Chemical Oceanography Organic Matter Cycling

Dr. David K. Ryan Department of Chemistry University of Massachusetts Lowell & Intercampus Graduate School of Marine Sciences and Technology

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

Organic Compounds in the Sea

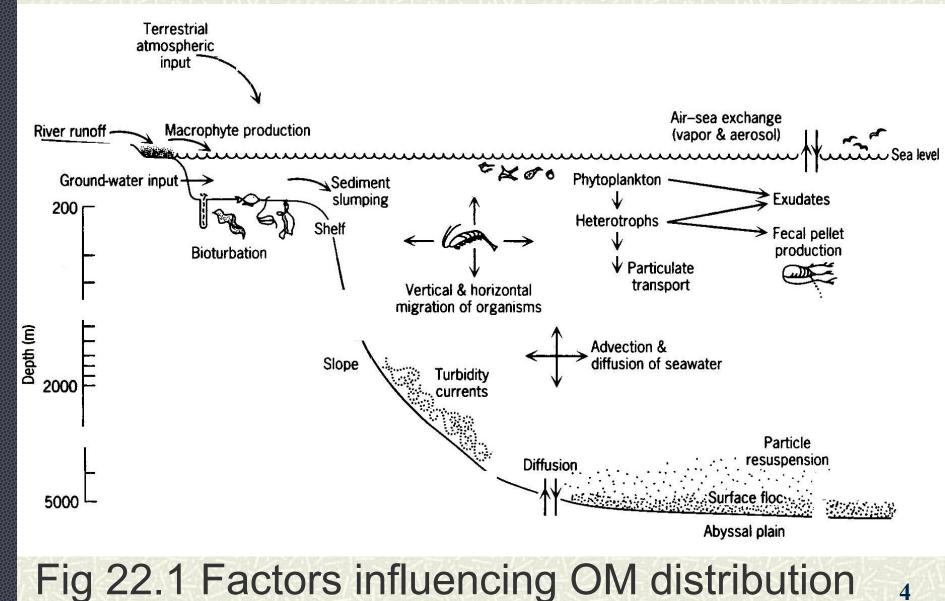
- **#** Where do they come from?
- **#** What are they?
- **#** Why are they important?
- **#** Where do they go?

Read: Emerson & Hedges Chapters 8 & 11 Libes Chapters 22 & 23 (posted on website)

Organic compounds produced during Primary Production

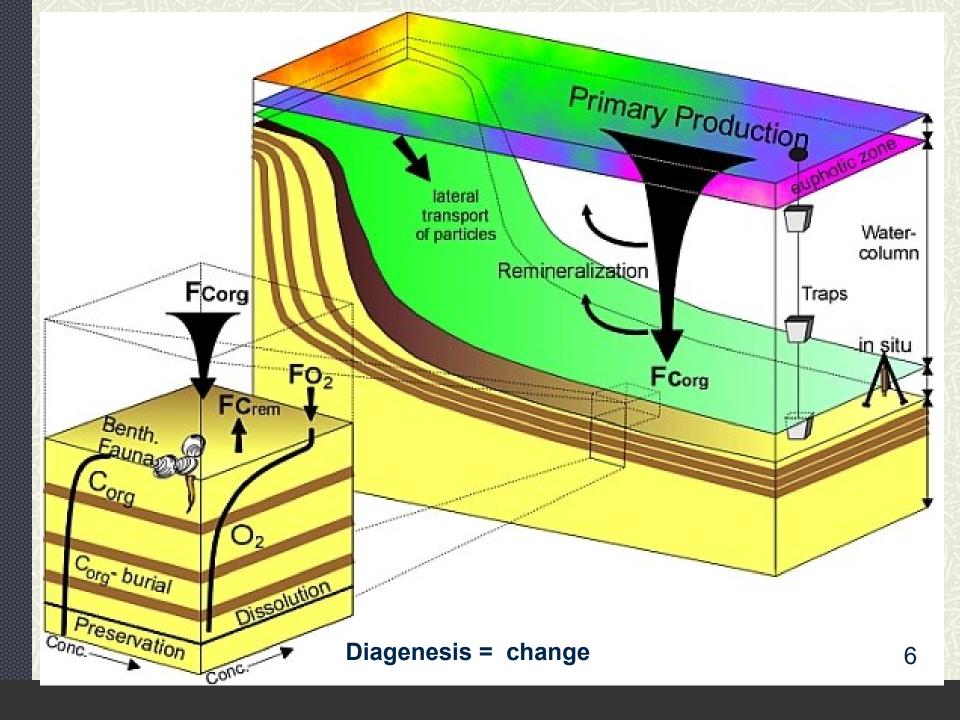
- Phytoplankton fix CO₂ to make "soft parts" (organic) (Broecker & Peng, Chapter 1)
- Consumed by other organisms to make their soft tissue
- All organisms exude and excrete soluble organic compounds
- Particulate organics arise from dead organisms (detritus) and fecal material from live organisms

Libes

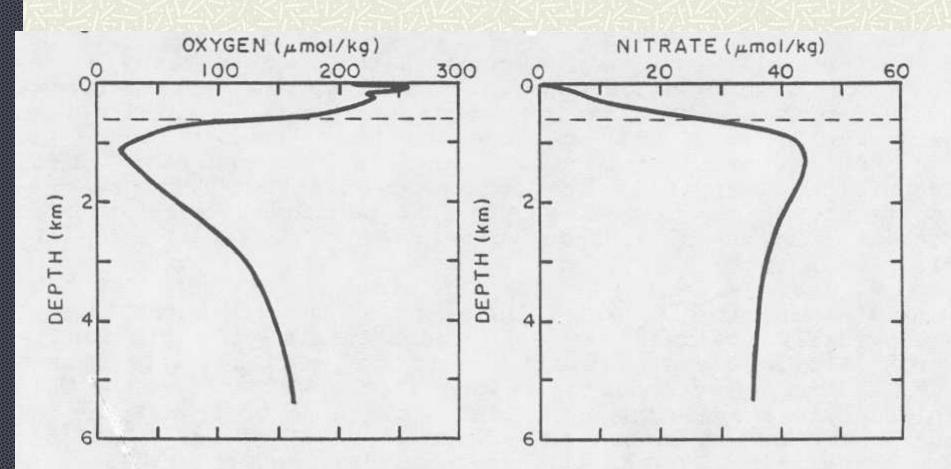


Primary Production continued

- # Organic particles sink under the influence of gravity
- **#** Become degraded by bacteria as they sink
- Consequently, the destruction of organic matter occurs at greater depth than formation
- Destroyed organics are remineralized to inorganic species (e.g., CO₃²⁻ & NO₃⁻)
- **#** Deep ocean becomes enriched in nutrients



Broecker & Peng Figure 1.1



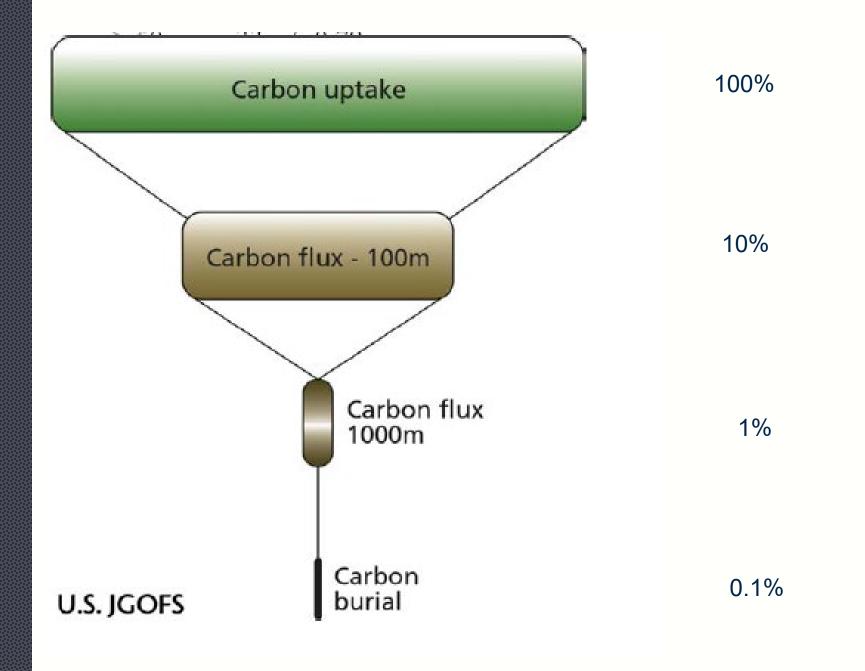
7

Primary Production continued

Large particles are more likely to make it all the way to the sediments and be buried
Greater than 99% of organic matter is remineralized, very little reaches sediments
Is there a consequence of the above info for large scale iron fertilization of the oceans?

Primary Production continued

- Large particles are more likely to make it all the way to the sediments and be buried
- Greater than 99% of organic matter is remineralized, very little reaches sediments
- Is there a consequence of the above info for large scale iron fertilization of the oceans?
 Yes, stimulating primary production at the surface results in an increased production of particulate organic material that is remineralized at greater depths and stores carbon in the deep ocean.



Marine Snow



Marine Snow

Verdugo et al., 2004 "The oceanic gel phase: a bridge in the DOM–POM continuum" Marine Chemistry 92, 67-85.

Handout posted on website, Course Materials

Nomenclature & Units for Carbon

Organic compounds are carbon containing (except oxides, carbonate minerals, elemental)
The symbol for carbon is C

Organic materials in the ocean are sometimes discussed as a whole, including all compounds regardless of structure

Specifying concentrations is best done in grams or moles of carbon (C) per L or kg of seawater
 μM C or mg C/L or mg C/kg

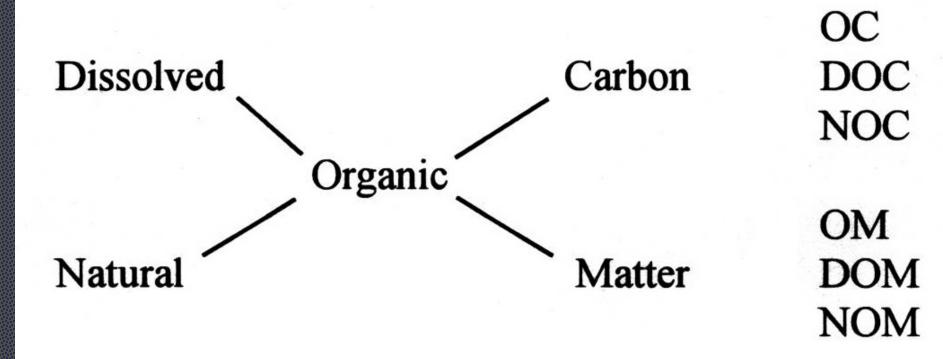
TABLE 9.7 Levels of Dissolved and Particulate Organic Material in Natural Waters				
Source	Dissolved	Particulate		
Seawater				
Surface	75–150 μM	1–17 µM		
Deep	4-75	0.2-1.3		
Coastal	60-210	4-83		
Estuarine	8-833	8-833		
Drinking water	17			
Ground water	58			
Precipitation	92			
Oligotrophic lake	183	80		
River	420	170		
Eutrophic lake	830-4,170	170		
Marsh	1,250	170		
Bog	2,500	250		

Concentrations of organic material expressed in μ M = micromoles of C per liter of solution

Millero, 1996 Table 9.8 in Millero, 2007

14

Nomenclature & Units for Carbon



DOC is most common abbreviation – specifies **C** DOM or NOM concentrations may differ from DOC by a factor of 2 to account for % C (Ryan 2013)

TABLE 22.1 Operationally Defined Fractions of Organic Matter^a

Operational Fraction

Particulate organic matter Dissolved organic matter Particulate organic carbon Dissolved organic carbon Dissolved inorganic carbon Particulate organic nitrogen Dissolved organic nitrogen Dissolved inorganic nitrogen

POM DOM POC DOC DIC PON DON DIN

Libes, 1992

^aAlso included are some inorganic fractions.

Relatively New Nomenclature CDOM is colored or chromophoric DOM Term used to distinguish light absorbing material from OM that has no light absorption or color

- Typically measured spectrophotometrically by:
- UV/vis absorption measurements
- Fluorescence spectrometry

Humic Materials or Humic Substances

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

Organic Compounds in the Sea

- **Where do they come from?**
- **#** What are they?
 - Hydrocarbons
 - 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 Compounds in the Sea

Where do they come from?

- Primary Production
- Riverine and Terrestrial Runoff

To a much lesser extent

- Atmospheric Deposition
- Sediment Diffusion & Resuspension
- Groundwater input
- Vents, etc.

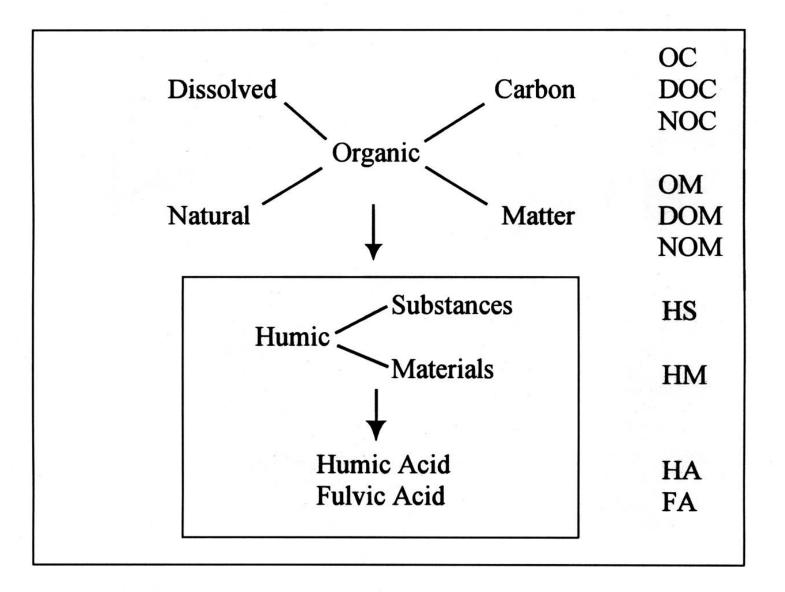
Average Concentrations of Organic Compounds in Baltic and North Sea Water

Components	Concentration $(\mu g \ C \ liter^{-1})$	
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 μ g C liter ⁻¹	
Approximate total	4000 µg C liter ⁻¹	

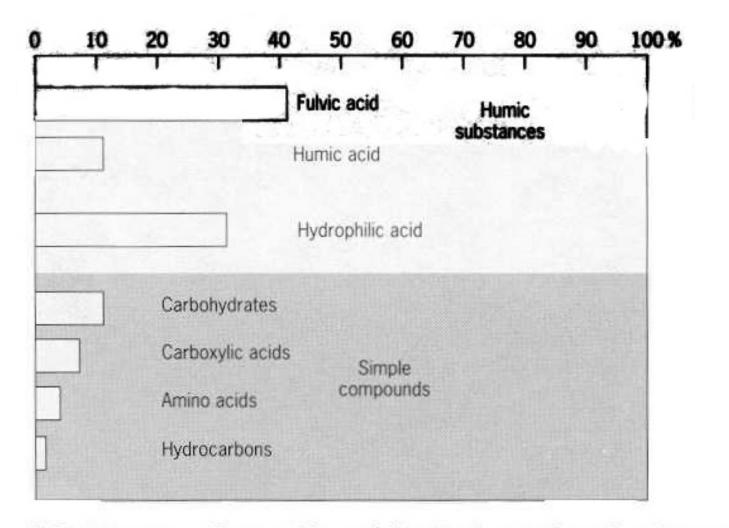
Morel, 1983

Average Concentrations of Organic Compounds in Baltic and North Sea Water

Components	Concentration $(\mu g \ C \ liter^{-1})$	
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	What is this stuff?
Aldehydes	5	
Hydrocarbons	5	
Urea	10	Morel, 1983
Uronic acids	18	1,10101, 1903
Approximate identified total	340 μ g C liter ⁻¹	
Approximate total	4000 μ g C liter ⁻¹	22

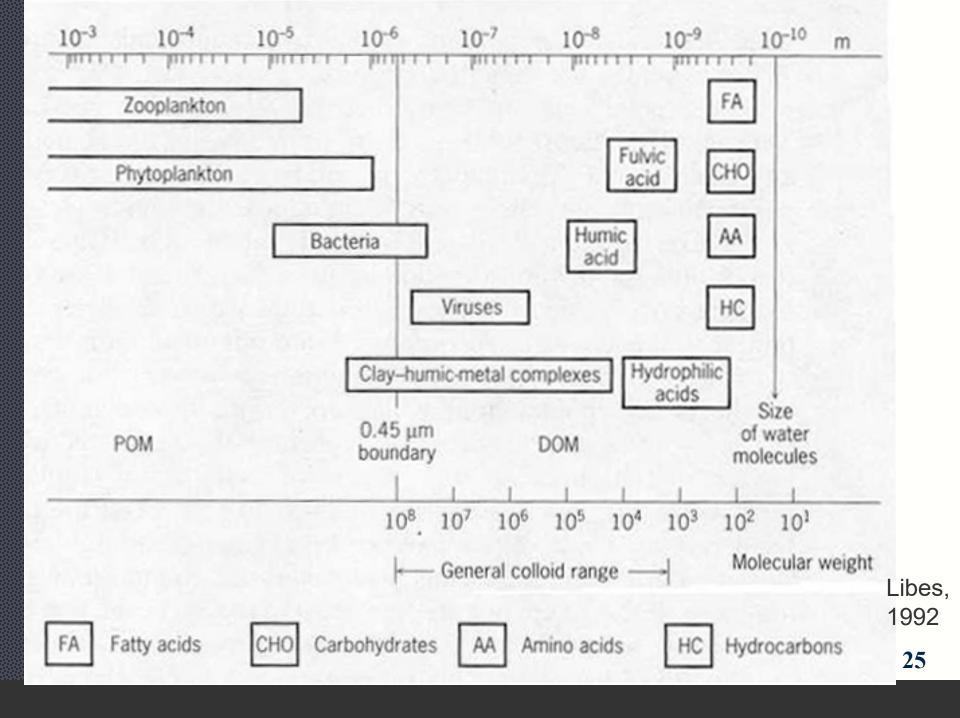


Ryan (2000)

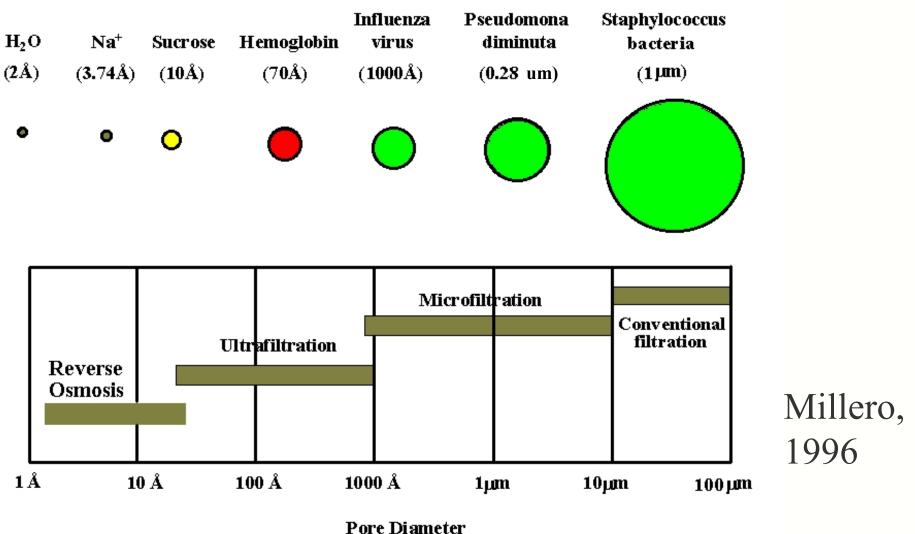


Libes, 1992

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. 20



PORE SIZE OF FILTRATION PROCESSES



Organic Compounds in the Sea

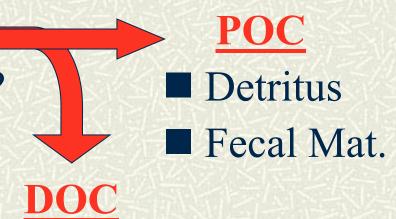
- **Where do they come from?**
 - Primary Production
 - Riverine and Terrestrial Runoff

To a much lesser extent

- Atmospheric Deposition
- Sediment Diffusion & Resuspension
- Groundwater input
- Vents, etc.

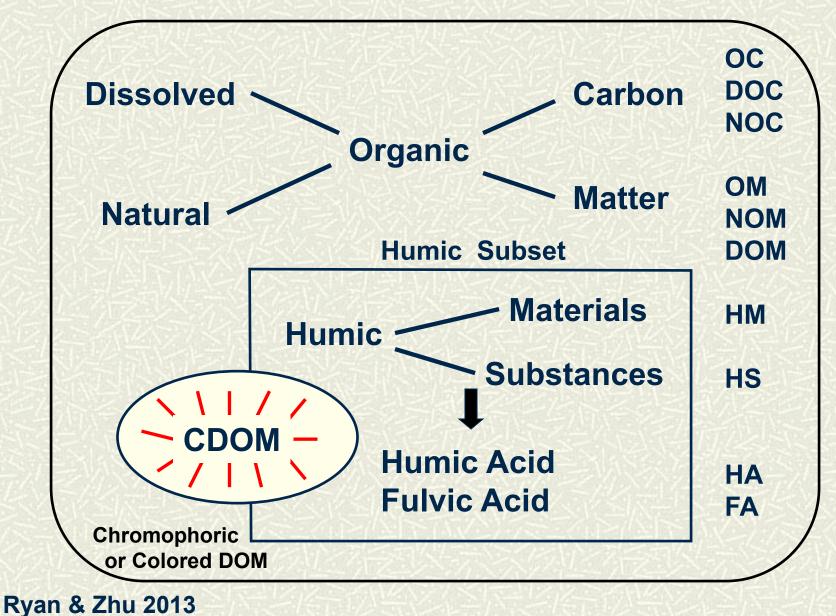
Organic Compounds in the Sea

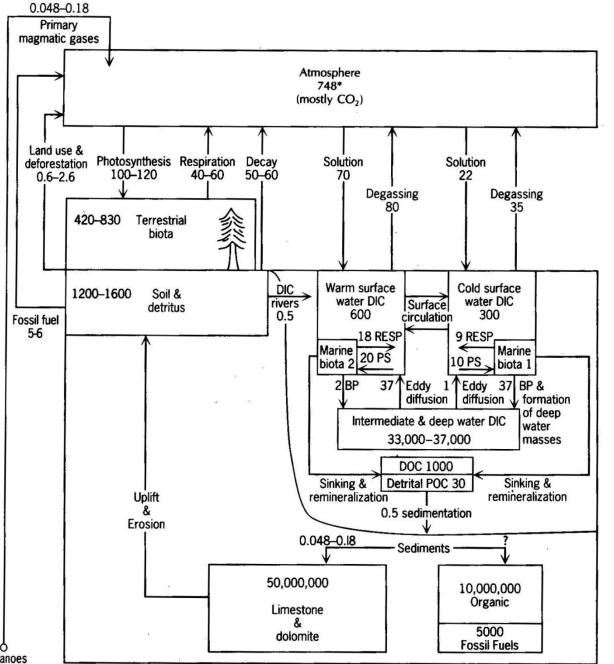
- **#** Where do they come from?
- **What are they?**
- **#** Why are they important?
- **#** Where do they go?



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

All Dissolved Organic Compounds

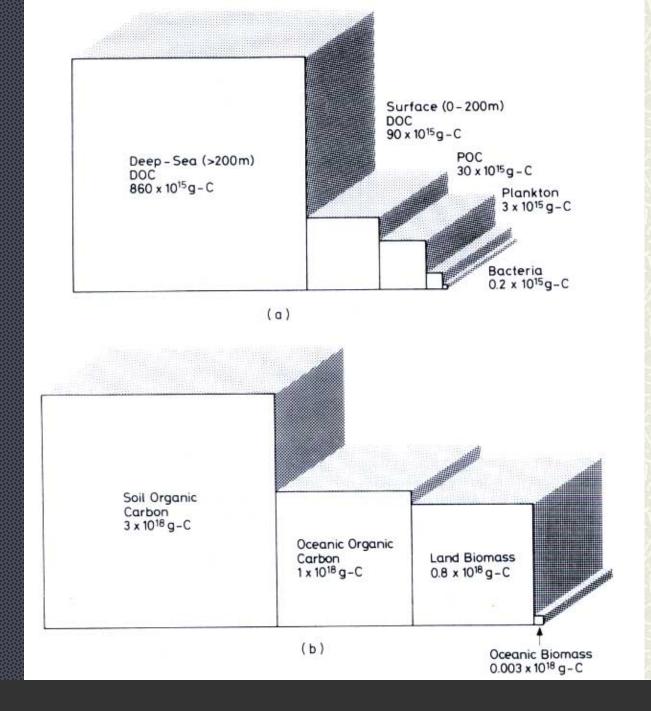




Carbon Cycle Libes, 1992

Inventories in $10^{15} \text{ g C} = \text{BMT}$

Fluxes (arrows) 10¹⁵ g C/yr



Distribution of Organic Carbon

(a) Major compartments in the global ocean

(b) Major compartments for the planet

Cauwet, 1978