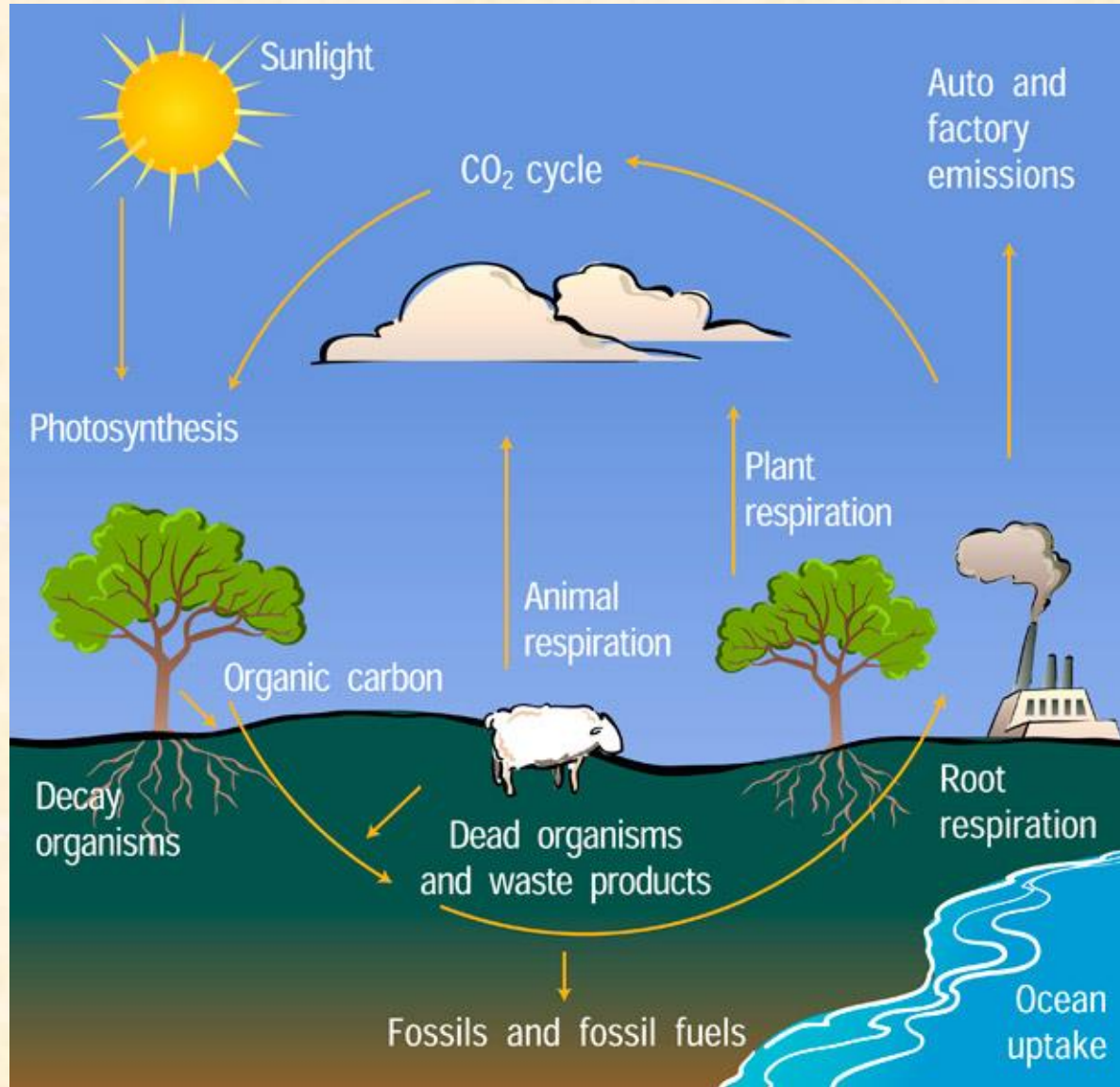
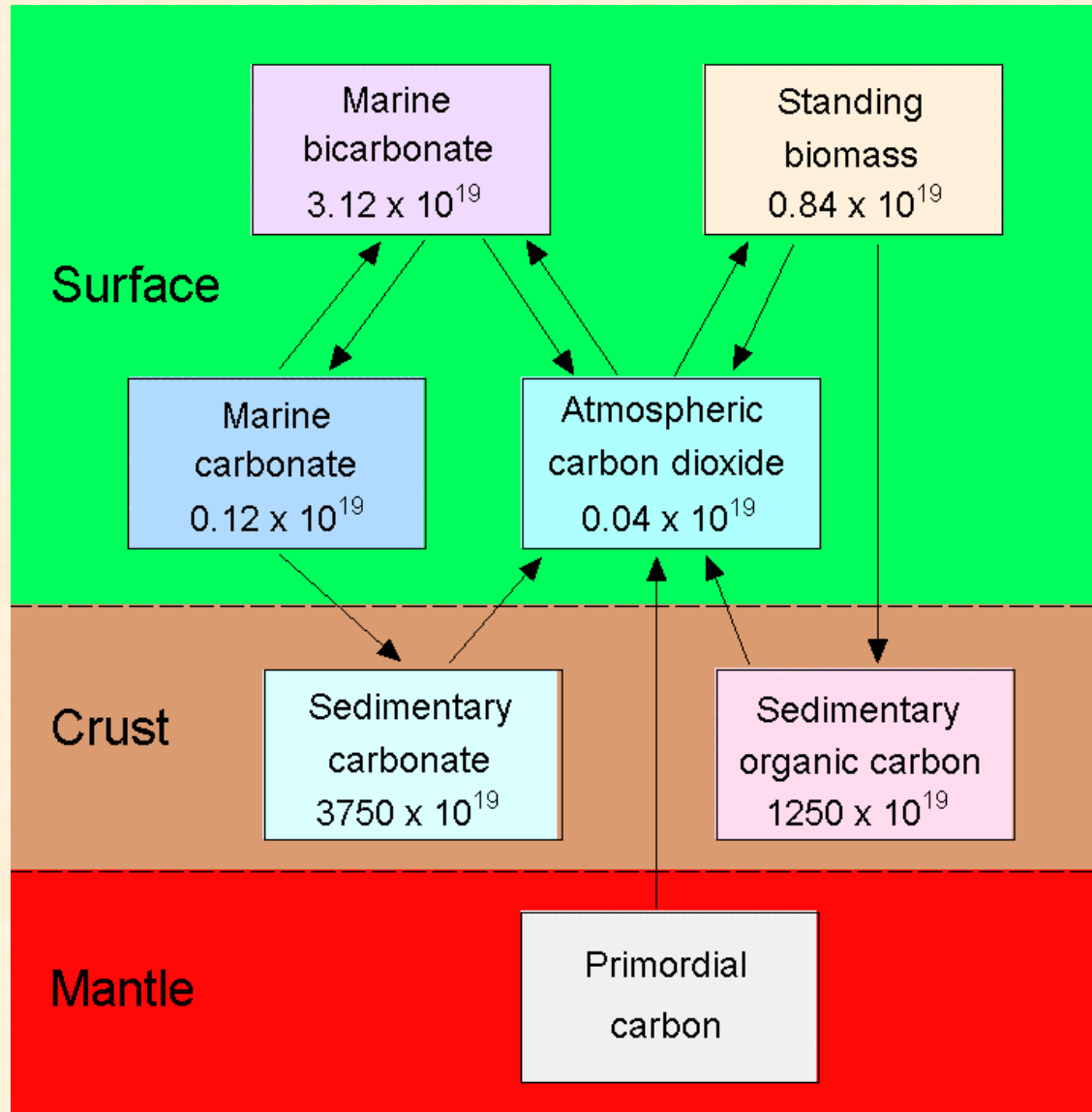


# Carbon in the Environment



# Natural Sources of Carbon Compounds



**Humic Substances:** a general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight, and refractory.

•**Humin:** that fraction of the humic material that is insoluble in water at all pH values.

•**Humic acid:** that fraction of the humic material that is soluble in water at pH values greater than 2.

•**Fulvic acid:** that fraction of the humic material that is soluble in water at all pH values.

•***Humic and Fulvic acids are the major components of both freshwater and marine DOC. (although there are significant differences in the types of humic substances that occur in these 2 environments.)***

# Humus

<b>Humin</b> Insoluble base Insoluble acid	<b>Humic Acid</b> Soluble base Insoluble acid	<b>Fulvic Acid</b> Soluble base Soluble acid
--	---	--

Decreasing Molecular Weight

1,000,000?      100,000      10,000      1000

Increasing Oxygen Percent

25?      30      45      50

Increasing Acidity and Ion Exchange Capacity

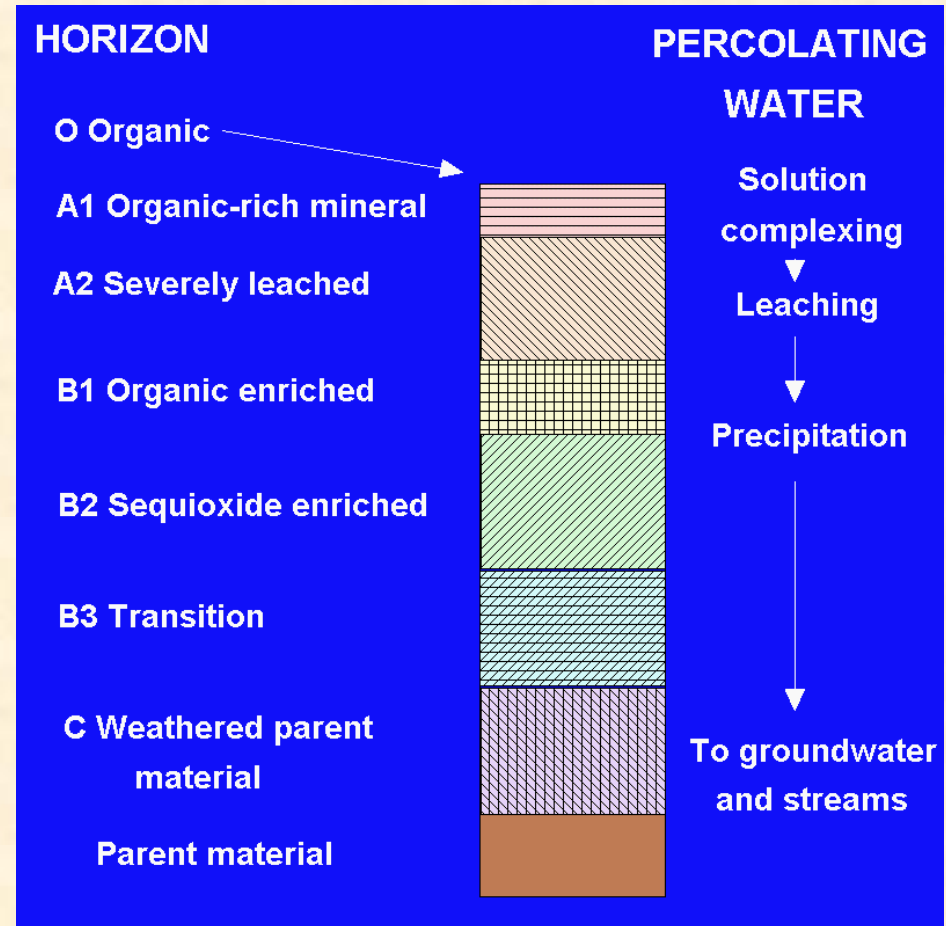
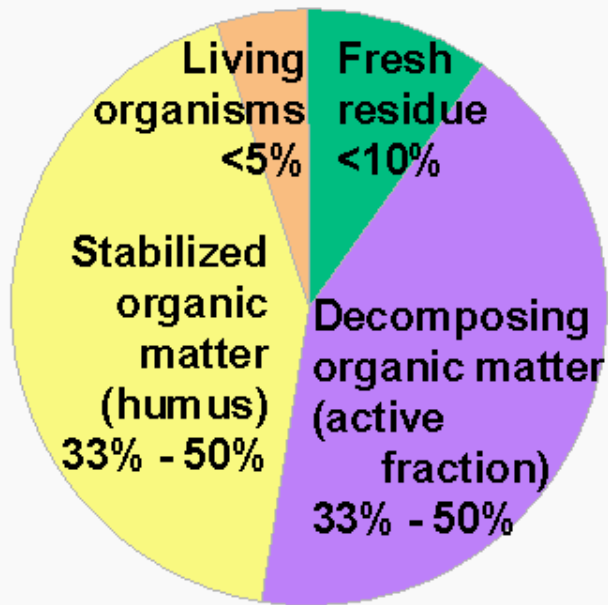
100?      300      500      1000

**Table 5-4. Compositon of humic substances in various environments**

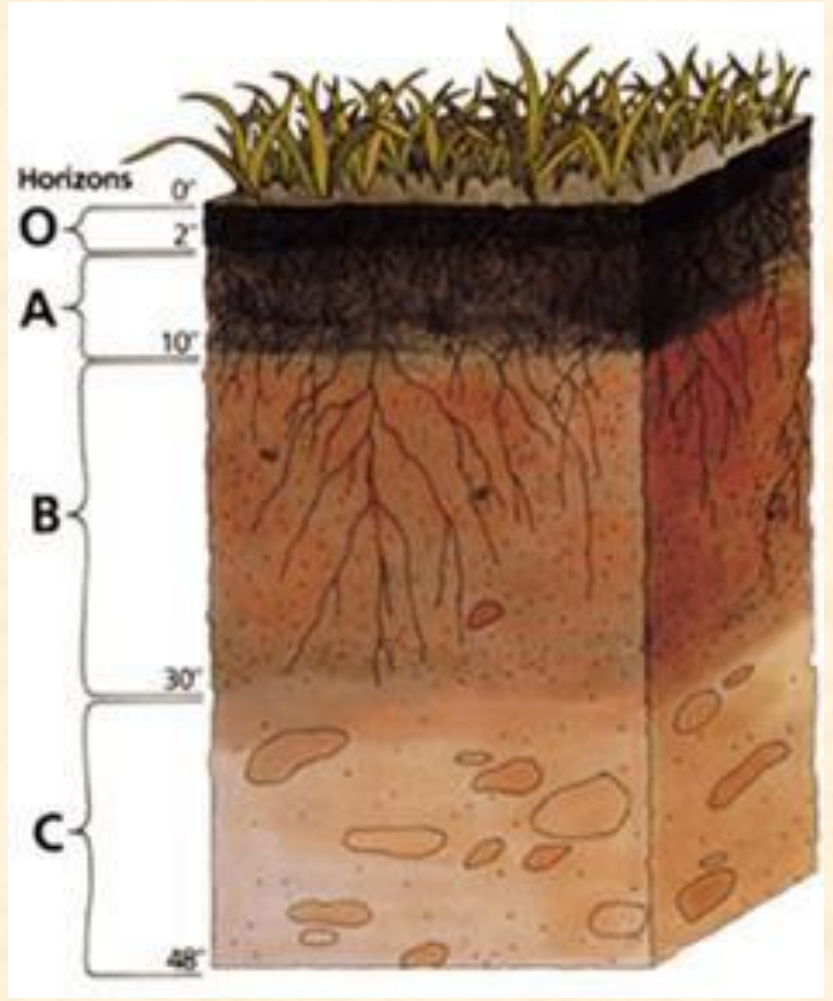
	Soil	Ground water	Surface water	Lake Sediments	Sea water	Marine sediments
Aromatic hydrocarbons	20 - 35%	-	17 - 30%	<15%	<15%	<15%
H/C	0.5 - 1.0	0.7 - 1.2	0.7 - 1.1	1.0-1.6	1.6	1.0 - 1.5
Molecular weights	$10^3 - 10^6$	$500 - 10^4$	$<10^4$	$10^3 - 10^6$	$<10^3$	-



# Soil Organic Matter



**Soil:** a complex system of air, water, decomposing organic matter, living plants, and animals, in addition to the residues of rock weathering, organized into definite structural patterns as dictated by the environmental conditions.





**Gelisols** - soils with permafrost within 2m of the surface.



**Histosols** - organic soils.



**Spodosols** - acid forest soils w/ a subsurface accumulation of metal-humus complexes.



**Andisols** - soils formed in volcanic ash.



**Oxisols** - intensely weathered soils of tropical and subtropical environments.



**Vertisols** - clayey soils with high shrink/swell capacity.



**Aridisols** -  $\text{CaCO}_3$ -containing soils of arid environments with subsurface horizon development.



**Ultisols** - strongly leached soils with a subsurface zone of clay accumulation and <35% base saturation.



**Mollisols** - grassland soils with high base status.



**Alfisols** - moderately leached soils with a subsurface zone of clay accumulation and >35% base saturation.

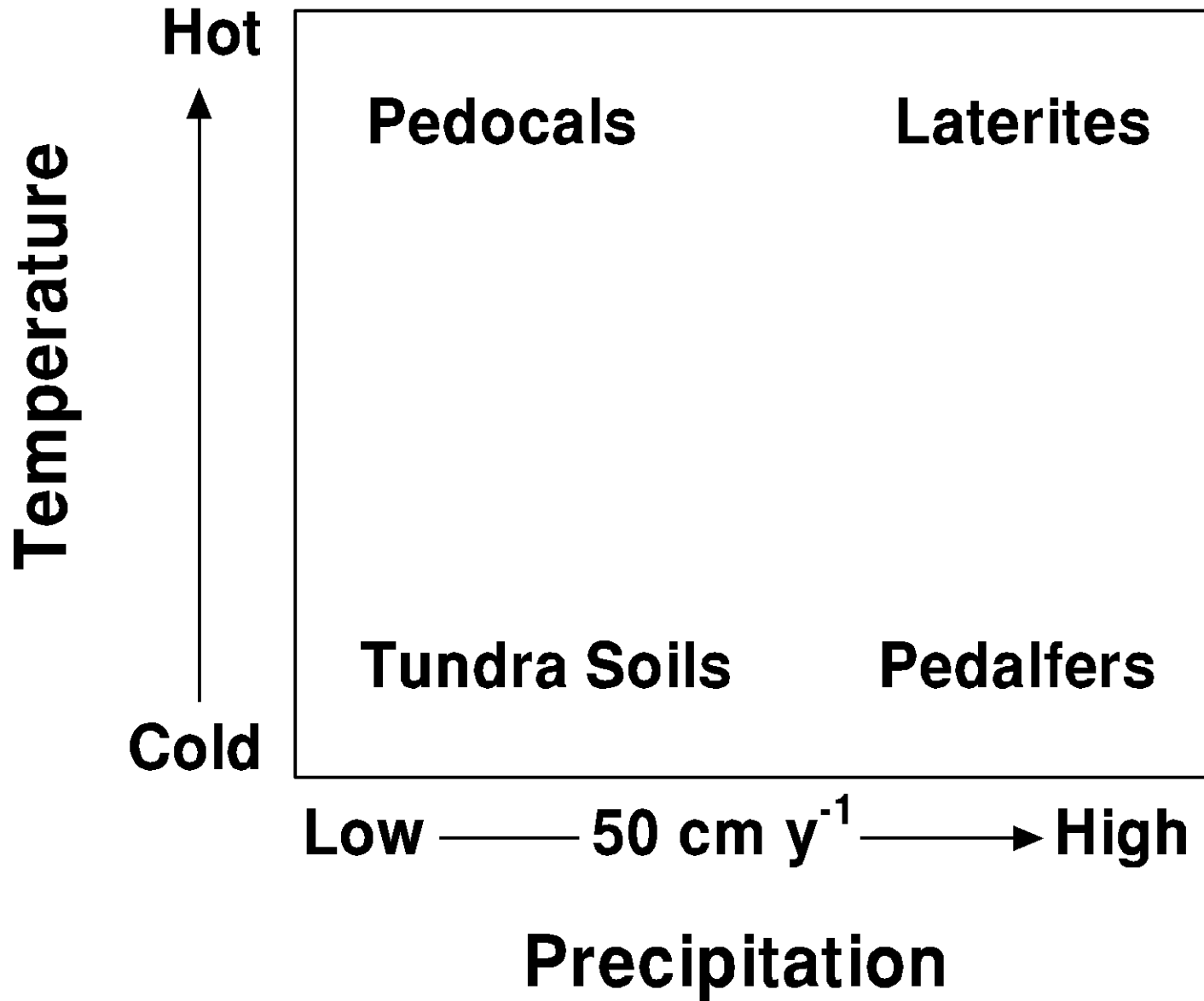


**Inceptisols** - soils with weakly developed subsurface horizons.

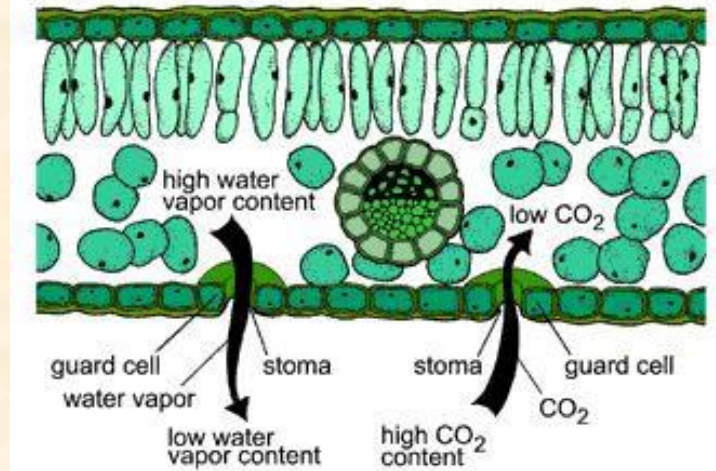
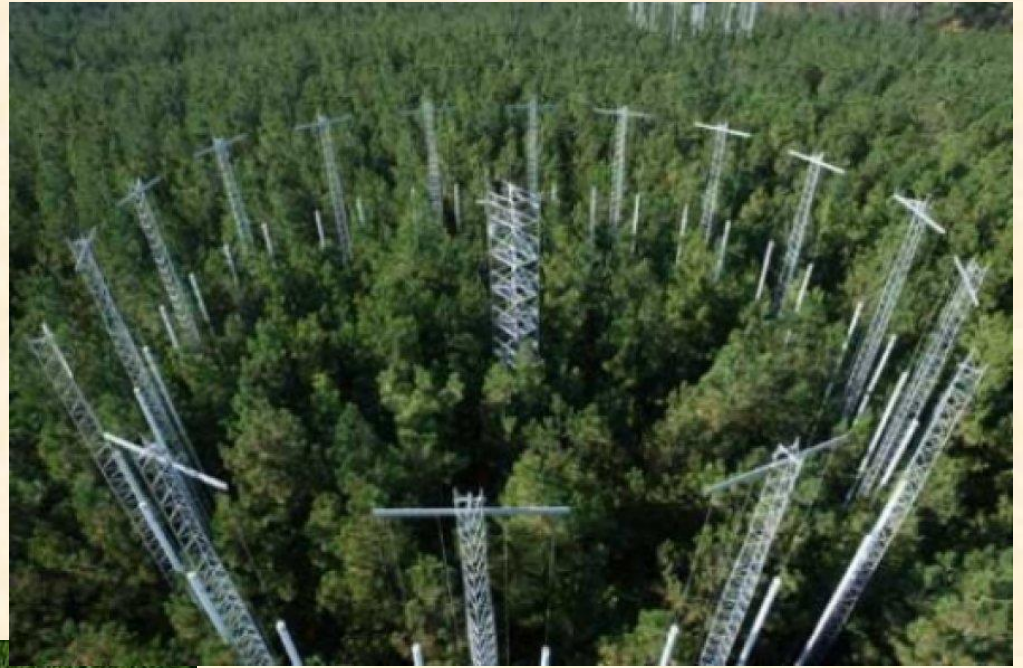
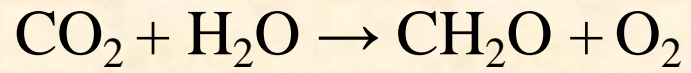


**Entisols** - soils with little or no morphological development.



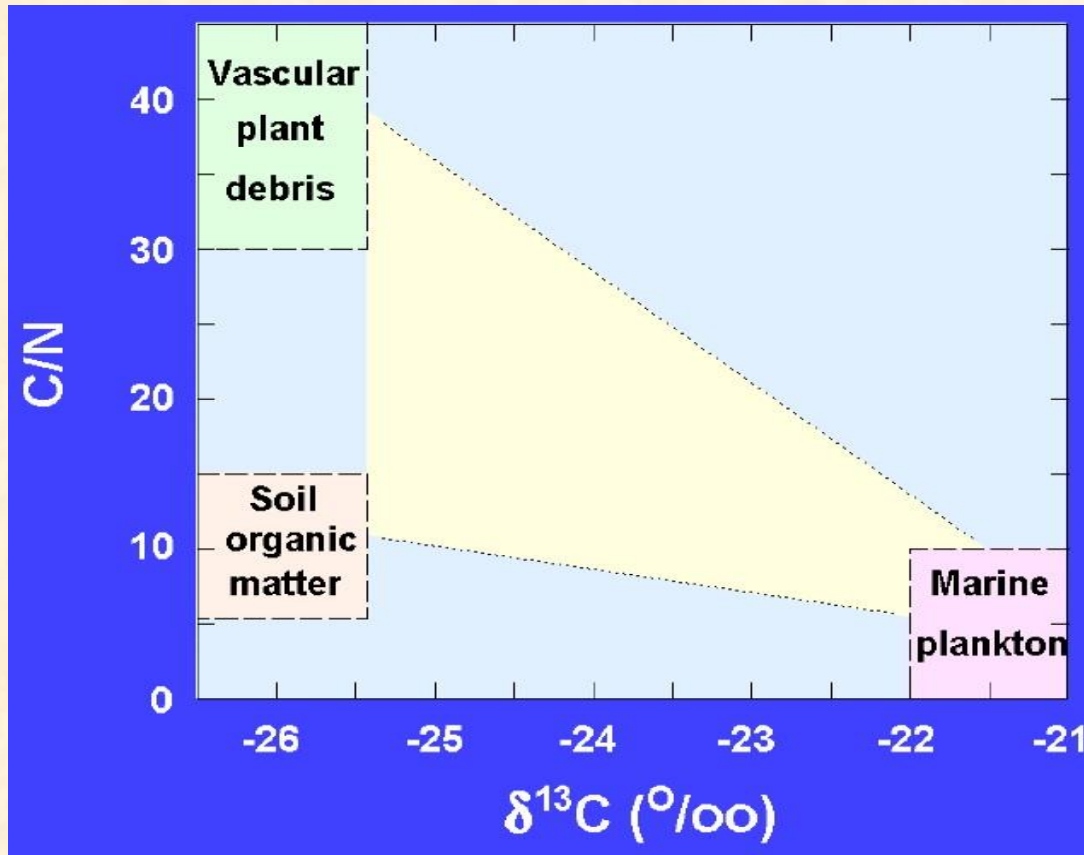


# Soil and Carbon Sequestration



# Marine Organic Matter

Marine and terrestrial sedimentary environments differ in a number of important ways. Marine sediments have a greater porosity and a narrower range of pH (7-8 versus 4.0 – 8.5) than terrestrial sediments.



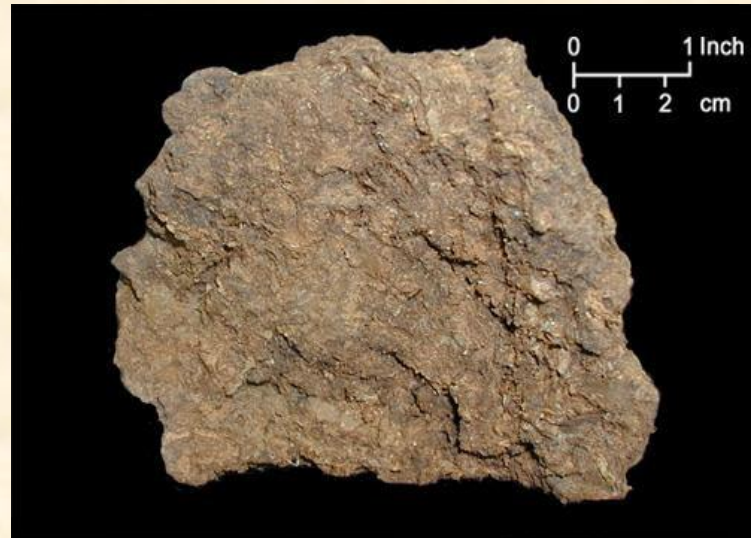
Different environments contain different organisms and as a result have different C/N ratios and  $\delta^{13}\text{C}$  values.

**Coal:** carbonaceous sediment composed most often of the remains of spores, algae, fine plant debris and noncarbonaceous ash.

**Humic coals:** derived from humic substances via a peat stage.

**Sapropelic coals:** formed from fairly fine-grained organic muds in quiet, oxygen-deficient shallow waters.

**Peat:** Unconsolidated, semicarbonized plant remains with high moisture content. Not true coal.

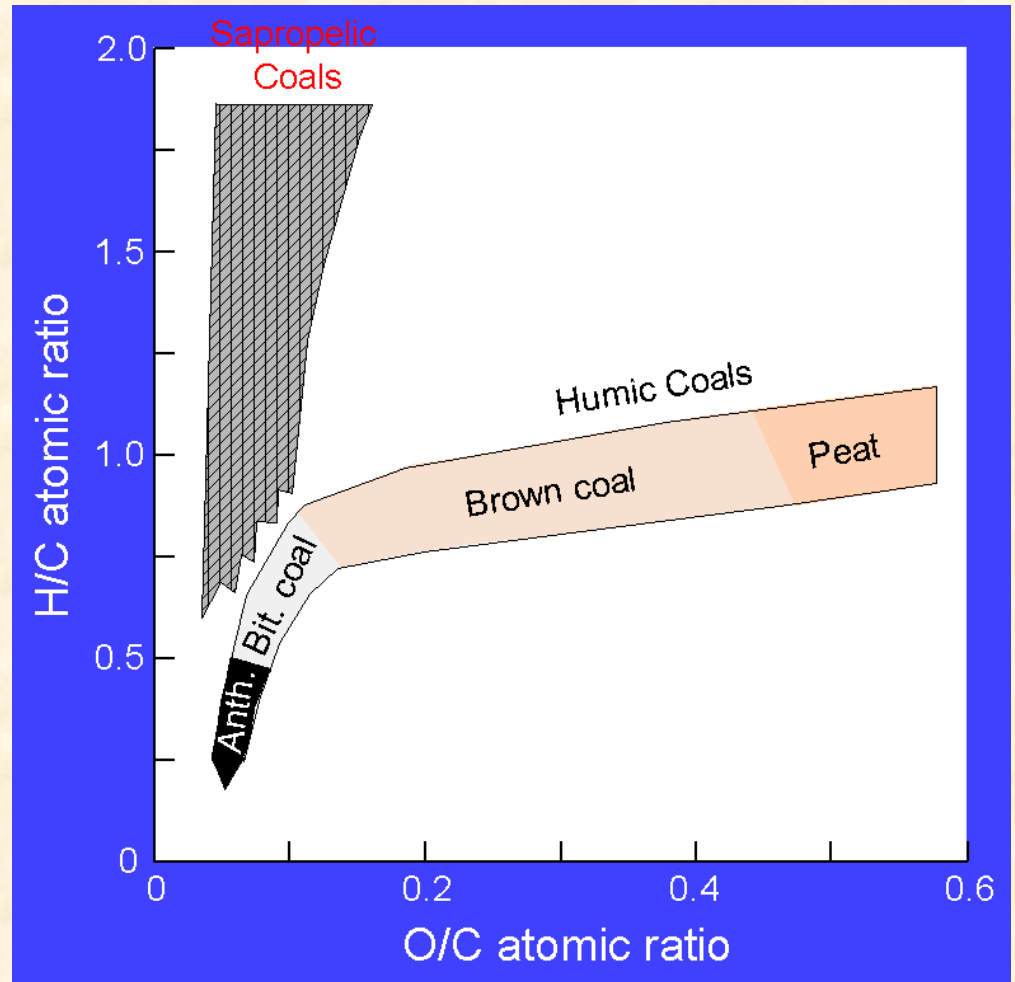


Lignite: (brown coal) coal with high moisture content and commonly retain many of the structures of the original woody plant fragments.



Bituminous: coals that are hard, black coals with a higher carbon content than lignite and commonly display alternating bright and dull bands.

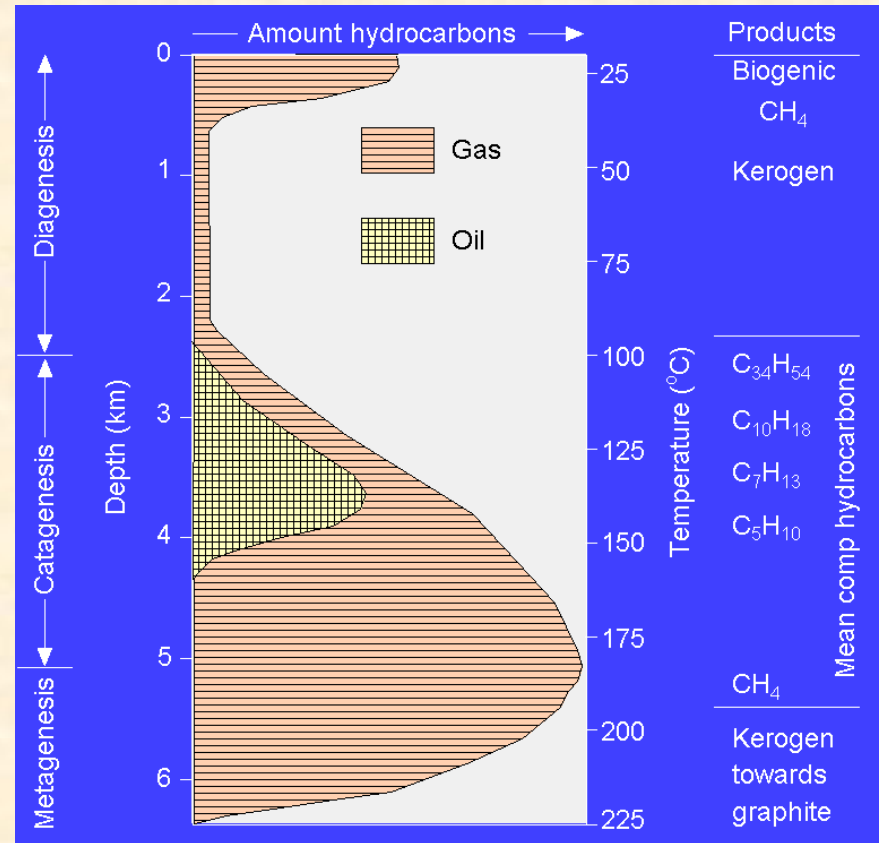
**Anthracite:** hard, black, dense coal commonly containing more than 90% carbon. Anthracite is hard and shiny and breaks with conchoidal fracture.



**Petroleum:** any hydrocarbon-rich fluid (liquid or gas) derived from kerogen by increases in pressure and temperature.

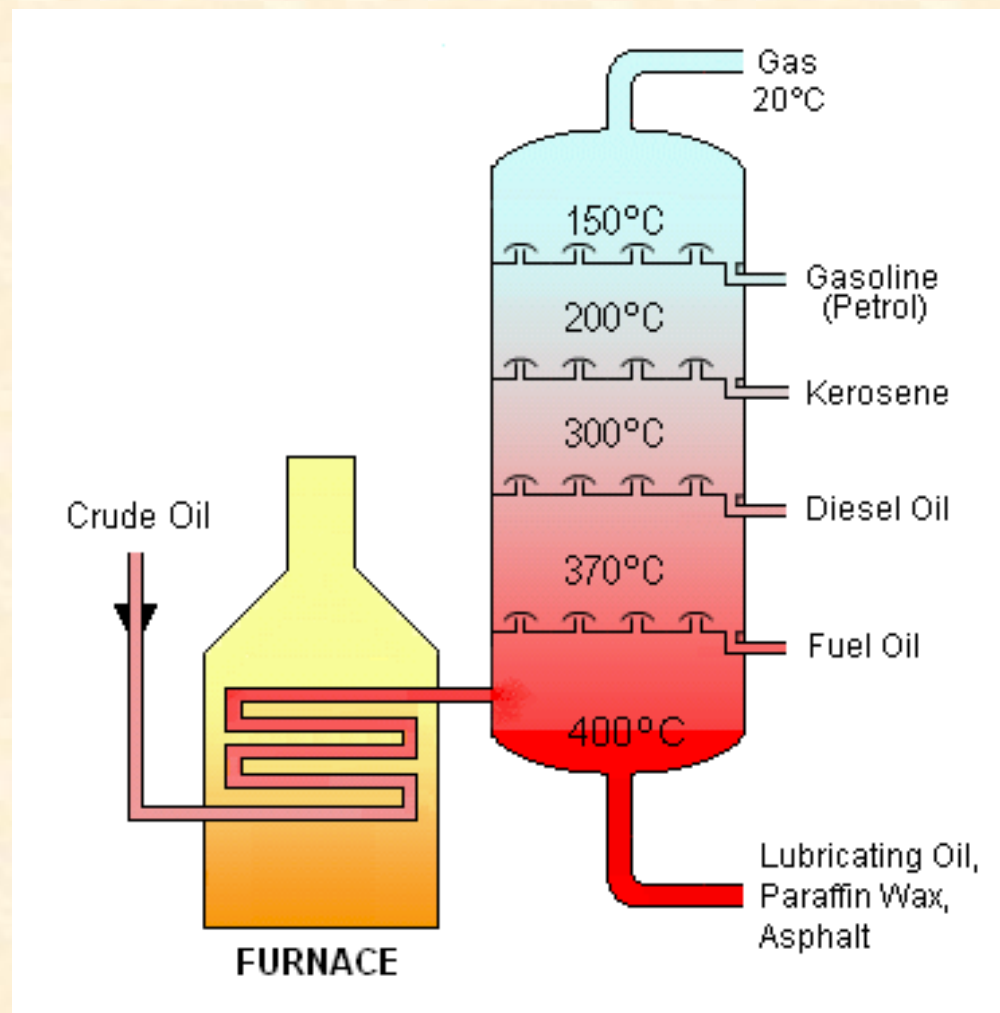
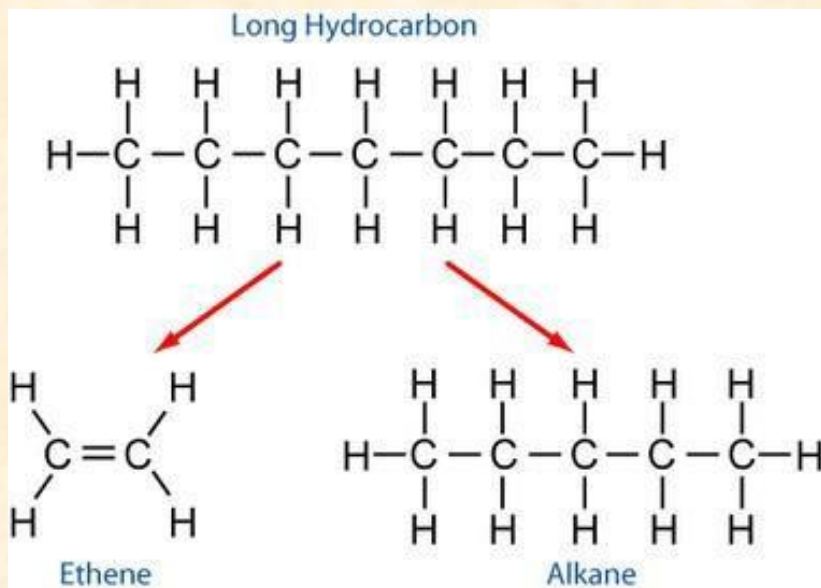
**Kerogen:** a polymeric organic material that occurs in sedimentary rocks in the form of finely disseminated organic macerals—the preserved remains of plant material.

**Diagenetic environment:** the environment in which processes occur at pressures and temperatures greater than those of the weathering environment, but below those required to produce metamorphism.



**Cracking:** the process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules (e.g. light hydrocarbons) by the breaking of carbon-carbon bonds in the precursors.

The *rate* of cracking and the end products are strongly dependent on the temperature and presence of any catalysts.





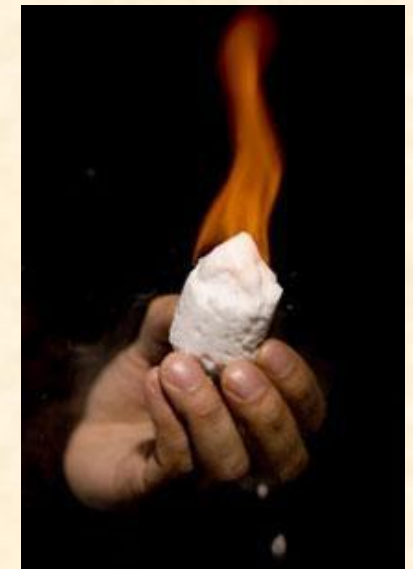
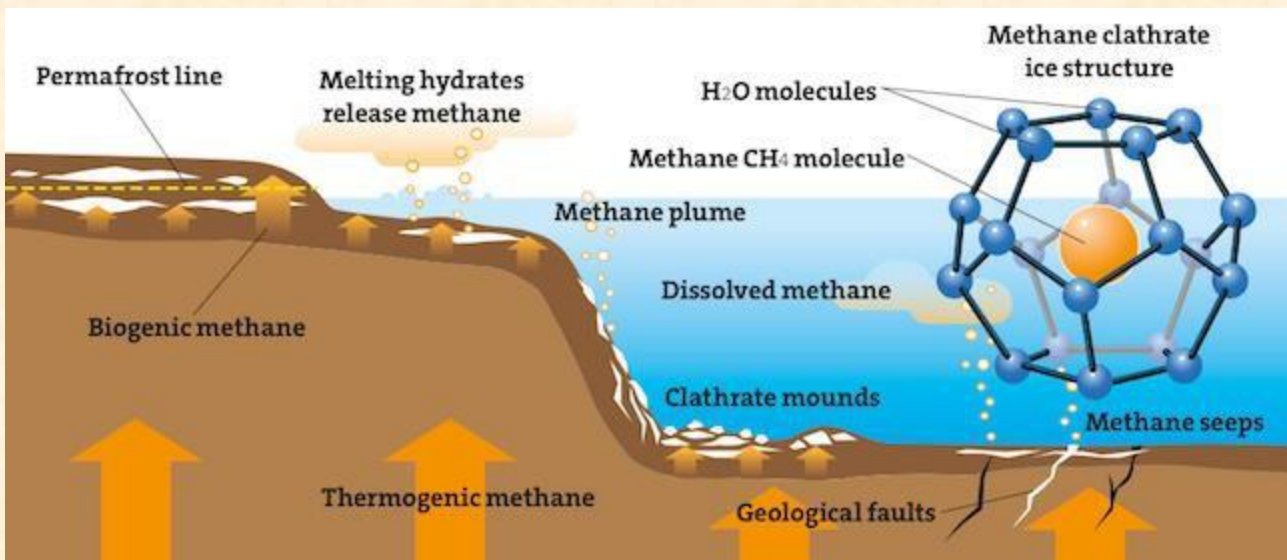
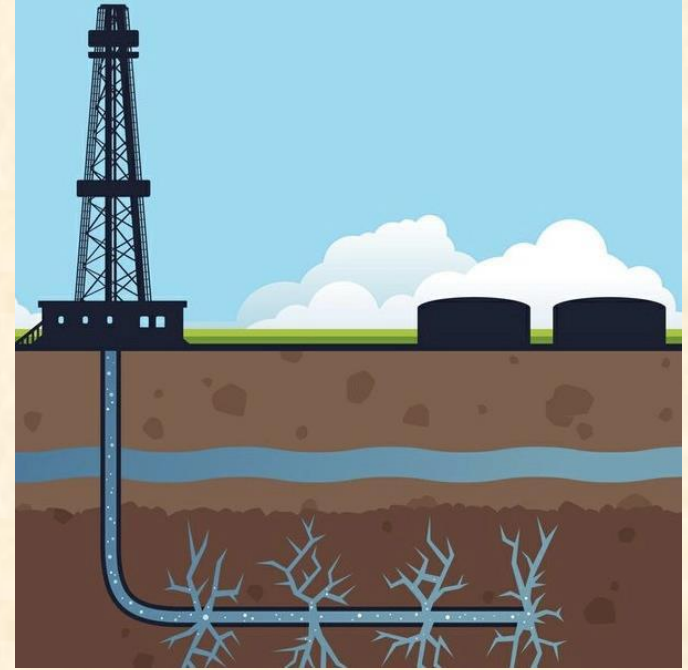
**Sweet** crude oil has a low sulfur content.

**Sour** crude oil has a high sulfur content.

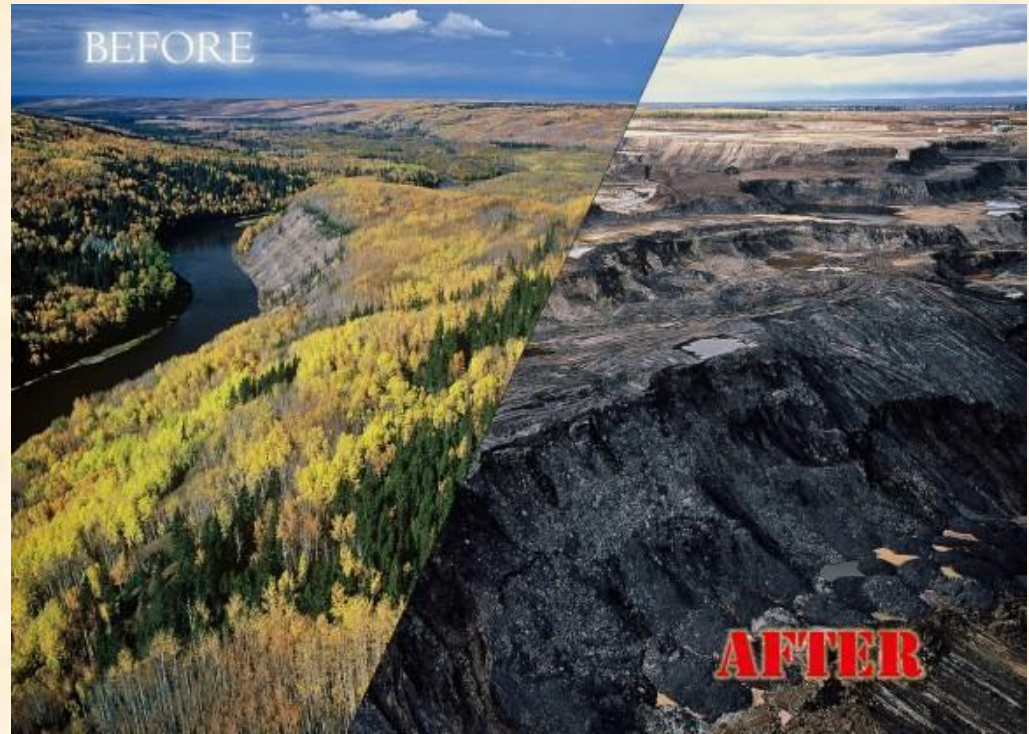
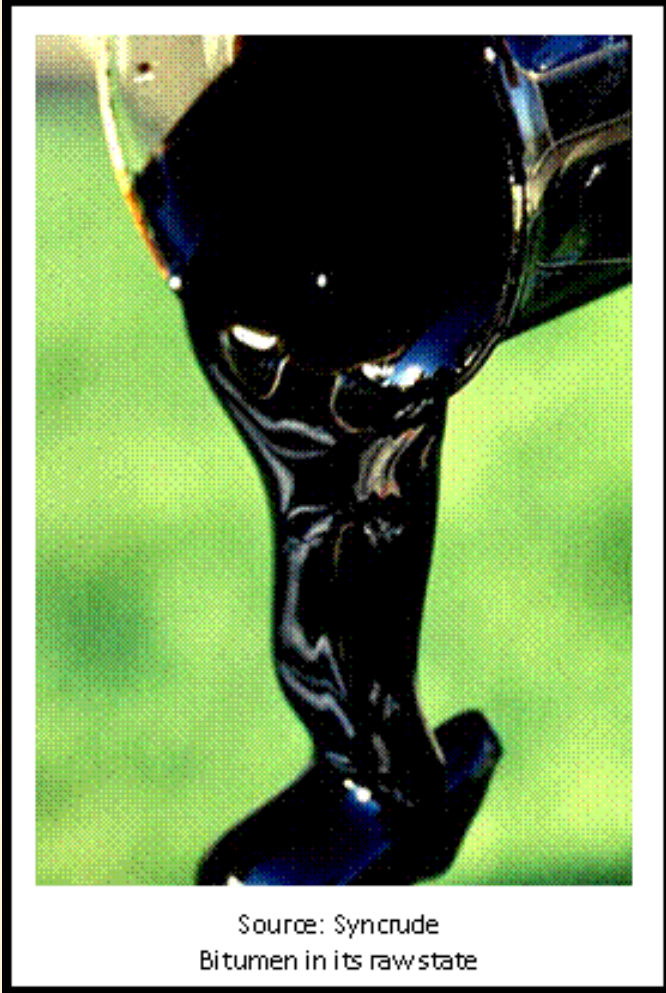
<b>Elemental Composition of Crude Oil</b>	
Element	Abundance (wt. %)
C	82.2 – 87.1
H	11.8 – 14.7
S	0.1 – 5.5
O	0.1- 4.5
N	0.1 – 4.5
Others	< 0.1

Why would the percentage of S and N be important?

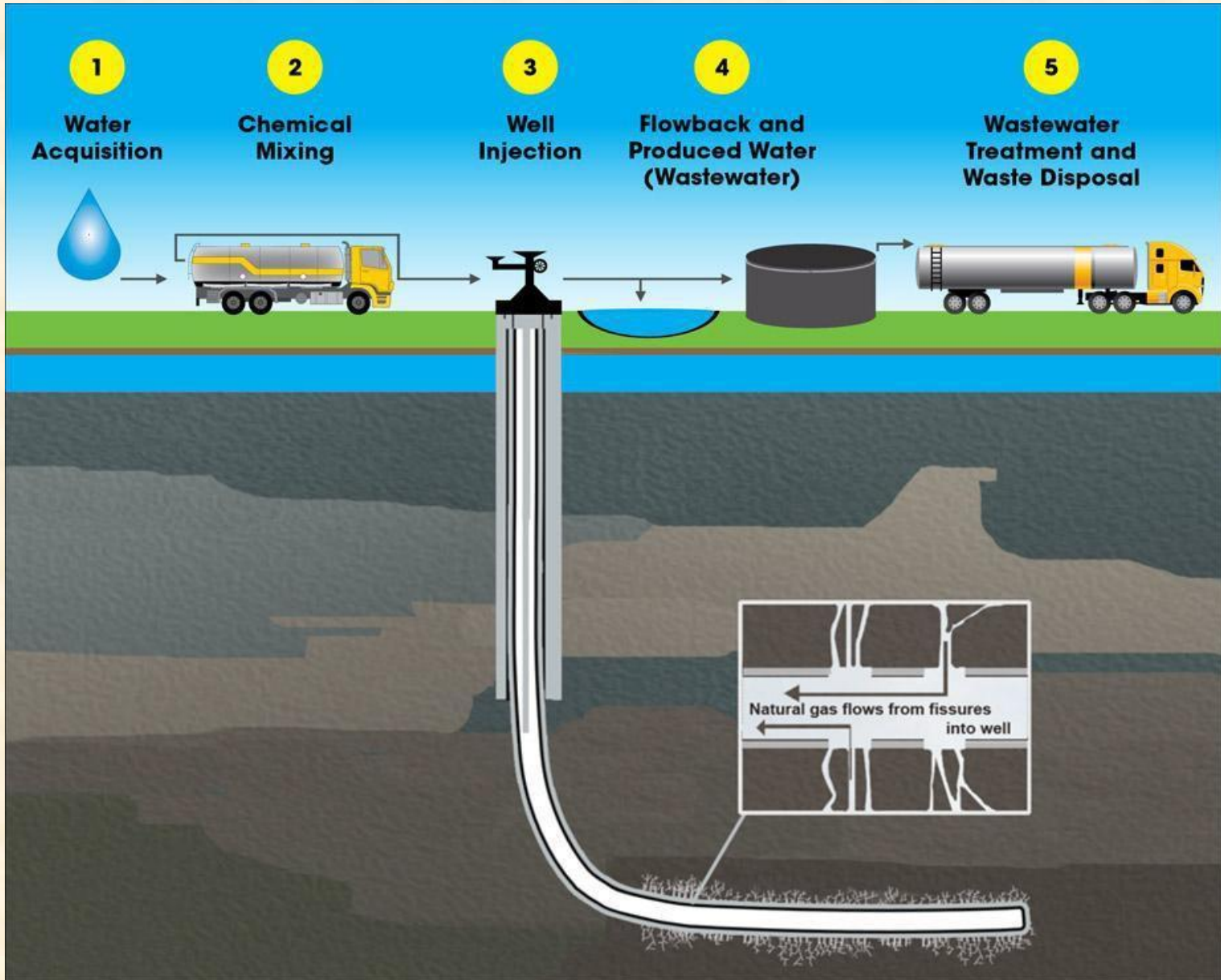
# Tar Sands, Hydraulic Fracturing and Methane Clathrates (Hydrates)



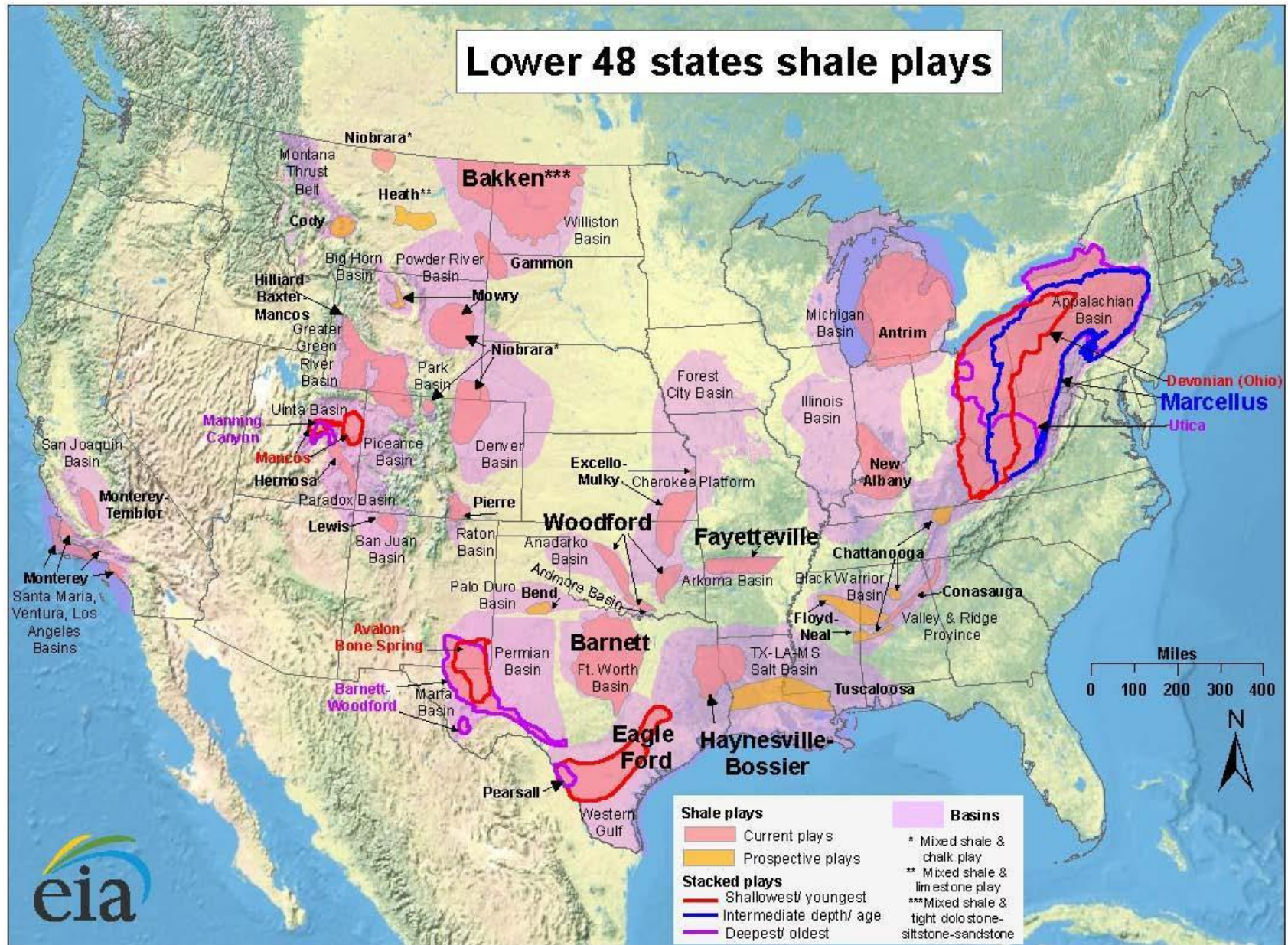
# Alberta Tar Sands



# Hydraulic Fracturing



# Lower 48 states shale plays



Source: Energy Information Administration based on data from various published studies.  
Updated: May 9, 2011



# Methane Hydrates or Clathrates

©NewScientist

## Global reserves of methane clathrates

Ice deposits containing natural gas within their crystals are found both under the sea and in permafrost. Globally, more carbon may be trapped in these methane clathrates than in all the traditional sources of fossil fuel

● Known occurrence    ● Occurrence inferred from geological data



**ALASKA**  
Between 0.7 and 4.4 trillion m<sup>3</sup> of methane clathrate found. 0.9 trillion m<sup>3</sup> could heat 100 million homes for a decade

**JAPAN**  
50 trillion m<sup>3</sup> of methane clathrate found. Enough to supply Japan with natural gas for centuries

One way of releasing the methane is to pump another gas, such as CO<sub>2</sub>, into the clathrate to take its place. The methane then shoots up the wellhead to the surface to be collected

If uncontrolled, a release could trigger explosions within the clathrate reserves that might cause landslides or tsunamis

● Clathrate

Released methane expands to **160** times the volume of the clathrate it came from

# Natural carbon inputs to surface and ground waters.

**TOC** is the total organic carbon and is composed of the DOC and the POC.

**DOC** is dissolved organic carbon—can pass through a 0.45 $\mu$ m filter.

**POC** is particulate organic carbon—carbon particulate matter retained by a 0.45 $\mu$ m filter.

Sources of carbon can either be ***allochthonous*** (from outside the aquatic system) or ***autochthonous*** (from within the aquatic system).

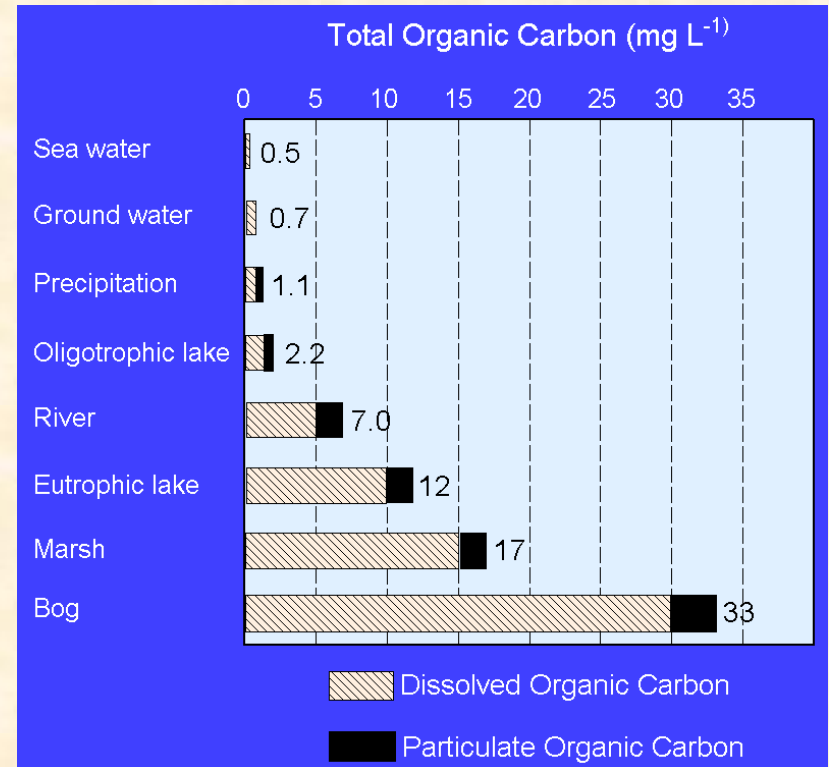
The concentrations of organic carbon vary greatly with differing aquatic systems, as does DOC / POC.

*In general:*

Surface waters have higher TOC than deep waters, because of photosynthetic organisms.

Coastal waters have a higher TOC than open ocean waters, because of land inputs.

Groundwater has a low carbon content, because organic carbon is used as a food supply by heterotrophic microbes.



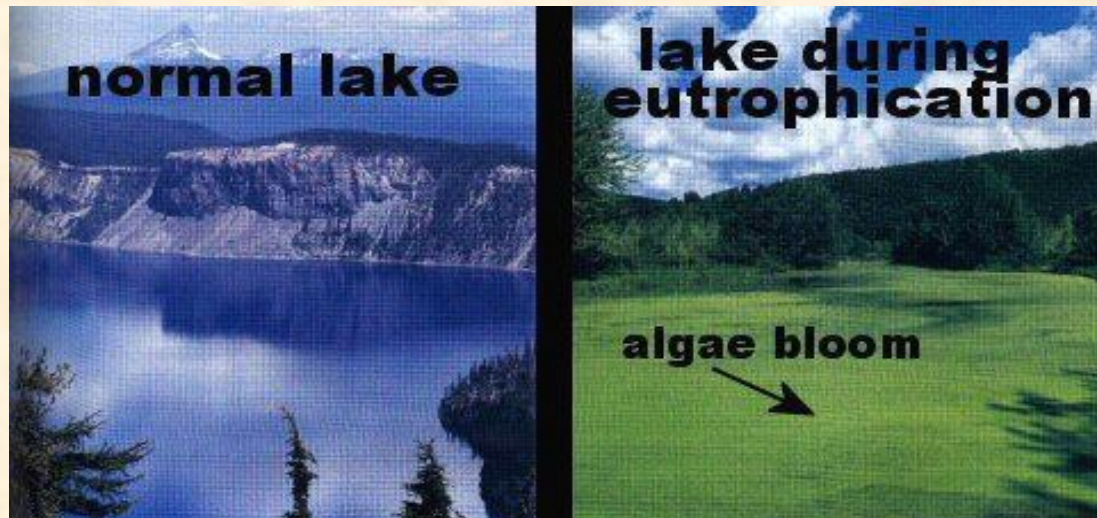


## Anthropogenic Carbon inputs to surface and ground waters

**Organic carbon:** Think waters overrun by septic systems...

If these effluents contain nutrients (N, K, P) which are often limited in the natural environment, it can lead to eutrophication.

**BOD:** (biological oxygen demand) the capacity of the organic matter in a sample of natural water to consume oxygen. The BOD should be much lower than 8.7 mg O<sub>2</sub>/L (O<sub>2</sub> saturation value at 25°C). The median BOD for unpolluted waters in the United States is 0.7 mg O<sub>2</sub>/L



**Pesticides:** chemicals used to control the growth of unwanted organisms.

**Insecticides:** a pesticide used to control insects. **Herbicide:** a pesticide used to control plant growth. **Fungicide:** a pesticide used to control the growth of various types of fungus.

**Hard pesticides:** typically organochlorine compounds that are persistent in the environment, but have low toxicity in mammalian systems.

**Soft pesticides:** Typically organophosphorus compounds and carbamates that have short residence times in the environment, but are often highly toxic.

**LD<sub>50</sub>:** the amount of the chemical per unit of body mass required to produce death in 50% of an exposed animal population.

Bioconcentration factor: (BCF) the expression of the tendency of a particular organic chemical in water to concentrate in fatty tissue.

$$\log \text{BCF} = 0.935 \cdot \log K_{\text{OW}} - 1.495$$

Where  $K_{\text{OW}} = [\text{S}]_{\text{octanol}} / [\text{S}]_{\text{water}}$  and

$[\text{S}]_{\text{octanol}}$  is the concentration of the chemical in the alcohol: 1-octanol and  $[\text{S}]_{\text{water}}$  is the concentration of the chemical in water.

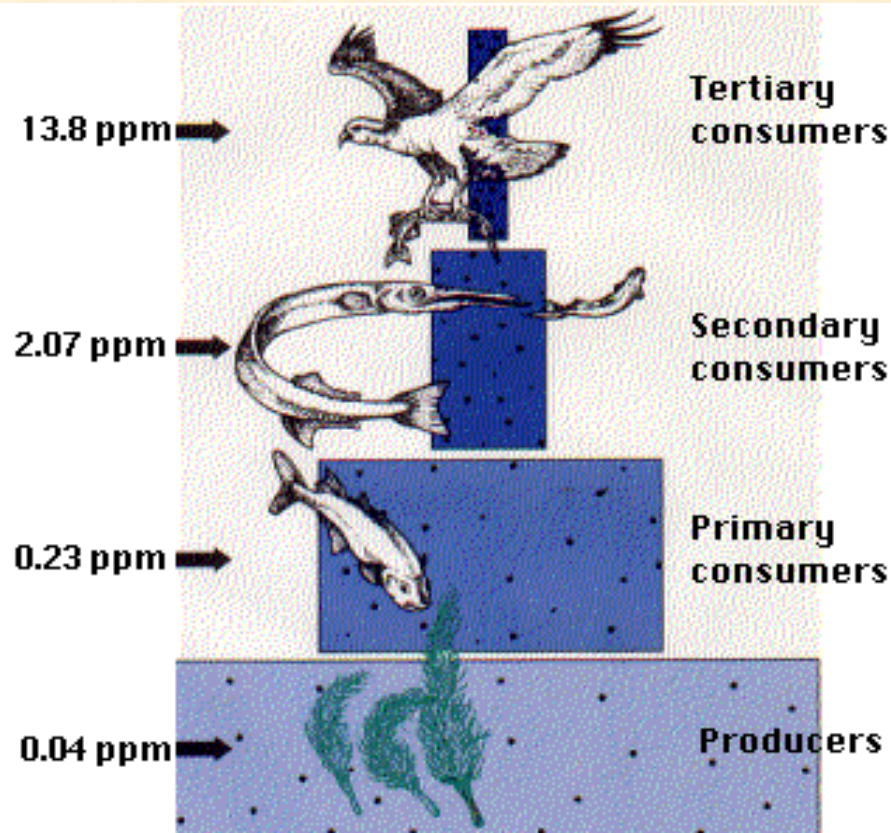
The higher the  $K_{\text{OW}}$  value, the more strongly a chemical is partitioned into the fatty tissue.

Chemicals with  $\log K_{\text{OW}}$  values of 7 to 8 or greater tend to be strongly adsorbed to sediments and are unlikely to enter living tissue.

**Table 5-9. Data for selected pesticides**

Pesticide	Solubility in H <sub>2</sub> O (mg kg <sup>-1</sup> )	LD <sub>50</sub> ( mg kg <sup>-1</sup> )	log K <sub>ow</sub>	log BCF
<i>Hard</i>				
HCB	0.0062	3,500 - 10,000	5.3	3.5
DDT	0.0034	115	3.9 - 6.2	2.2 - 4.3
Toxaphene	n/a	85	2.9 - 3.3	1.2 - 1.6
Dieldrin	0.20	46	5.1 - 6.2	3.3 - 4.3
Mire x	0.20	700	5.8	3.9
<i>Soft</i>				
Malathion	145	1,375 - 2,800	2.7	1.0
Parathion	24	3.6 - 13	n/a	
Atrazine	30	1,870 - 3,080	2.3	0.7

Biomagnification: the bioaccumulation of a substance up the food chain by transfer of residues of the substance in smaller organisms that are food for larger organisms in the chain.

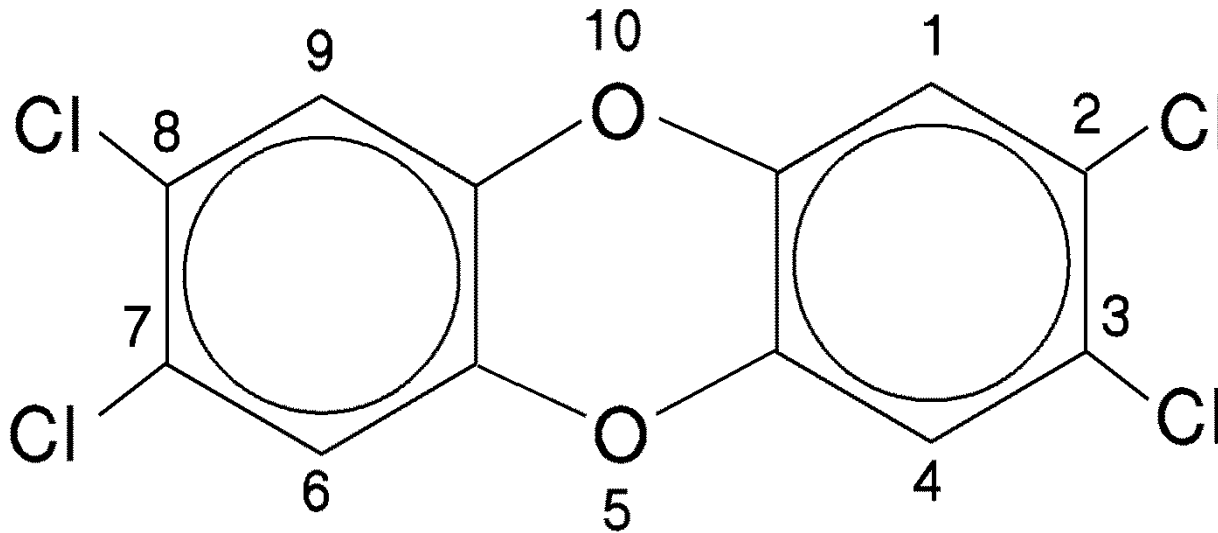


The numbers are representative values of the concentration in the tissues of **DDT** and its derivatives (in parts per million, ppm)

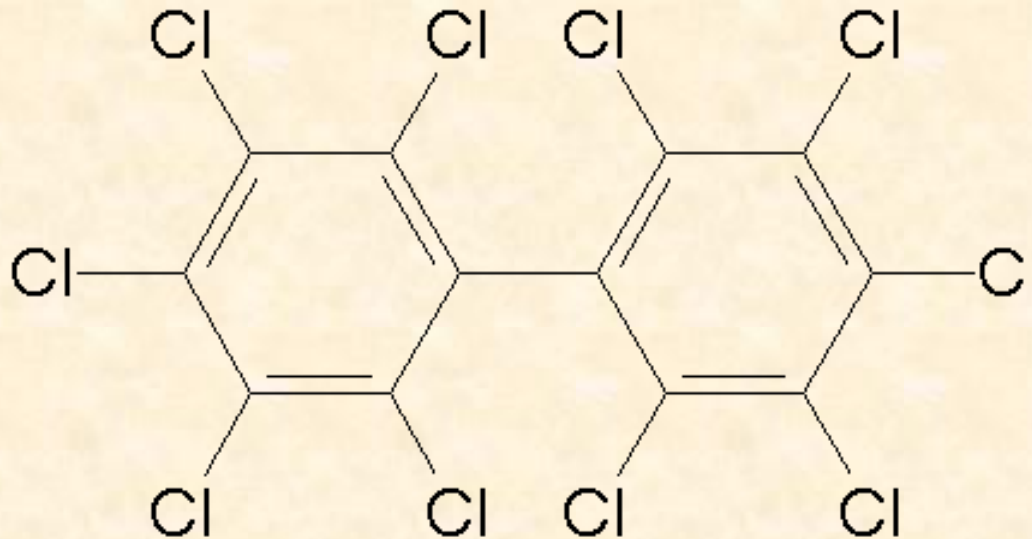
Recall that roughly 10% of the biomass from the lower trophic level is transferred to the next level, but ALL of the pesticide is transferred.

## Dioxins, PCBs, and Dibenzofurans (DFs)

**Dioxin:** the byproduct of pesticide manufacture and by the incomplete combustion of PCBs during waste incineration. They have high thermal stability and do not decompose until the temperature exceeds 700°C. The basic structure is two benzene rings connected by an oxygen-containing cyclic hydrocarbon. The benzene rings have from one to eight chlorine atoms substituting for hydrogen giving a total of 75 possible derivatives.

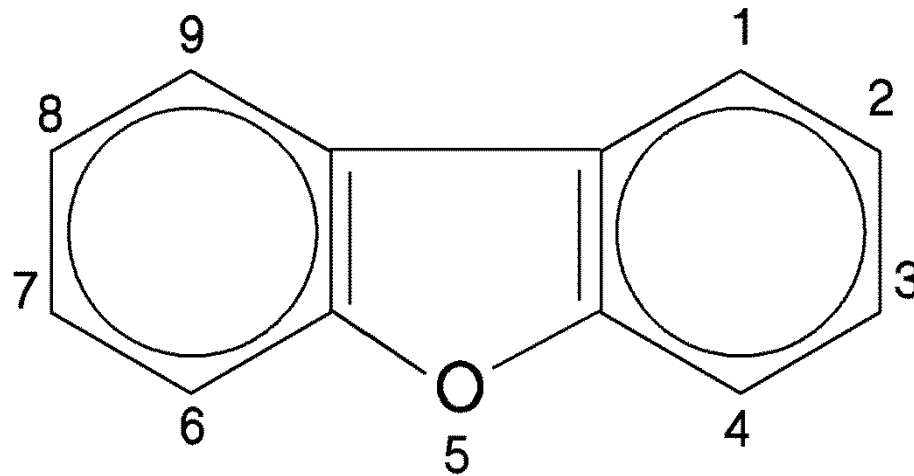


**PCBs:** (polychlorinated biphenyls) two benzene rings joined by a single bond with attached chlorine atoms. PCBs have very high chemical, thermal, and biological stability; low vapor pressures; and high dielectric constants. For this reason they have wide industrial applications. They accumulate in the environment and subsequently in the fatty tissues of birds and fish. They are ubiquitous.



**Dibenzofurans:** produced when PCBs are heated in the presence of oxygen. Their structure is that of 2 benzene rings joined by a furan ring (4 carbons and one oxygen joined in a ring structure.) Furans with intermediate amounts of Cl have a toxicity similar of that to TCDD—Dioxin.

## Dibenzofuran



Benzene ring

Furan

Benzene ring



The relative toxicity of these chemicals is measured using the Toxicity Equivalence factors (TEQ). By multiplying the TEQ specific to the dioxin, etc. one can determine the relative detrimental health effects as equivalents to TCDD. FYI: The  $LD_{50}$  for TCDD in hamsters is  $\sim 0.046\text{mg/kg}$ .

#### Example 5-4

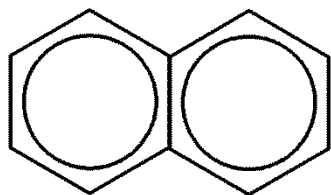
Suppose that an individual ingested 20 pg of 2,3,7,8-tetrachlorodibenzo-p-dioxin, 200 pg of octachlorodibenzo-p-dioxin, and 40 pg of 1,2,3,4,7,8,9-heptachlorodibenzofuran. Using the toxicity factors listed in table 5-10, determine the Toxicity Equivalence Factor for the sum of these exposures.

**Table 5-10. Toxicity e quivalence factors ( TEQ) for some important dioxins and furans**

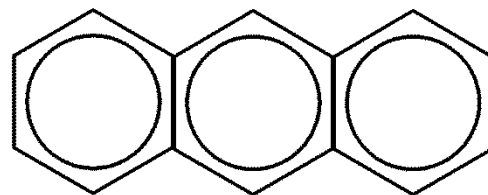
Dioxin or furan	TEQ
2,3,7,8-tetrachlorodibenzo-p-dioxin	1
1,2,3,7,8-pentachlorodibenzo-p-dioxin	0.5
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	0.1
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	0.1
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	0.1
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	0.01
octachlorodibenzo-p-dioxin	0.001
2,3,7,8-tetrachlorodibenzofuran	0.1
2,3,4,7,8-pentachlorodibenzofuran	0.5
1,2,3,7,8-pentachlorodibenzofuran	0.05
1,2,3,4,7,8-hexachlorodibenzofuran	0.1
1,2,3,7,8,9-hexachlorodibenzofuran	0.1
1,2,3,6,7,8-hexachlorodibenzofuran	0.1
2,3,4,6,7,8-hexachlorodibenzofuran	0.1
1,2,3,4,6,7,8-heptachlorodibenzofuran	0.01
1,2,3,4,7,8,9-heptachlorodibenzofuran	0.01
octachlorodibenzofuran	0.001

$$TEQ = (20\text{pg})(1) + (200\text{pg})(0.001) + (40\text{pg})(0.01) = 20.6\text{pg of TCDD}$$

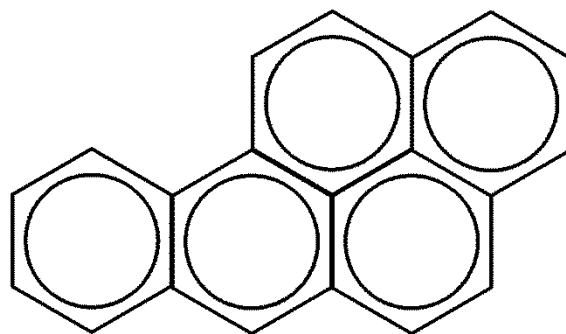
**PAHs (polycyclic aromatic hydrocarbons)** consist of fused benzene rings. The only PAH still commercially produced is naphthalene, whose vapor is toxic to some insects. PAHs are also produced by the incomplete combustion of wood and coal. They are found in creosote, which is a wood preservative. Certain PAHs are known carcinogens and tend to accumulate in fatty tissues.



Napthalene



Anthracene



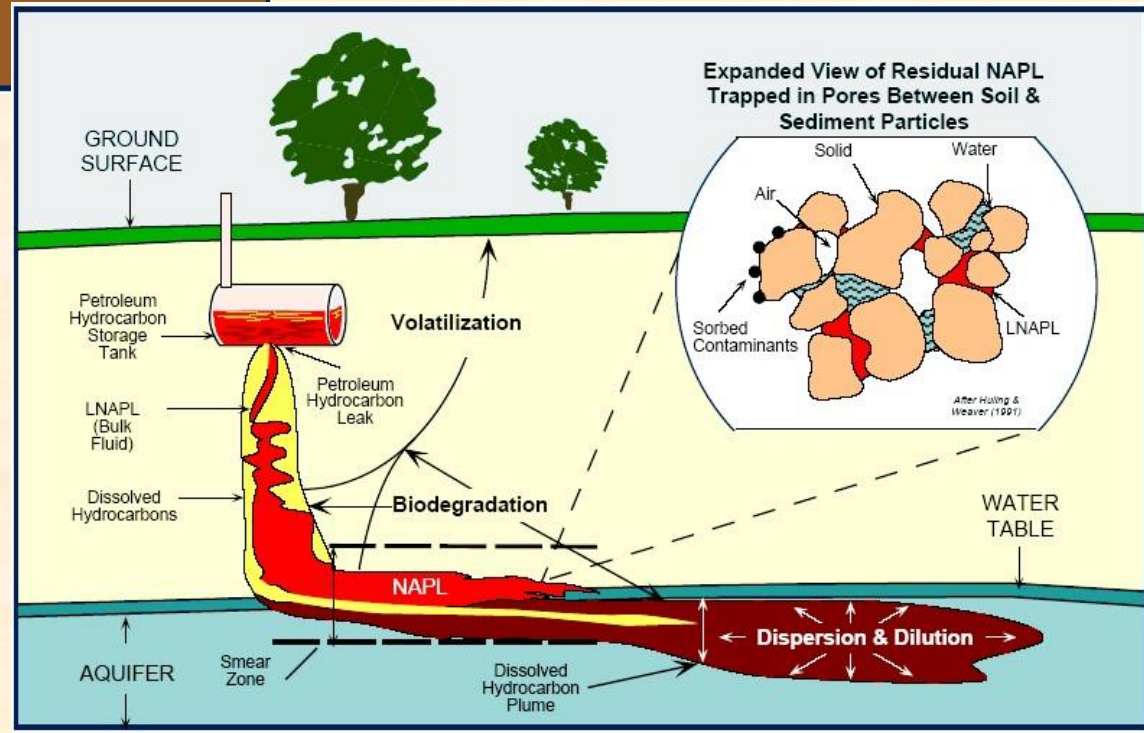
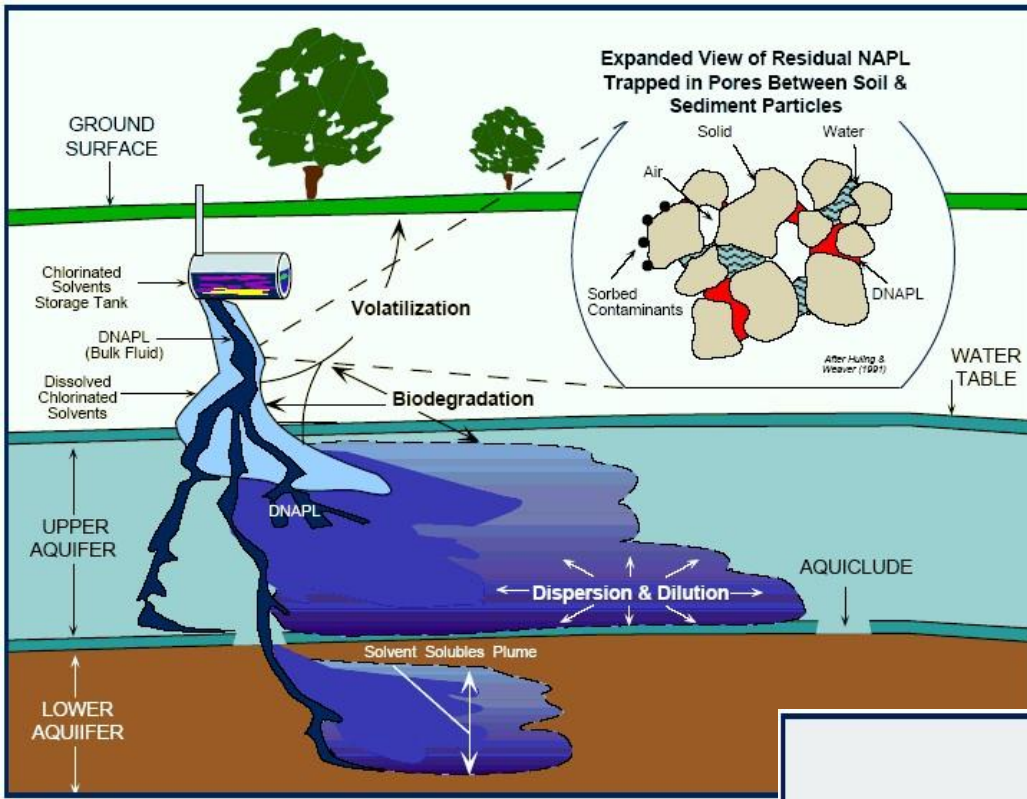
Benzo(a)pyrene

**NAPLs (nonaqueous-phase liquids):** hydrocarbons that have very low solubility in water. They are divided into two groups on the basis of their density.

**LNAPLs** are light nonaqueous-phase liquids and are less dense than water. As a result, they will float on the water table. LNAPLs are primarily petroleum and gasoline-related compounds.

**DNAPLs** are dense nonaqueous-phase liquids and are more dense than water. As a result, they can sink into the saturated zone. DNAPLs are mostly halogenated hydrocarbons and commonly occur as contaminants in groundwater.

# DNAPLs



# LNAPLs

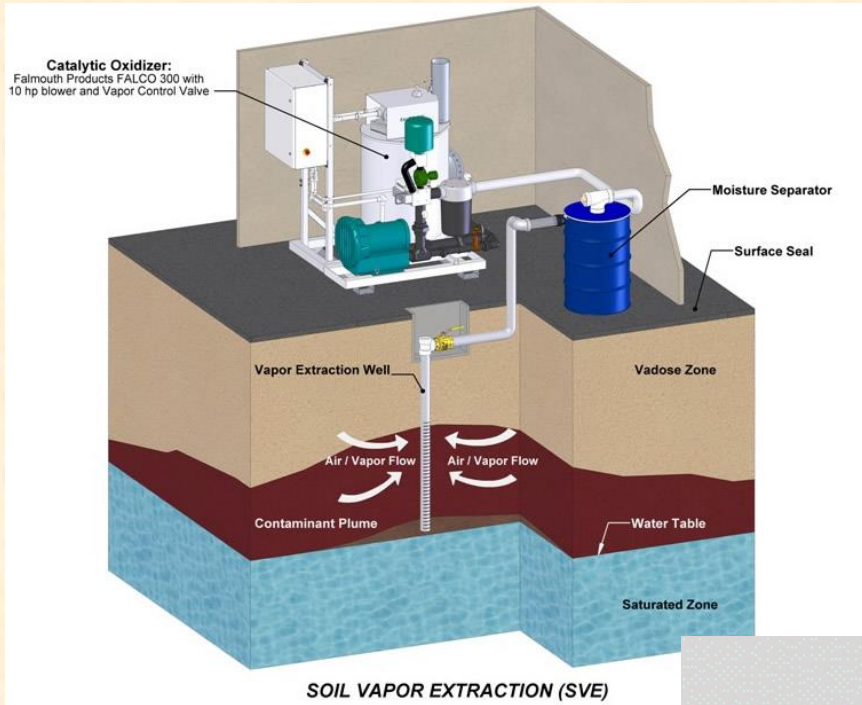
**Volatilization:** the tendency to readily go into the vapor state. Most organic compounds have a low volatility –they do not readily evaporate. However, low-molecular-weight, nonpolar molecules have the greatest vapor pressures of organic compounds. ---Think nail polish remover or gasoline---

The partitioning of an organic compound between liquid and vapor is often expressed in terms of a Henry's Law's constant.

$H_i = \text{Concentration in vapor state} / \text{Concentration in water}$ .

**Degradation Half-life:** the length of time it takes for 50% of an organic compound to be degraded.

$t_{1/2} = \ln 2 / k$  where  $k$  is the degradation (rate) constant for the compound.



## Remediation

**Soil vapor extraction (SVE)** uses vacuum pressure to remove volatile and some semi-volatile contaminants (VOCs and SVOCs) from the **soil**. The gas leaving the **soil** may be treated or destroyed, depending on local and state air discharge regulations.

*Air sparging*, also known as in situ air stripping and in situ volatilization, is an in situ remediation technique used for the treatment of saturated soils and groundwater contaminated by *volatile organic compounds (VOCs)*

