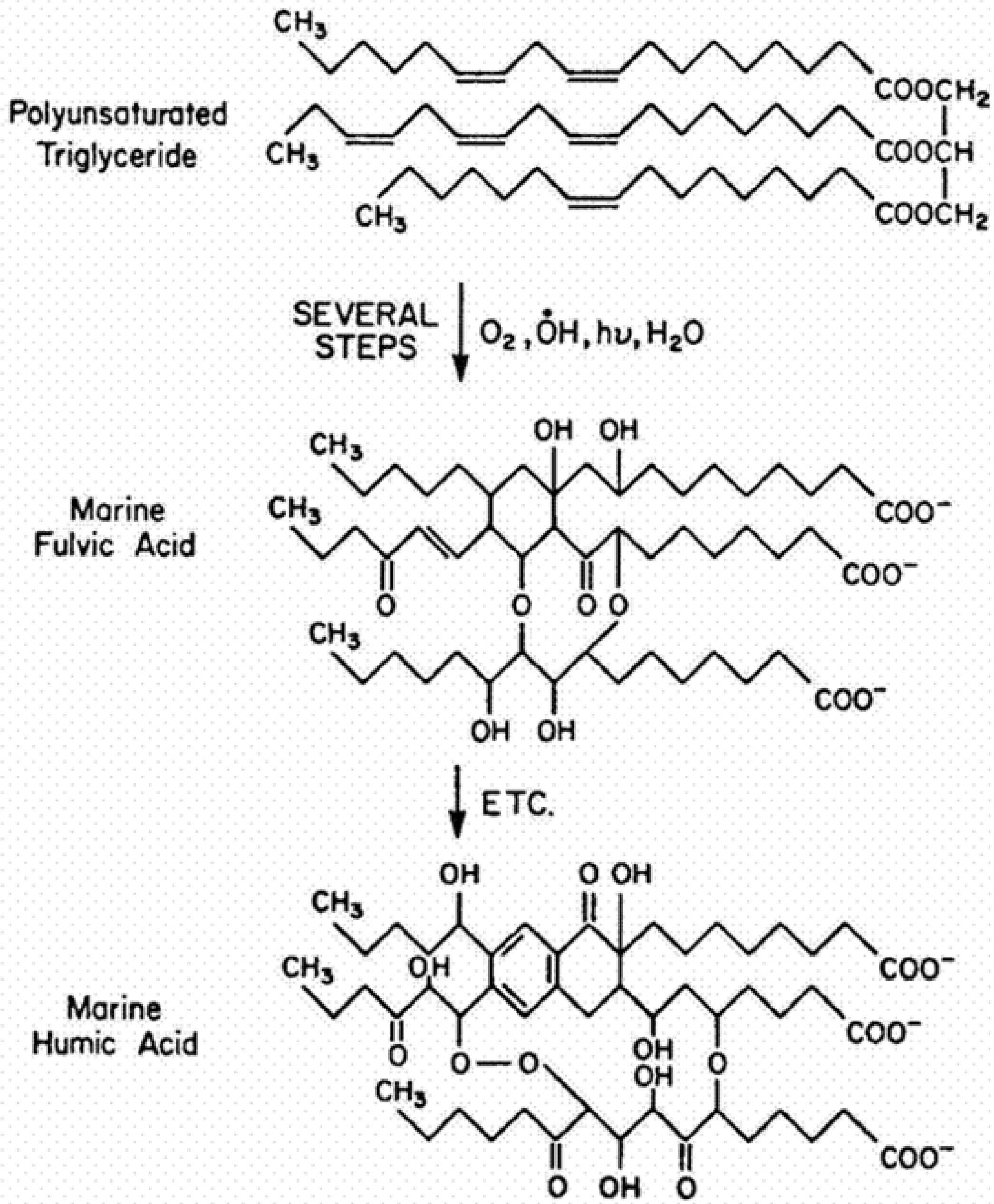


Sea Foam caused by naturally occuring surface active agents

Air-Sea Interfacial Chemistry





Morel & Hering, 1993

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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.

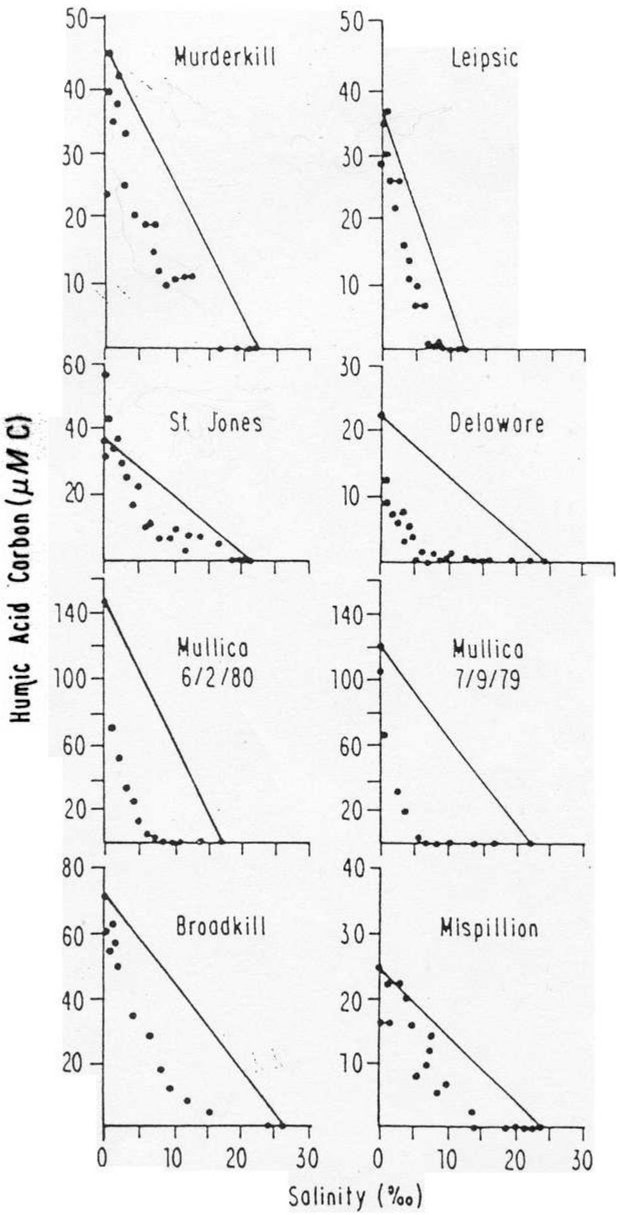

Figure 3. Humic acid carbon as a function of salinity. The standard error of the mean is 5%.

Fox, 1983

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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

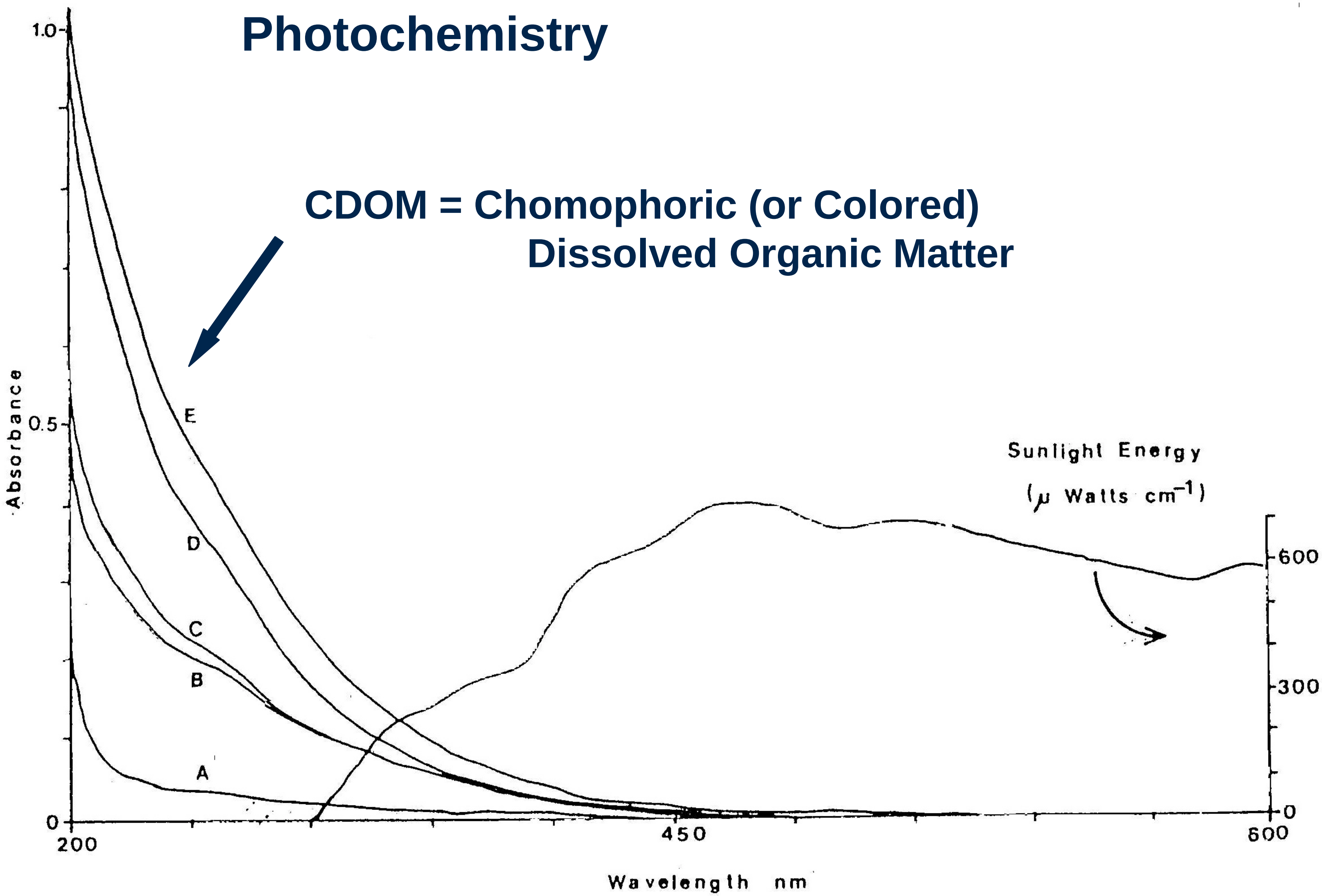

Figure 1. Absorption spectra (pathlength of 1 cm) of several waters and a generalized surface solar energy distribution (adapted from ref. 8). (DOC of waters: A = 3.0, B = 7.8, C = 13.4, D = 13.4, E = 15.4 mg L^{-1}).

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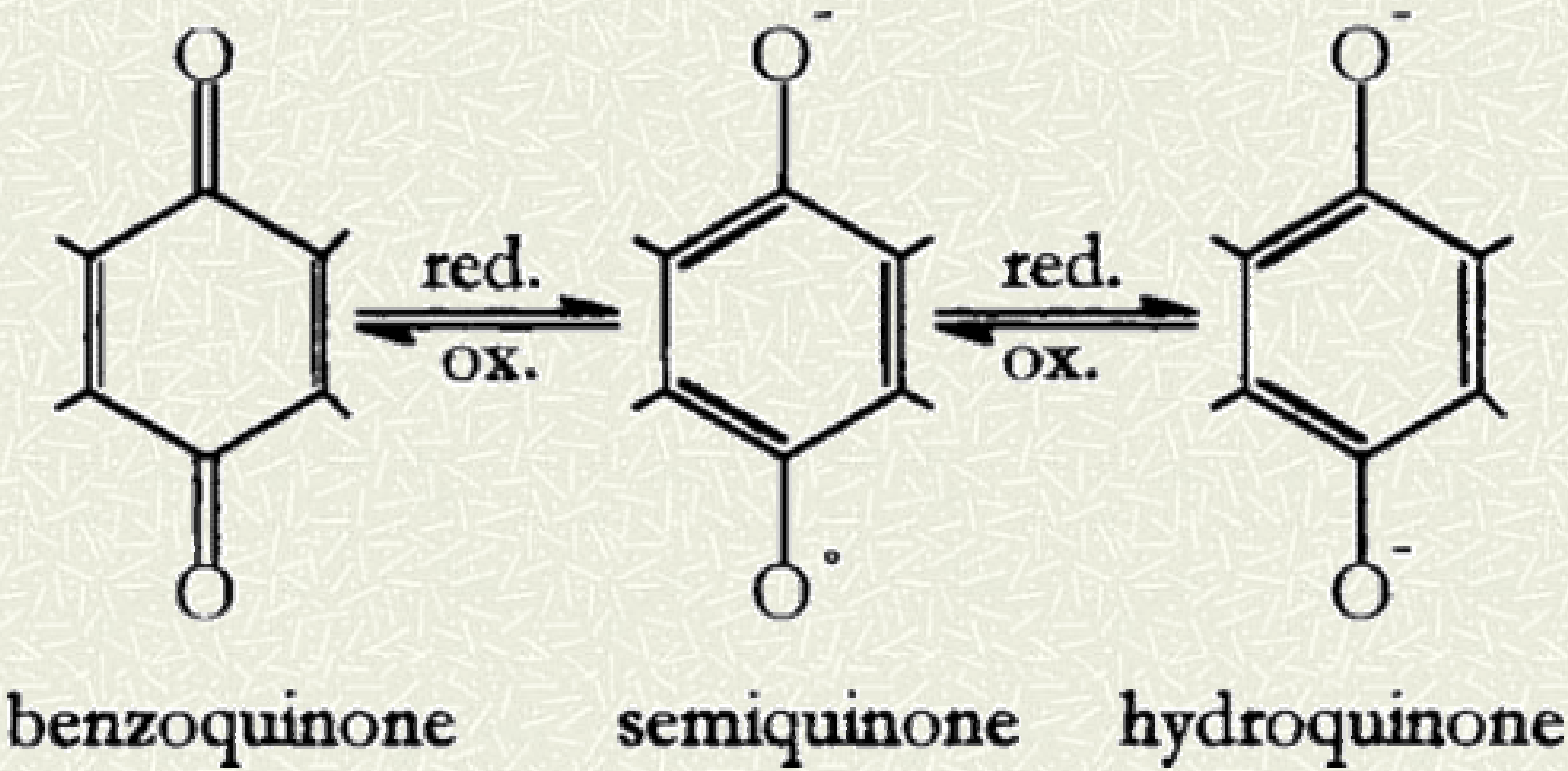
The quinone radical is known to be present in humic material



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

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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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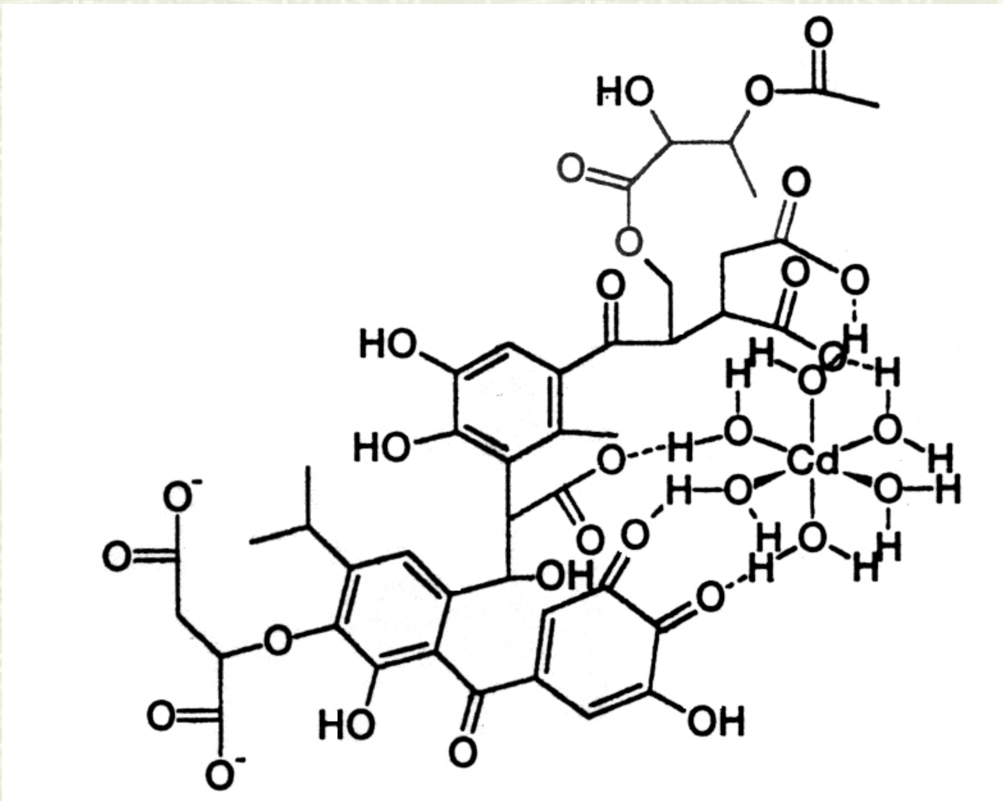
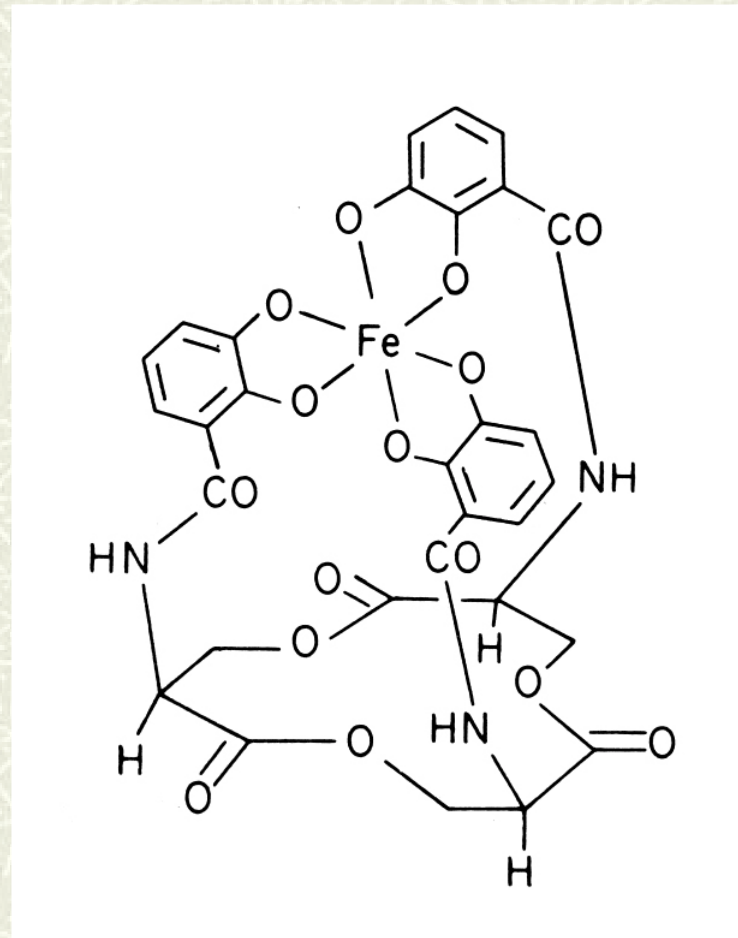
Metal Complexation by Humics



Leenheer et al. (1998)



Morel (1983)

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

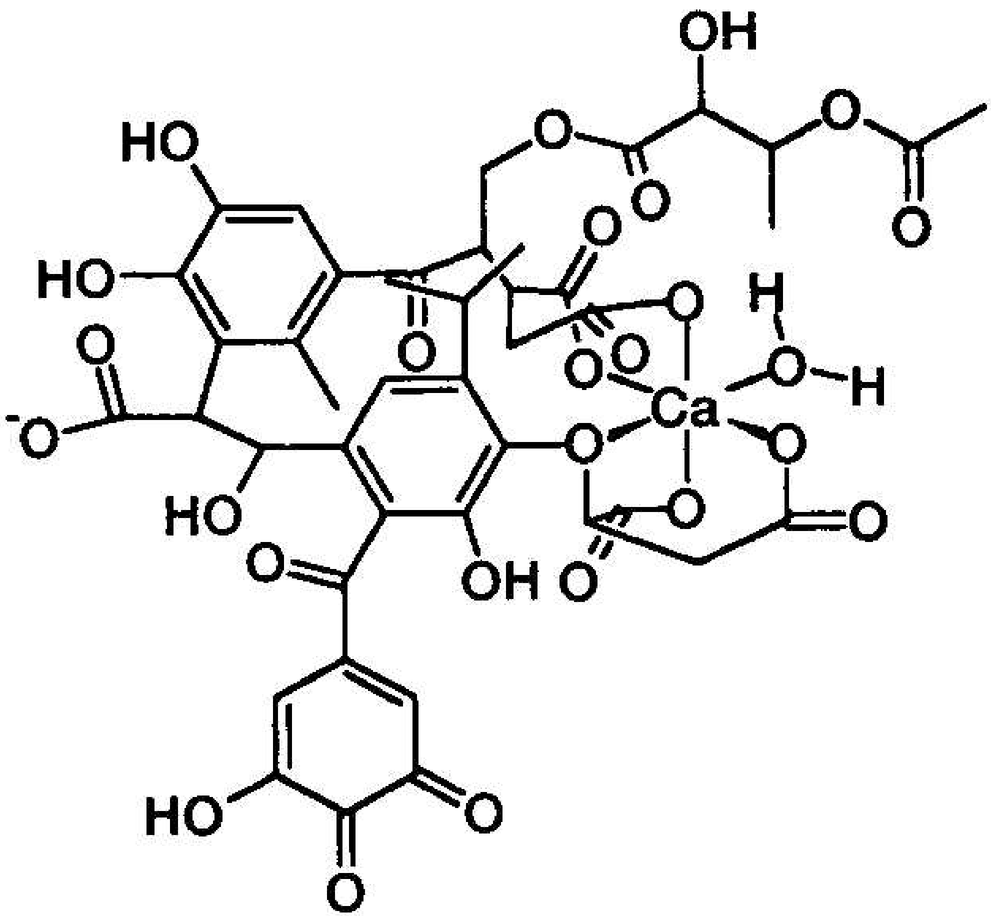

FIGURE 6. Structural model of a calcium inner-sphere complex

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

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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

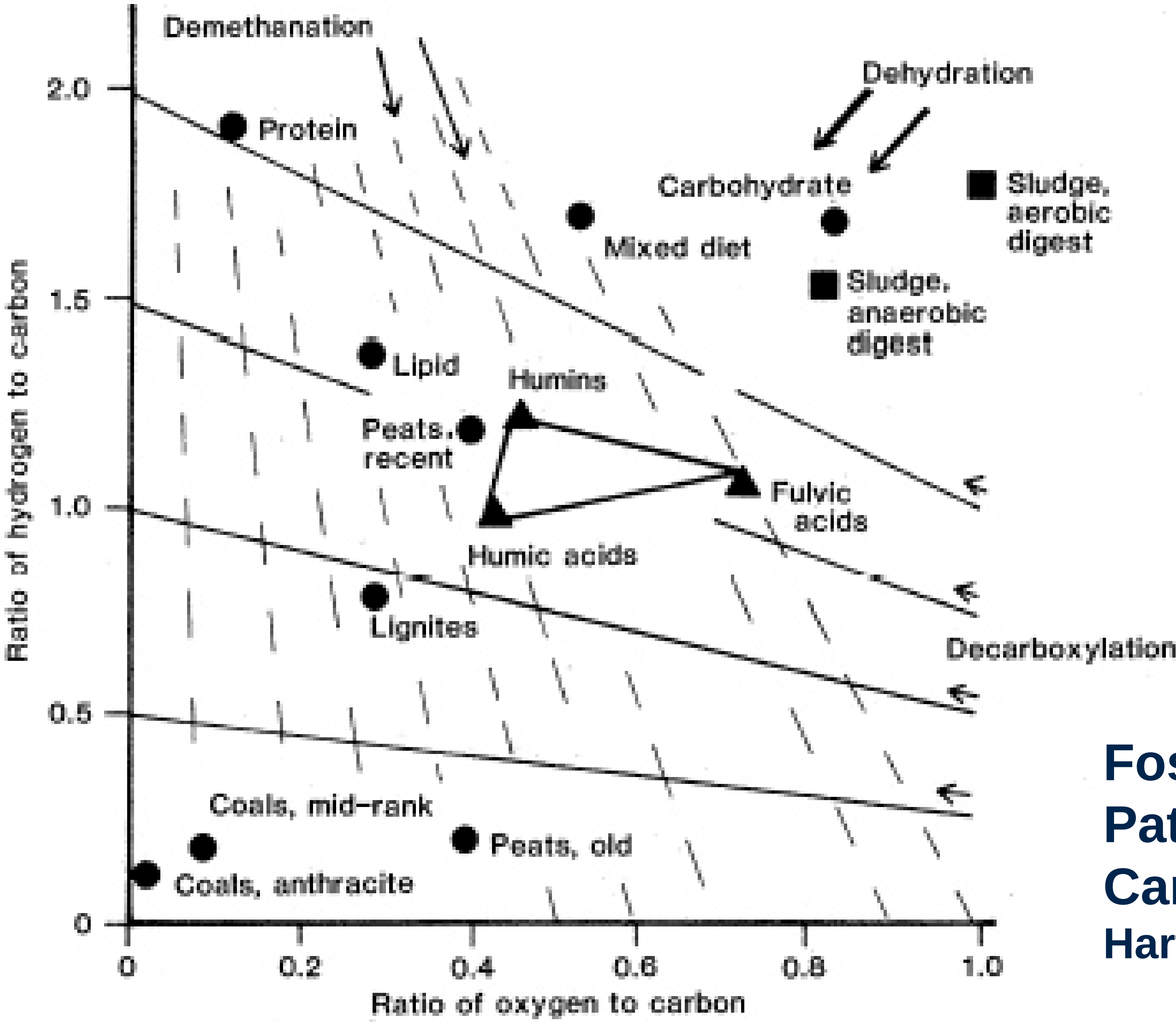
Sludge Decomposition and Stabilization

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

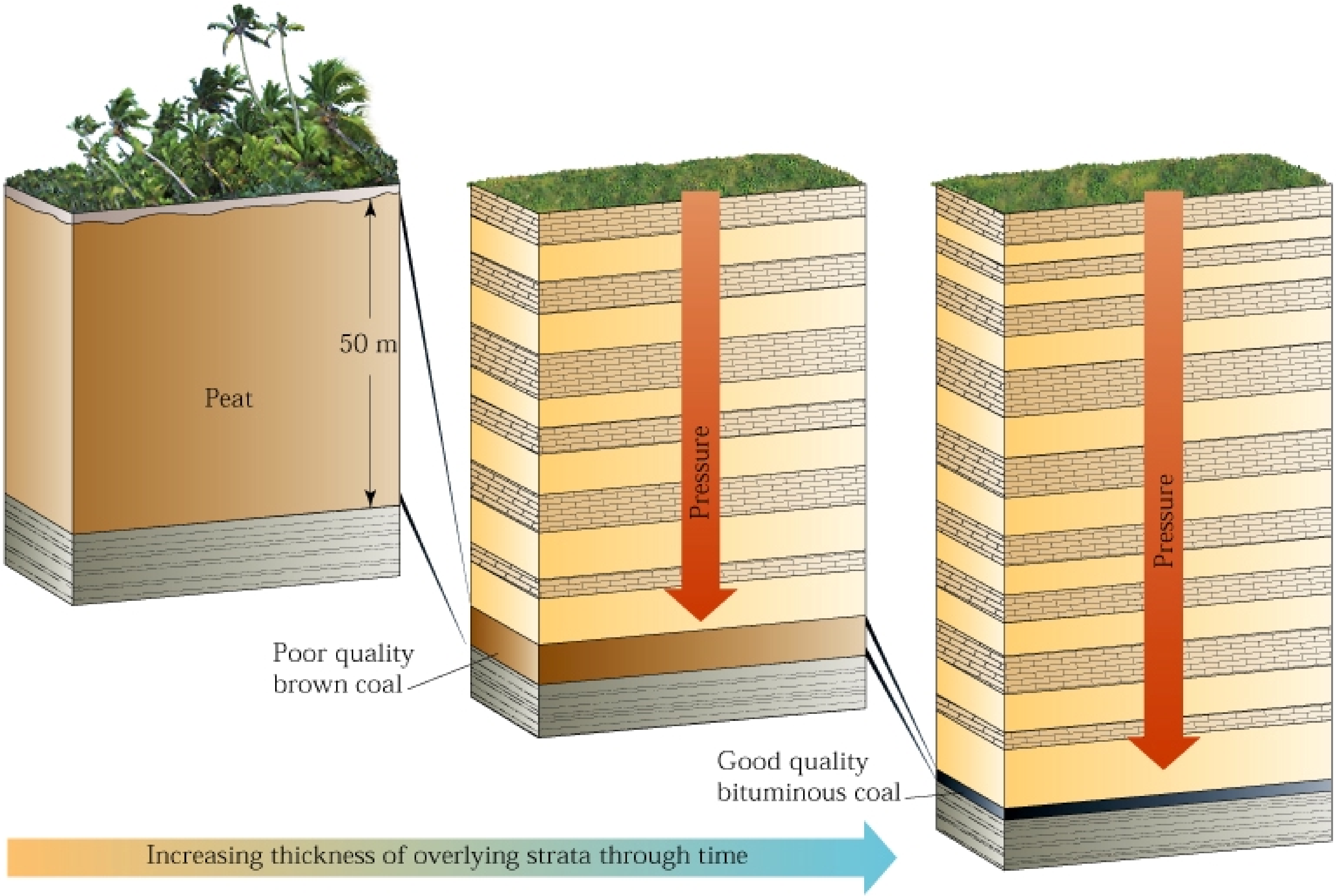


Fossilization Pathway of the Carbon Cycle

Hartenstein, 1981

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

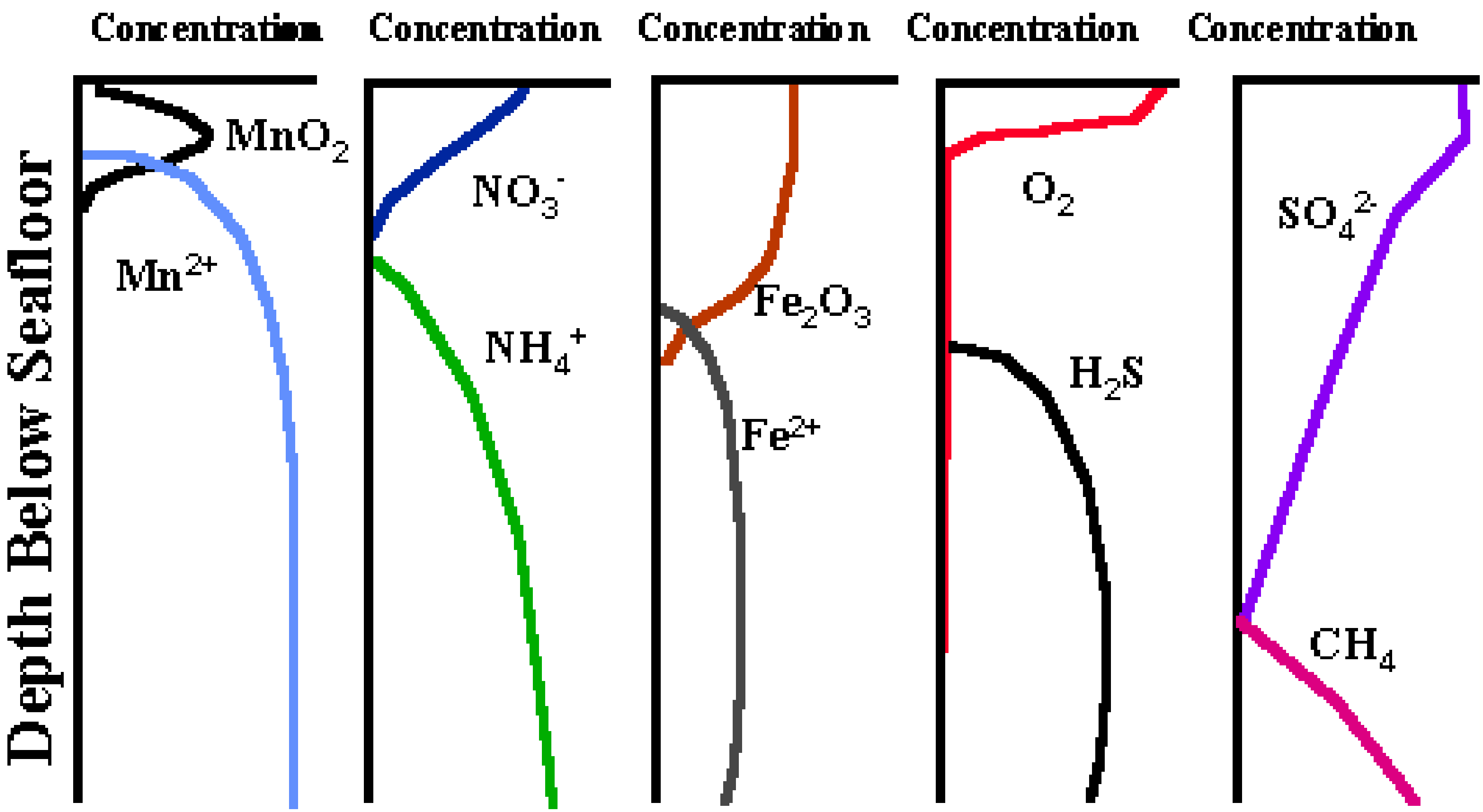
Applied Geochemistry, Vol. 11, pp. 711–720, 1996

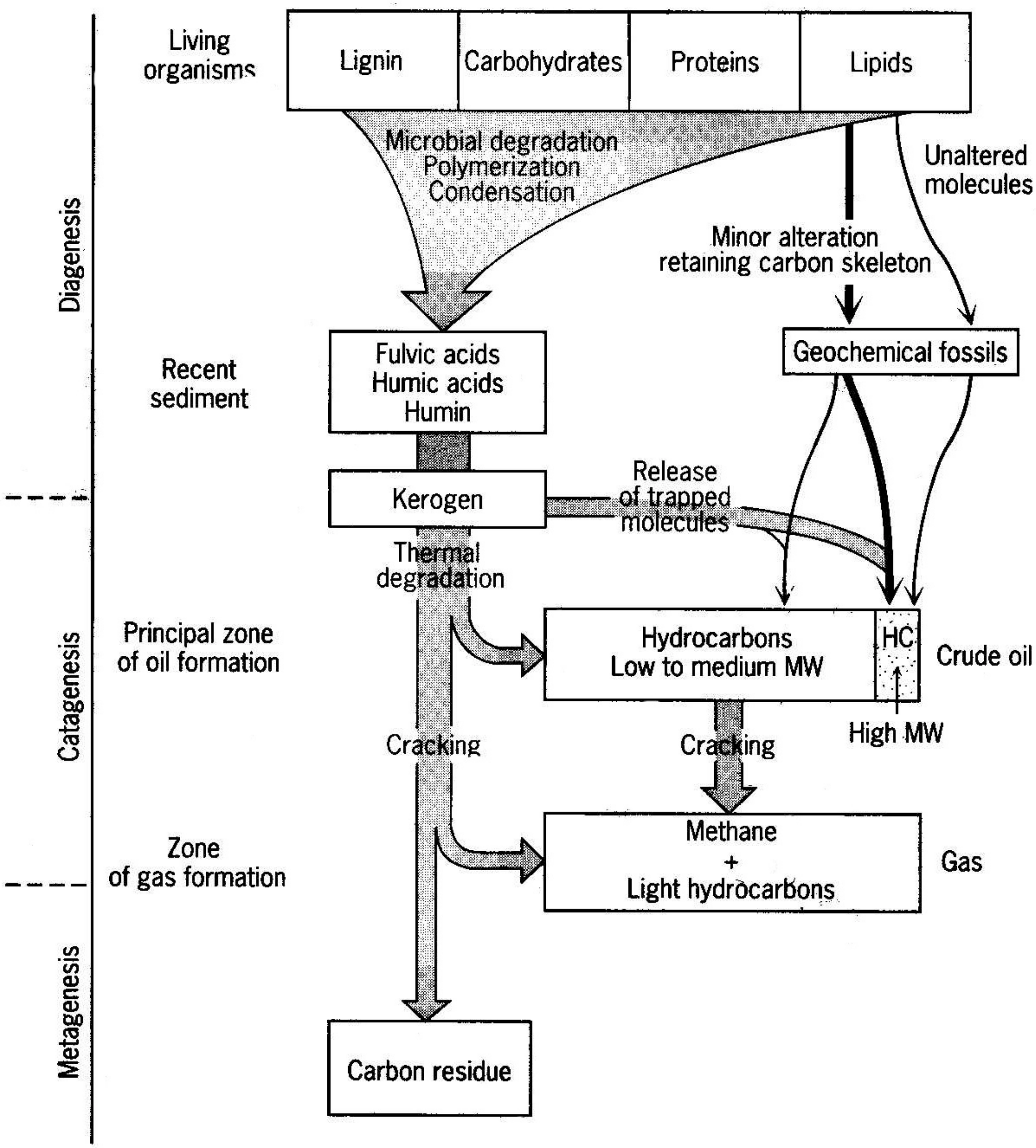
0883–2927/96 $15.00 + 0.00

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.

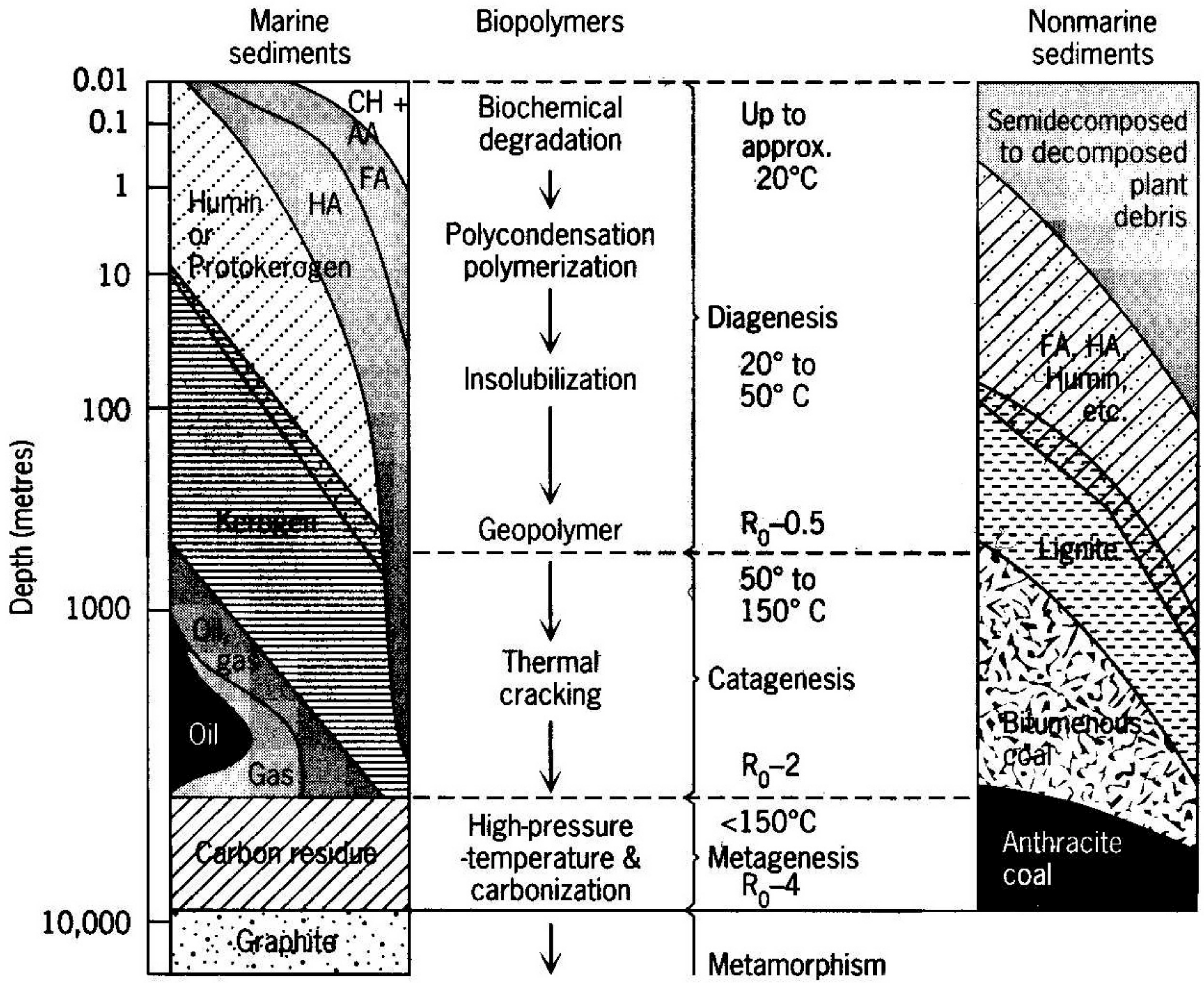
Sediment Diagenesis includes more than Organic Matter Transformations – Many redox processes occur





Petroleum Maturation Process

Libes, 1992



Evolution of Fossil Fuels

Libes, 1992

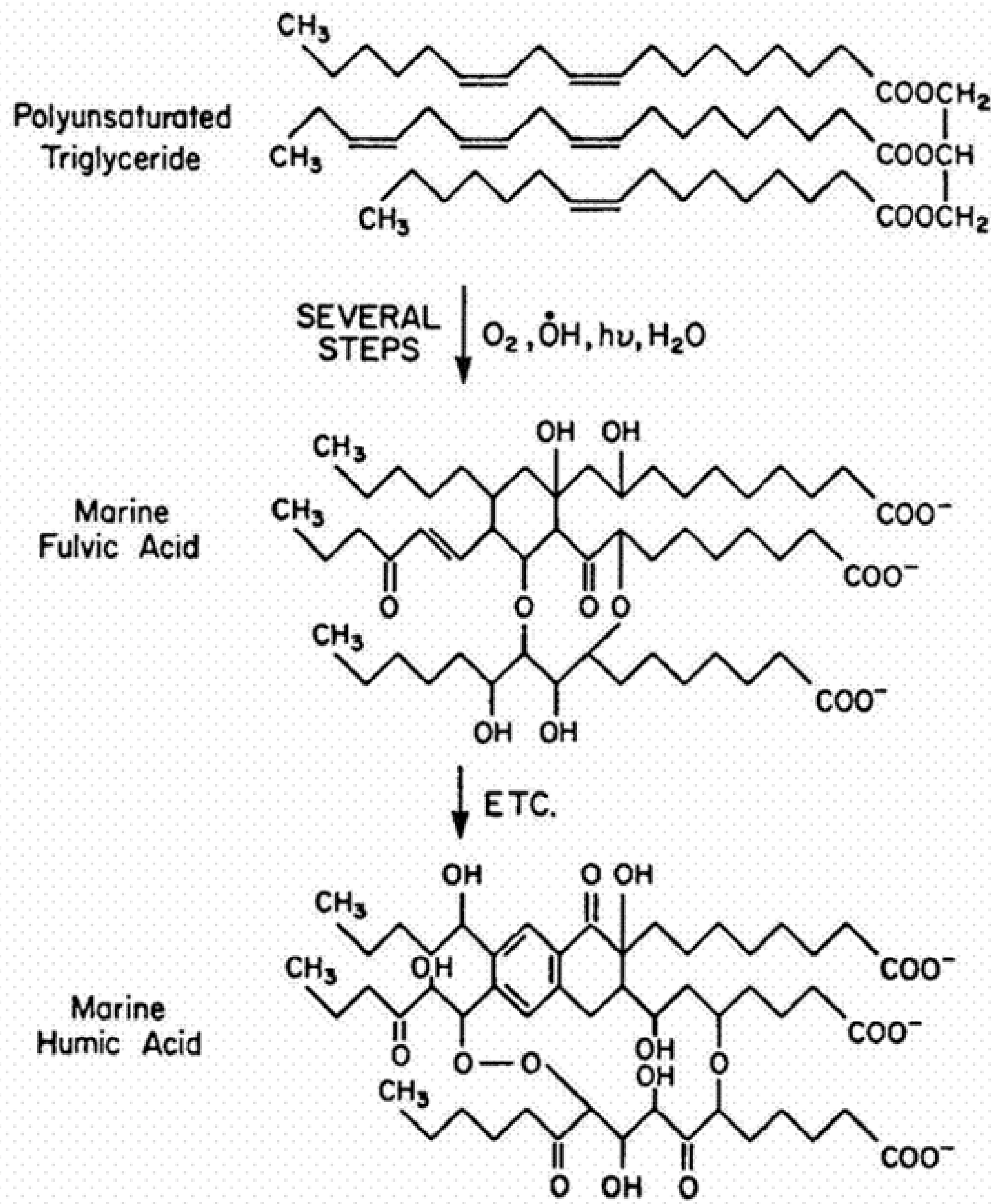


Figure 6.13 A possible pathway for the formation of marine humic acids from a triglyceride. From Harvey et al., 1983.

Morel & Hering, 1993