

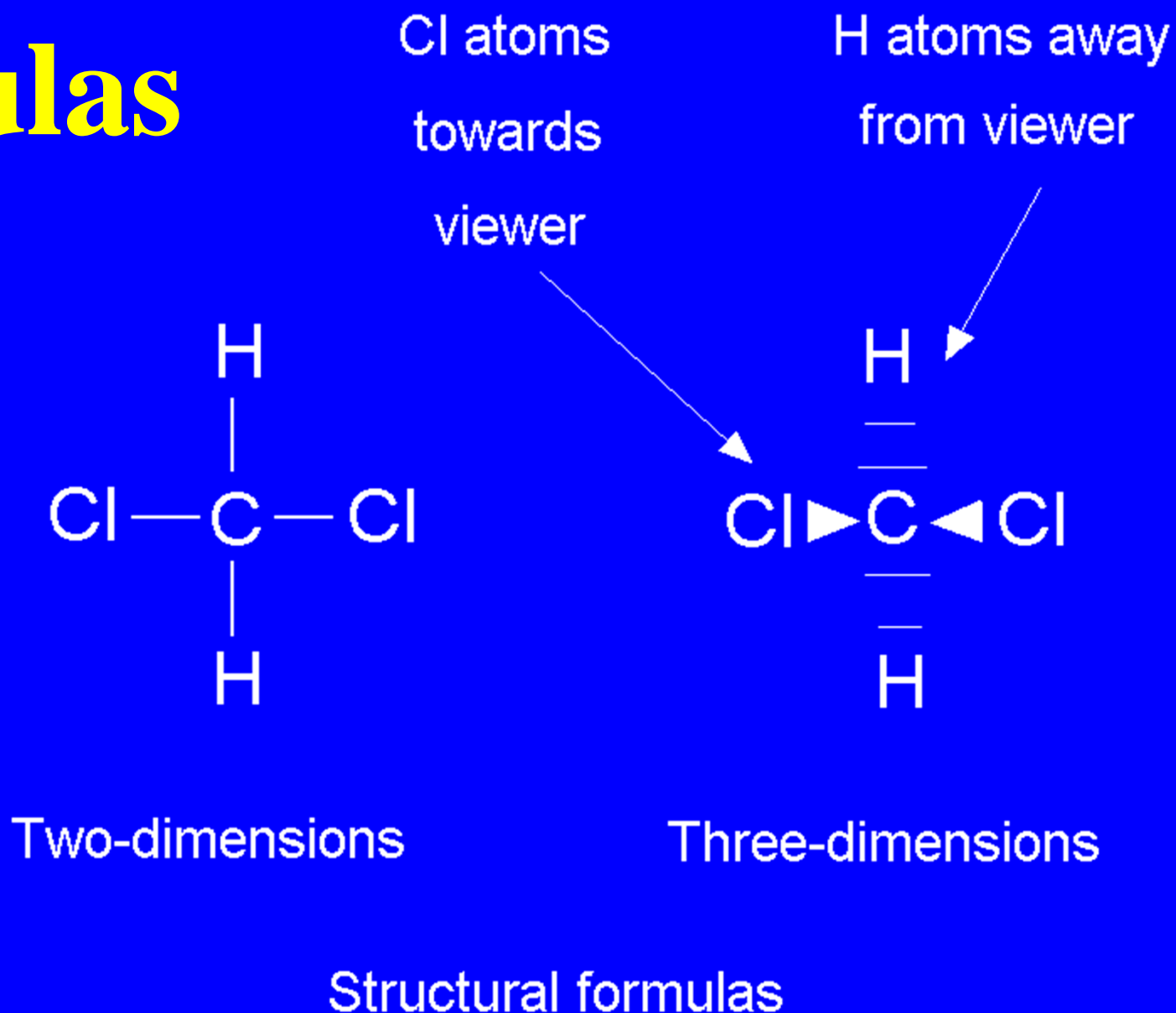
# Carbon Chemistry

**Nelson Eby: Principles of  
Environmental Geochemistry**

# Basic Structures and Naming of Organic Compounds

- Single bonds
- Double bonds
- Triple bonds
- Unsaturated compounds
- Saturated compounds
- Functional group
- Systematic names
- IUPAC naming system

# Formulas



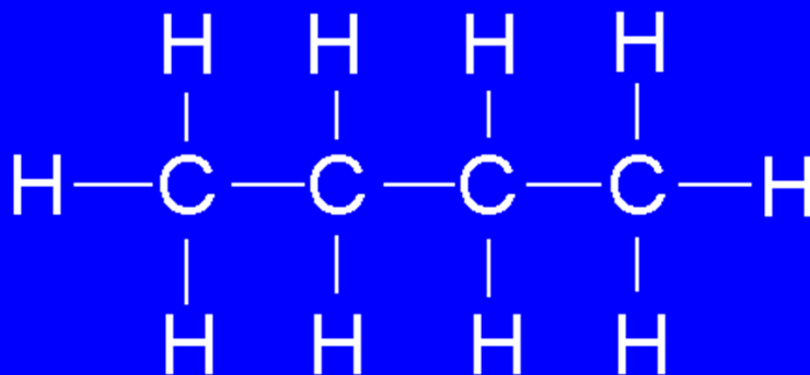
**Figure 5-1. Two- and three-dimensional structural formulas for dichloromethane,  $\text{CH}_2\text{Cl}_2$ .** In a two-dimensional representation, single, normal-weight lines indicate bonds extending away from the viewer and arrows indicate bonds extending toward the viewer.

# Butane

Condensed structural formula



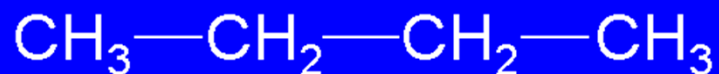
Structural formula



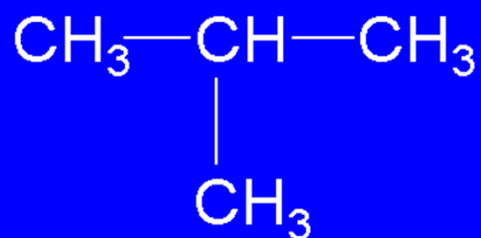
**Figure 5-2.** Relationship between the condensed structural formula and the structural formula of butane.



## Butane



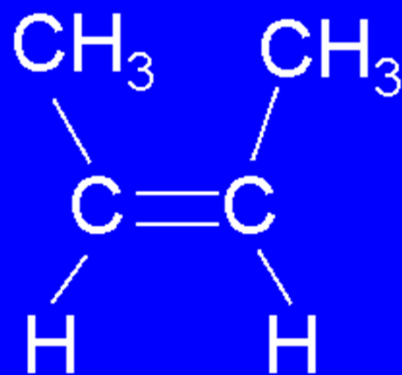
## 2-Methylpropane



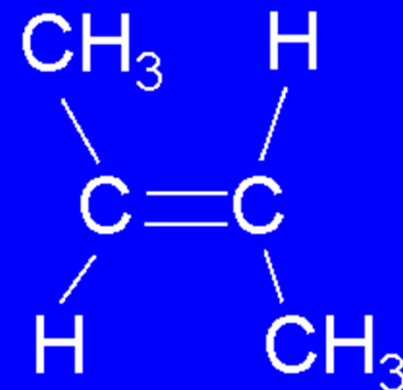
**Figure 5-3.** Isomers of  $\text{C}_4\text{H}_{10}$ . Both butane and 2-methylpropane have the same number of C and H atoms, but 2-methylpropane has a branched chain.

# ISOMERS

**Figure 5-4.** Examples of **geometric isomers**, *cis*-2-butene and *trans*-2-butene. In the first isomer, the two substituent groups are on the same side of the double bond. In the second isomer, the two substituent groups are on opposite sides of the double bond.



*cis*-2-butene



*trans*-2-butene

# VAPOR PRESSURE

*Vapor Pressure  $P^\circ$*  - the pressure of a compound in a gas phase in equilibrium with the liquid form of the compound.

The vapor pressure depends on the temperature (higher temperature = greater vapor pressure).

*Volatility* - the tendency of a compound to evaporate from a pure liquid of the compound.

Vapor pressure is a measure of volatility.

*NAPLs* - Non Aqueous Phase Liquids.

# RELATIVE VOLATILITIES OF ORGANIC COMPOUNDS

Volatility	Vapor Pressure (atm)	Compounds
Volatile	$>10^{-4}$	Light hydrocarbons; halogenated hydrocarbons
Semivolatile	$10^{-4}-10^{-11}$	Heavier hydrocarbons; most compounds with O, N, S and P
Nonvolatile	$<10^{-11}$	Other organics

# WATER SOLUBILITY

*Solubility* - the mass or number of moles of an organic compound in a unit volume or mass of water.

*Miscible* - completely soluble in water.

*Immiscible* - relatively insoluble in water and separates to form a nearly pure organic phase when mixed with water.

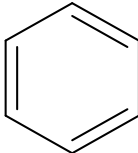
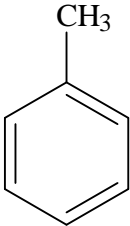
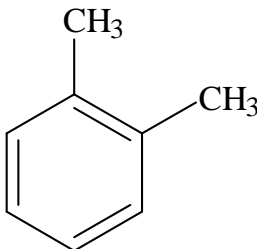
*Hydrophobic* - non-polar compounds with low water solubility.

*Hydrophilic* - polar compounds that readily dissolve in water.

# FACTORS GOVERNING WATER SOLUBILITY

- 1) **Polarity:** More polar organic compounds tend to have higher water solubilities. Less polar organic compounds are less soluble. In particular, compounds containing oxygen and nitrogen tend to be more water soluble.
- 2) **Molecular weight:** Given similar structures, compounds with higher molecular weights have lower aqueous solubilities. They also tend to be less volatile.

# SOLUBILITIES AS A FUNCTION OF MOLECULAR WEIGHT

Compound	Structure	Molecular Weight	Solubility (g m <sup>-3</sup> )
Benzene		78.0	1,780
Toluene		92.0	515
O-xylene		106.0	175

# DENSITY

The importance of density is in relation to the behavior of immiscible compounds in the subsurface.

Compounds with densities less than the aqueous phase will pool on the capillary fringe if enough of the compound is present (LNAPL's or floaters).

Compounds with densities more than the aqueous phase will sink until an impermeable barrier is reached (DNAPL's or sinkers).

# HENRY'S CONSTANT

The vapor pressure is only a measure of the volatility of a pure compound.

The volatility of an organic compound in an aqueous phase also depends on the solubility of that compound.

The important parameter describing this situation is the partitioning coefficient.

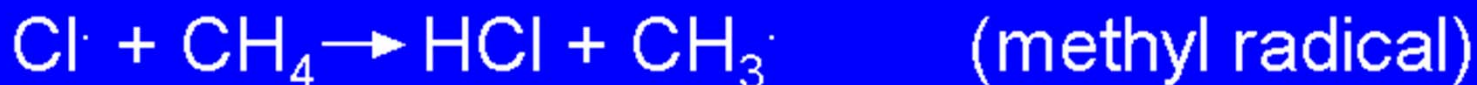
***Partitioning coefficient*** - the ratio of the abundances of a given compound in two phases in equilibrium.

***Henry's Law constant*** - the partitioning coefficient between a gas phase and liquid water.

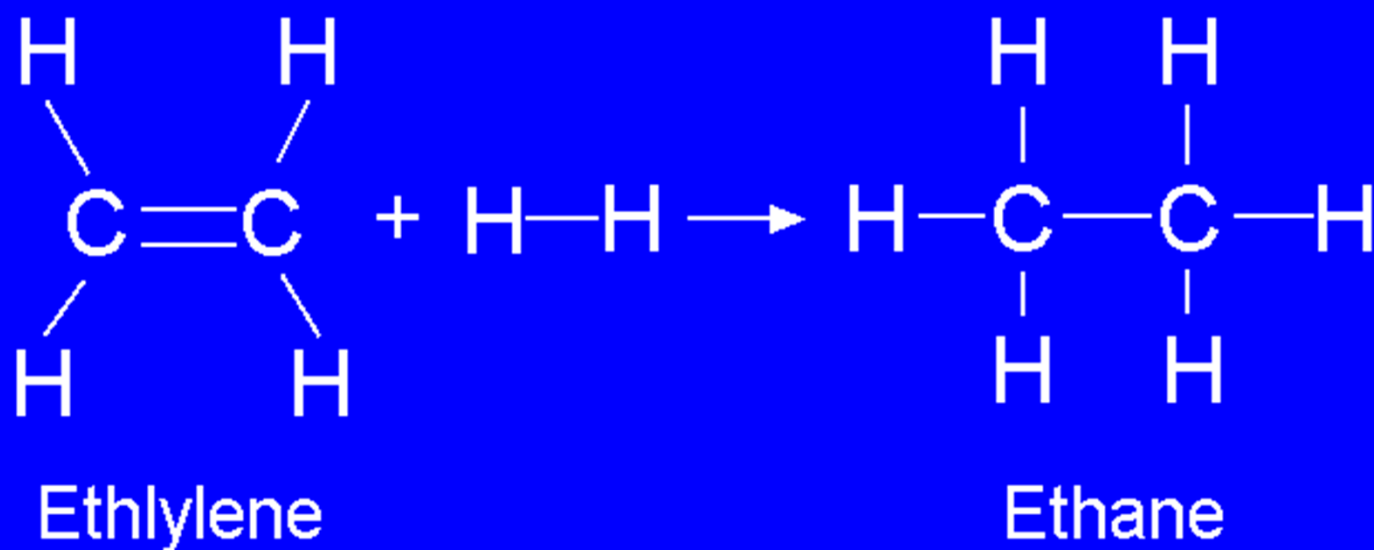


# Hydrocarbons

- **Contain only carbon and hydrogen**
- **Major types are alkanes, alkenes, alkynes and aromatic compounds**
- **Substitution reaction**
- **Addition reaction**



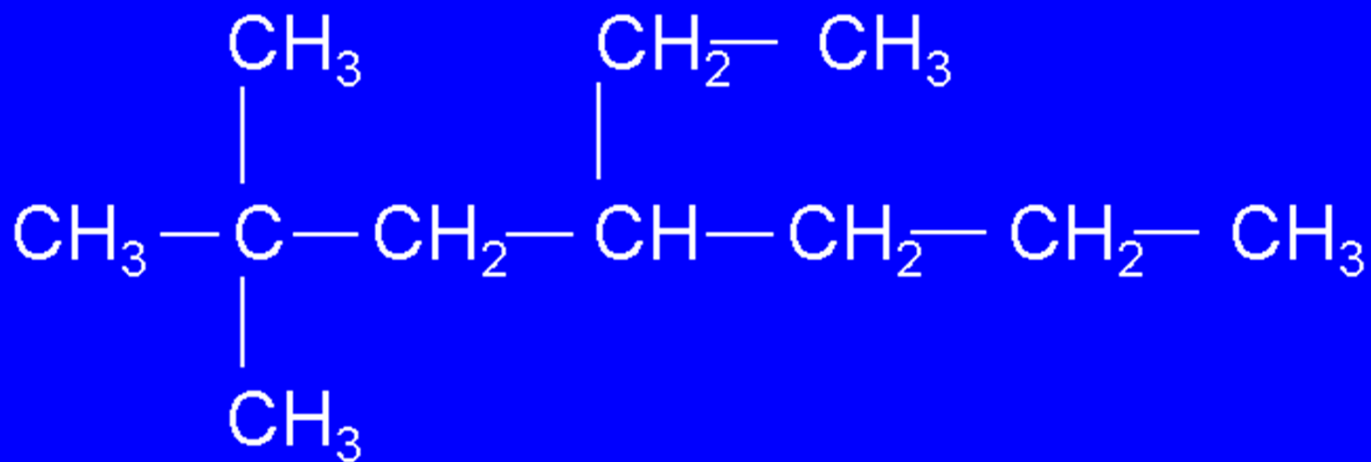
**Figure 5-5.** Example of a substitution reaction in which a hydrogen atom is replaced by a chlorine atom to produce chloromethane.



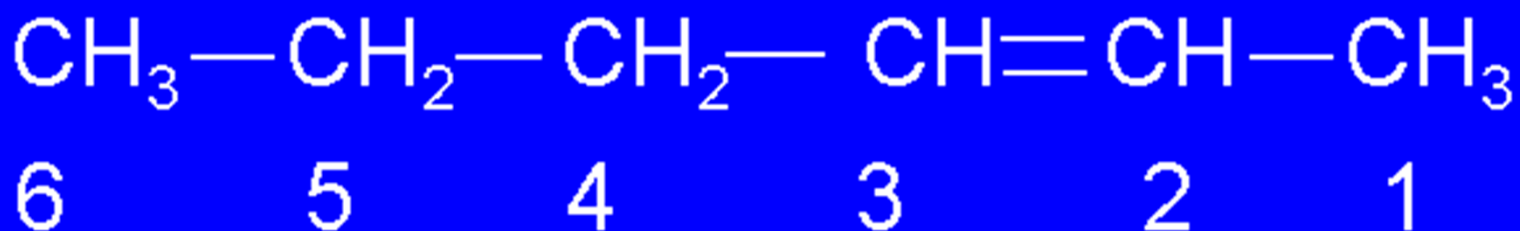
**Figure 5-6.** Example of an addition reaction in which hydrogen is added to ethylene to produce ethane (a hydrogenation reaction).

**Table 5-1. Prefixes for the number of carbon atoms**

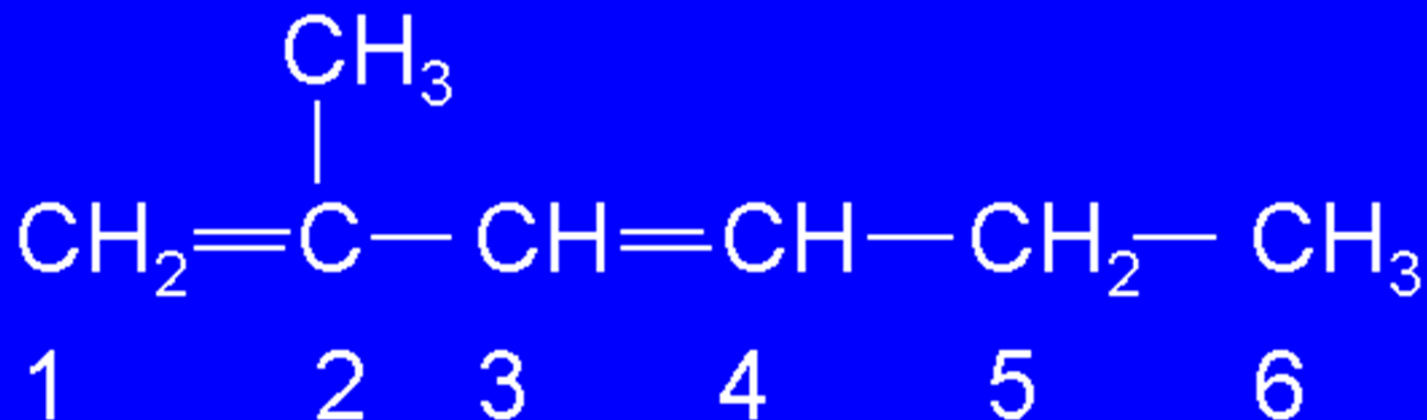
# C	Prefix	# C	Prefix	# C	Prefix
1	Meth	11	Undec	21	Henicos
2	Eth	12	Dodec	22	Docos
3	Prop	13	Tridec	23	Tricos
4	But	14	Tetradec	24	Tetracos
5	Pent	15	Pentadec	25	Pentacos
6	Hex	16	Hexadec	26	Hexacos
7	Hept	17	Heptadec	27	Heptacos
8	Oct	18	Octadec	28	Octacos
9	Non	19	Nonadec	29	Nonacos
10	Dec	20	Eicos	30	Triacont



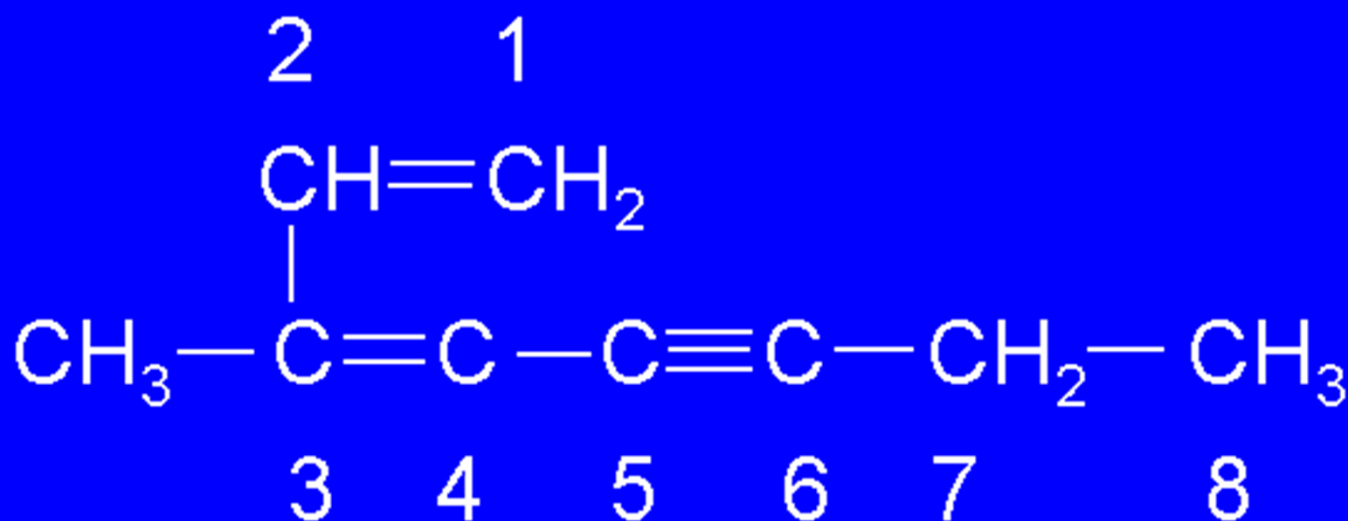
**Figure 5-7. Condensed structural formula for the alkane 4-ethyl-2,2-dimethylheptane.**



**Figure 5-8. Condensed structural formula for 2-hexene.**



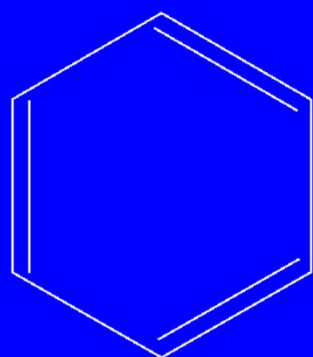
**Figure 5-9. Condensed structural formula for 2-methyl-1,3-hexdiene.**



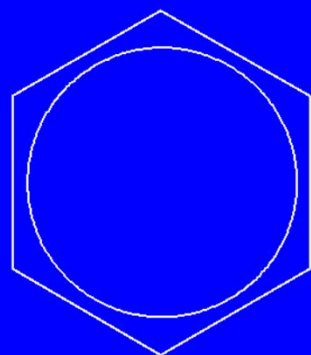
**Figure 5-10. Condensed structural formula for 3-methyl-1,3-octadien-5-yne.**

# Cyclic Hydrocarbons

- Aromatic Hydrocarbons
- Polycyclic Aromatic Hydrocarbons (PAH)

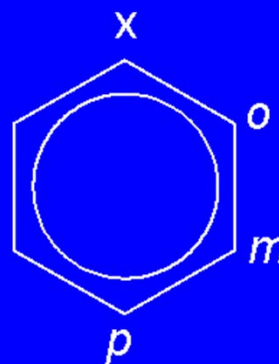


Benzene ring shown as  
alternating single and  
double bonds

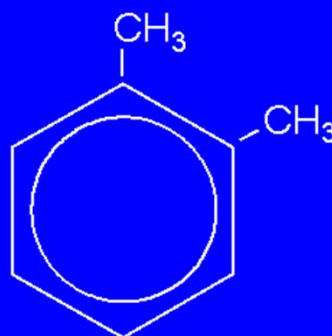


Benzene ring shown as  
a ring of delocalized  
electrons

**Figure 5-11.**  
**Representations of the  
benzene ring found in  
the literature.**

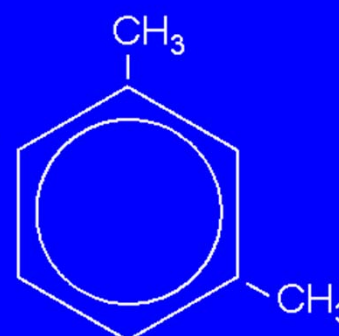


x is an substituent  
o = ortho position  
m = meta position  
p = para position



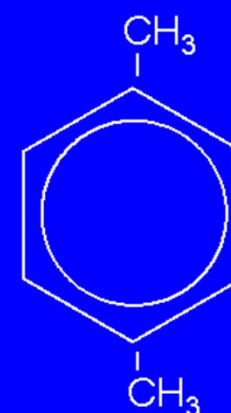
1,2-dimethylbenzene

*o*-xylene



1,3-dimethylbenzene

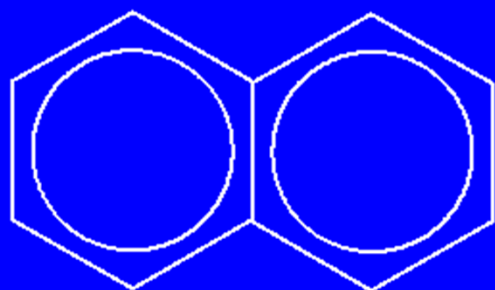
*m*-xylene



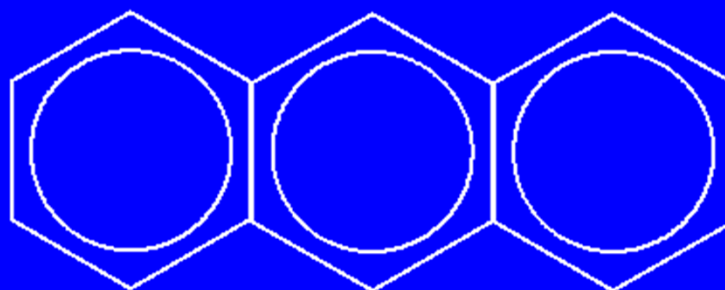
1,4-dimethylbenzene

*p*-xylene

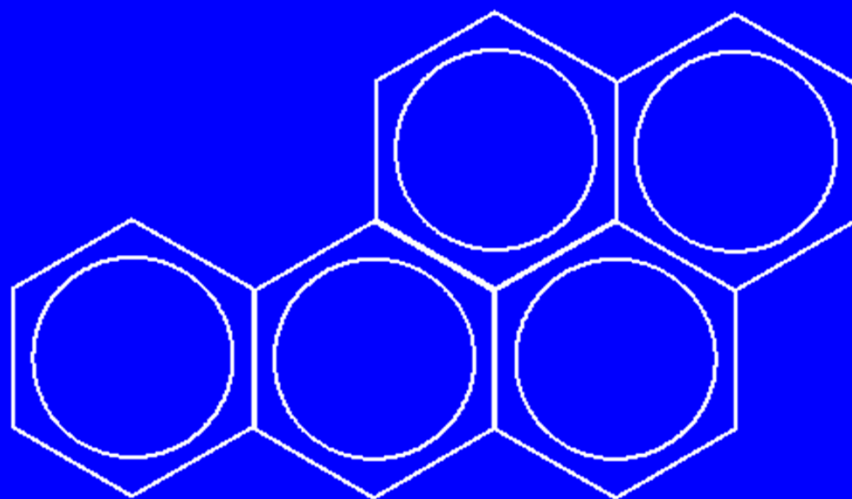
**Figure 5-12. Illustration of the naming  
conventions for the benzene ring using  
attached methyl groups. Note that while now  
shown on the diagram, the other sites are  
occupied by hydrogen atoms.**



Napthalene



Anthracene



Benzo(a)pyrene

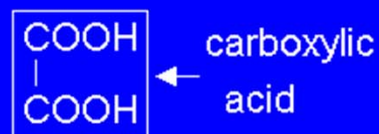
**Figure 5-13.** Examples of polycyclic aromatic hydrocarbons (PAHs) including the known carcinogen benzo(a)pyrene. Where the benzene rings do not share edges, hydrogen atoms are attached to the carbon atoms.



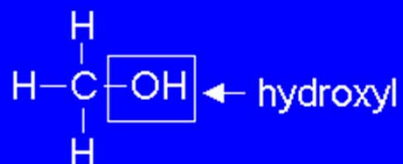
# Organochloride Compounds

- Chlorofluorocarbons
- Polychlorinated biphenyls (PCB's)
- Chlorinated phenols

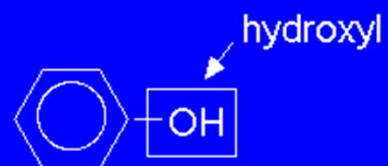
**Figure 5-14.** Examples of important functional groups. For each molecule the functional group is enclosed in a box and the name of the group is indicated by the arrow. The name of the compound is listed under each molecule.



Oxalic acid



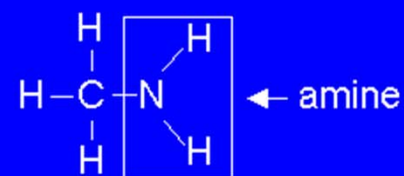
Methanol



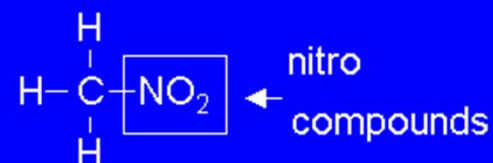
Phenol



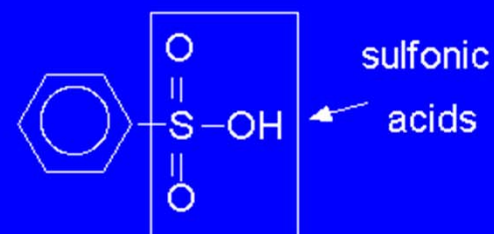
Formaldehyde



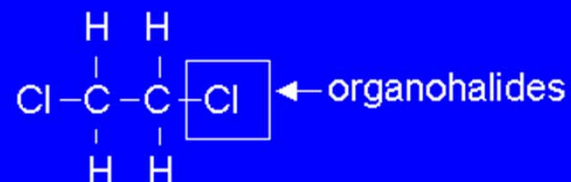
Methylamine



Nitromethane



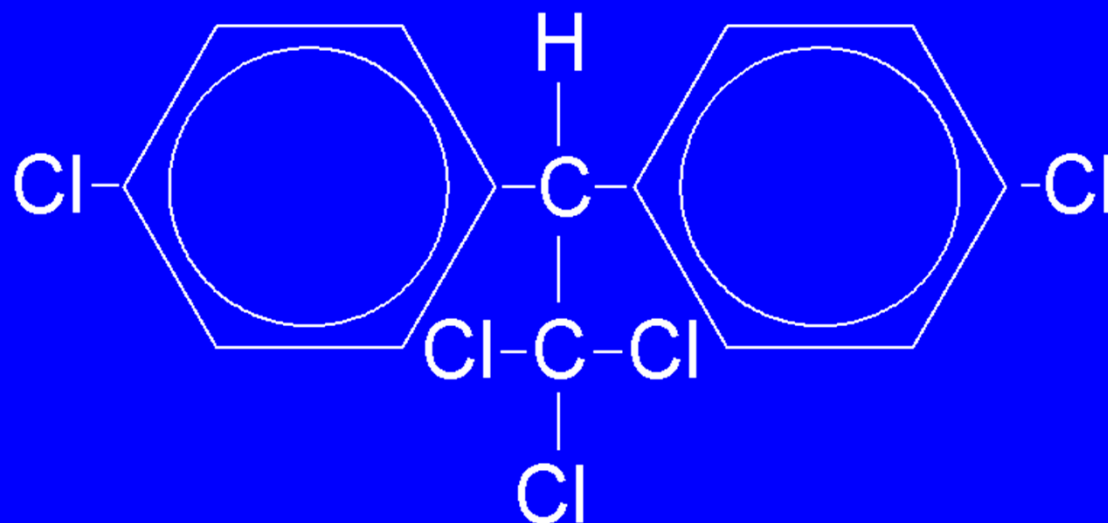
Benzenesulfonic acid



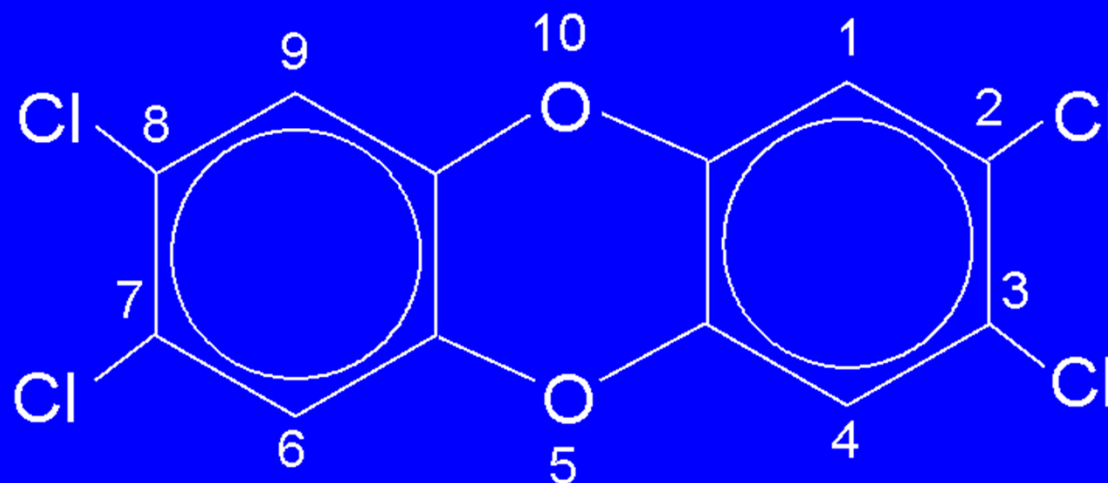
1,2-Dichloroethane

**Table 5-2. Examples of halogenated hydrocarbons**

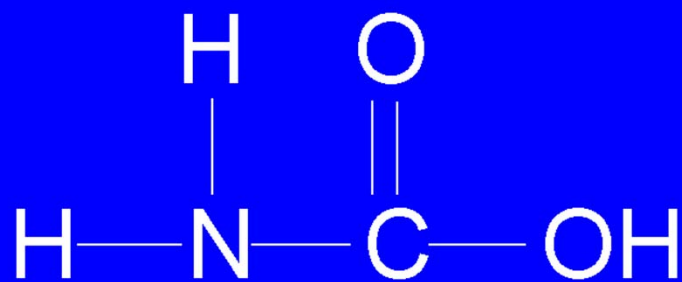
Name	Formula	Name	Formula
Chloromethane	CH <sub>3</sub> Cl	1,1,2,2-Tetrachloroethane	Cl <sub>2</sub> CH—CHCl <sub>2</sub>
Bromomethane	CH <sub>3</sub> Br	1,1,1,2-Tetrachloroethane	Cl <sub>3</sub> C—CH <sub>2</sub> Cl
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	Pentachloroethane	Cl <sub>3</sub> C—CHCl <sub>2</sub>
Trichloromethane	CHCl <sub>3</sub>	Hexachloroethane	Cl <sub>3</sub> C—CCl <sub>3</sub>
Tetrachloromethane	CCl <sub>4</sub>	2-Chloropropane	CH <sub>3</sub> —CHCl—CH <sub>3</sub>
Bromodichloromethane	CHCl <sub>2</sub> Br	1,2-Dibromo-3-chloropropane	BrCH <sub>2</sub> —BrCH—CH <sub>2</sub> Cl
Trichlorofluoromethane	CCl <sub>3</sub> F	Chloroethene	CH <sub>2</sub> =CHCl
Chlorodifluoromethane	CHClF <sub>2</sub>	1,1-Dichloroethene	CH <sub>2</sub> =CCl <sub>2</sub>
Dichlorodifluoromethane	CCl <sub>2</sub> F <sub>2</sub>	Trichloroethene	ClCH=CCl <sub>2</sub>
Chloroethane	CH <sub>3</sub> —CH <sub>2</sub> Cl	Tetrachloroethene	Cl <sub>2</sub> C=CCl <sub>2</sub>
1,2-Dichloroethane	ClCH <sub>2</sub> —CH <sub>2</sub> Cl	1-Chloropropene	ClCH=CH—CH <sub>3</sub>
1,1,1-Trichloroethane	CH <sub>3</sub> —CCl <sub>3</sub>	1,3-Dichloropropene	ClCH=CH—CH <sub>2</sub> Cl



**Figure 5-15.** Structure of DDT. The molecule consists of two benzene rings joined by a chlorinated ethane group. Each ring has a Cl atom substituting for a H atom. The IUPAC name for this molecule would be dichlorodiphenyltrichloroethane.

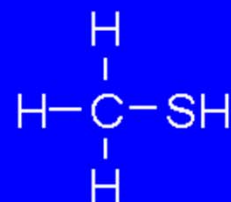


**Figure 5-16.** Structure of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The rings are numbered as shown. Note that the chlorine atoms occur in positions 2, 3, 7, and 8. The tetra prefix indicates that there are four chlorine atoms.



**Figure 5-17.** Carbamic acid.

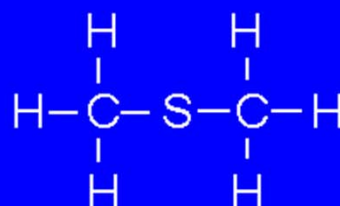
**Figure 5-18.** Examples of organosulfates. Thiols – methanethiol and benzenethiol, sulfides – dimethyl sulfide and dimethyl disulfide, thiourea – thiourea, sulfoxides – dimethylsulfoxide, sulfonic acids – benzenesulfonic acid, sulfates – methylsulfuric acid.



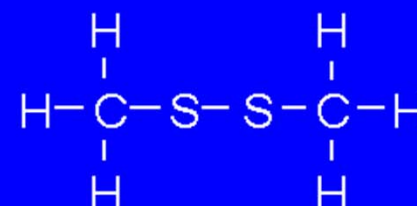
Methanethiol



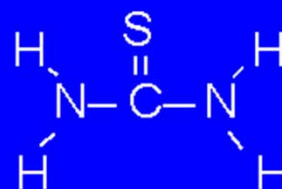
Benzenethiol



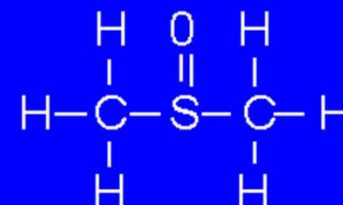
Dimethyl sulfide



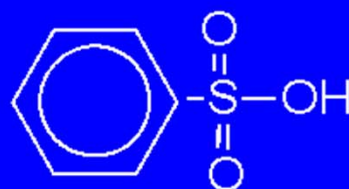
Dimethyl disulfide



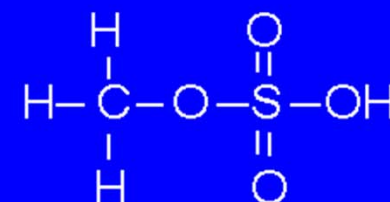
Thiourea



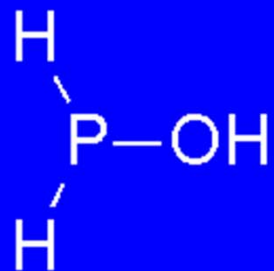
Dimethylsulfoxide (DMSO)



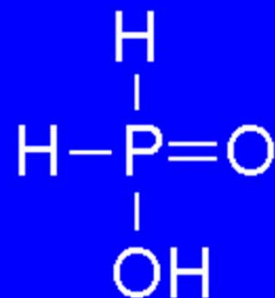
Benzenesulfonic acid



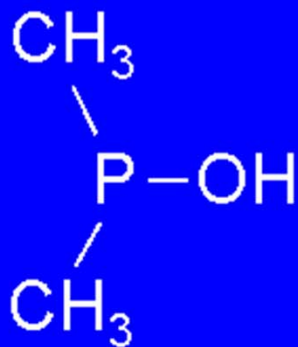
Methylsulfuric acid



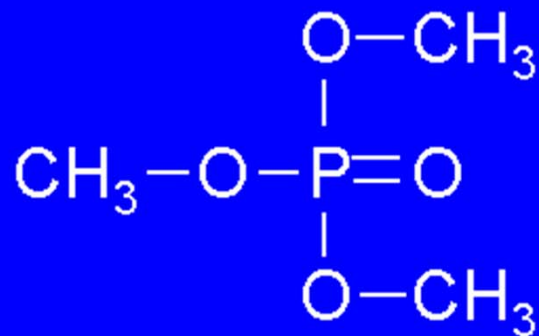
Phosphinous acid



Phosphinic acid

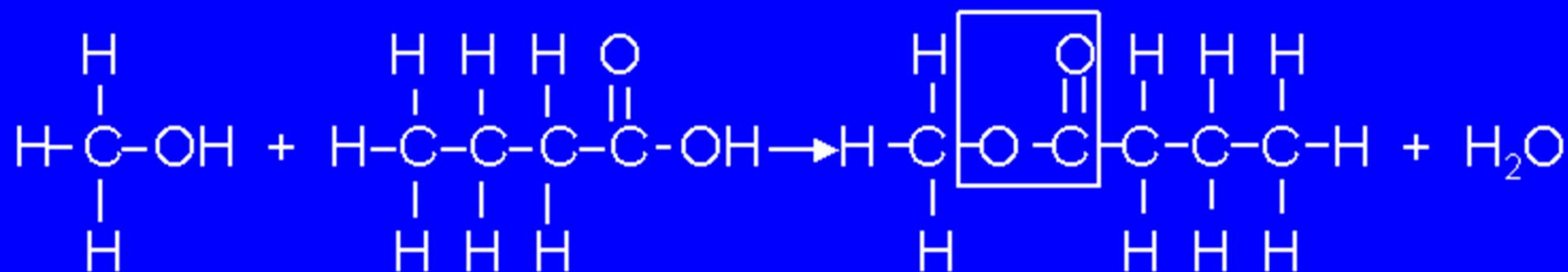


Dimethylphosphinic  
acid



Trimethyl phosphate

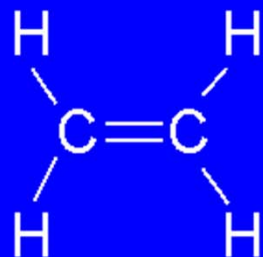
**Figure 5-19.** Examples of organophosphorus compounds. See text for description of naming conventions.



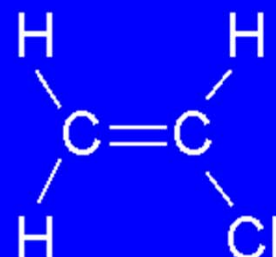
Methanol + Butanoic acid  $\longrightarrow$  Methyl butanoate

**Figure 5-20.** Condensation reaction between an alcohol (methanol) and a carboxylic acid (butanoic acid) to form an ester (methyl butanoate). Note that water is expelled during this reaction. The ester functional group is enclosed by the box.

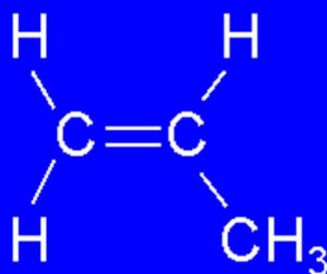
**Figure 5-21.** Examples of monomers used to build the common synthetic polymers. See text for examples of the uses of each synthetic polymer.



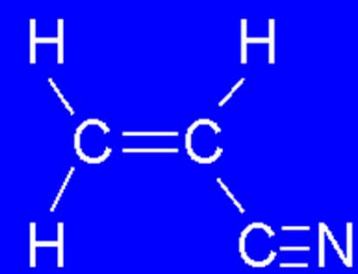
Ethylene



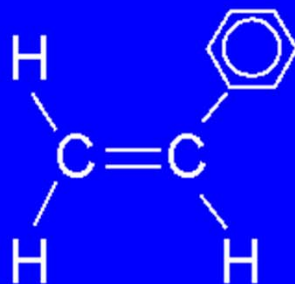
Vinyl chloride



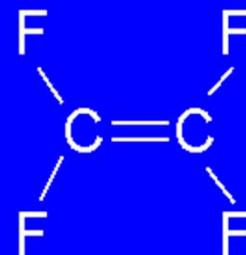
Propylene



Acrylonitrile



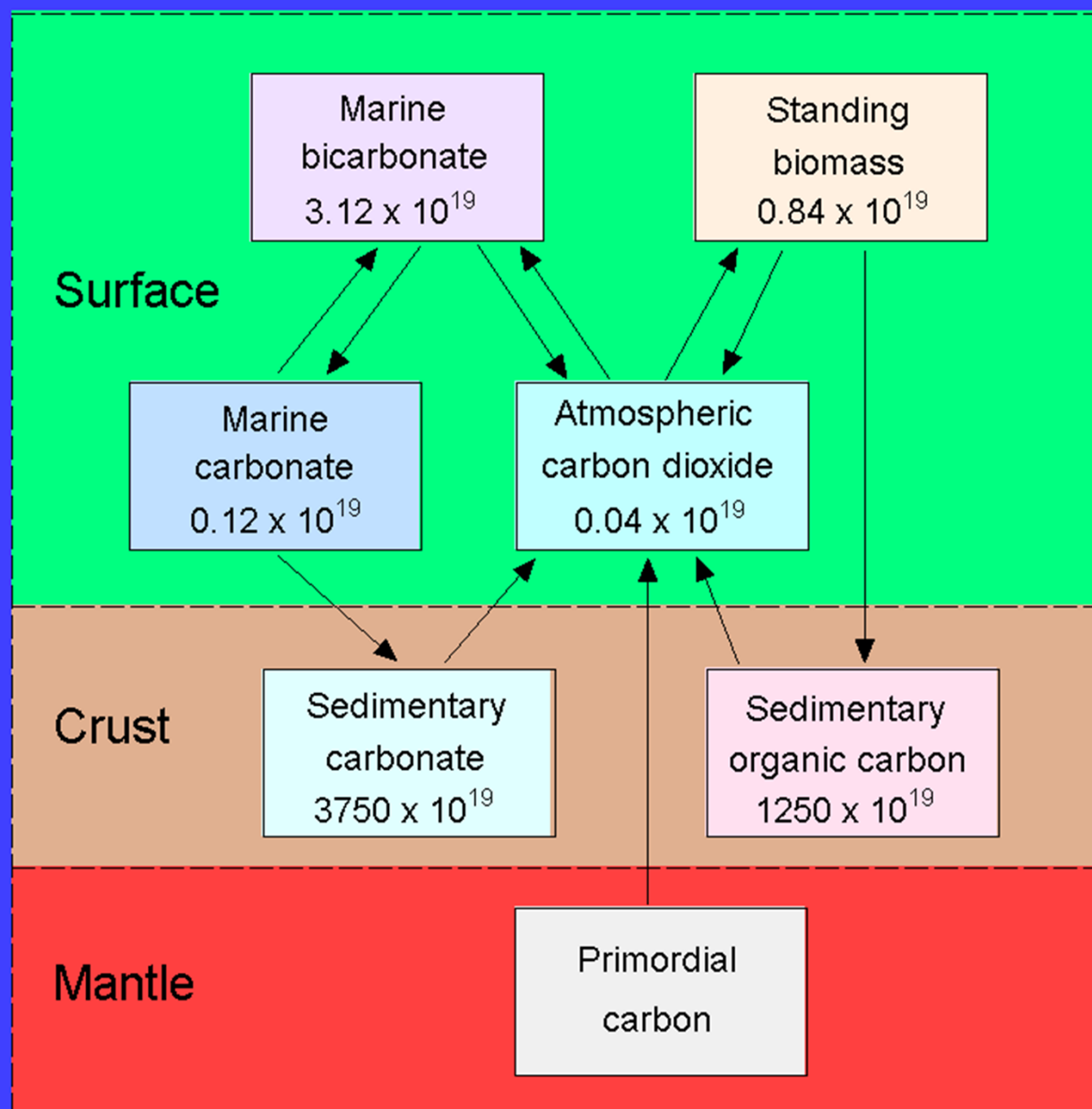
Styrene



Tetrafluoroethylene



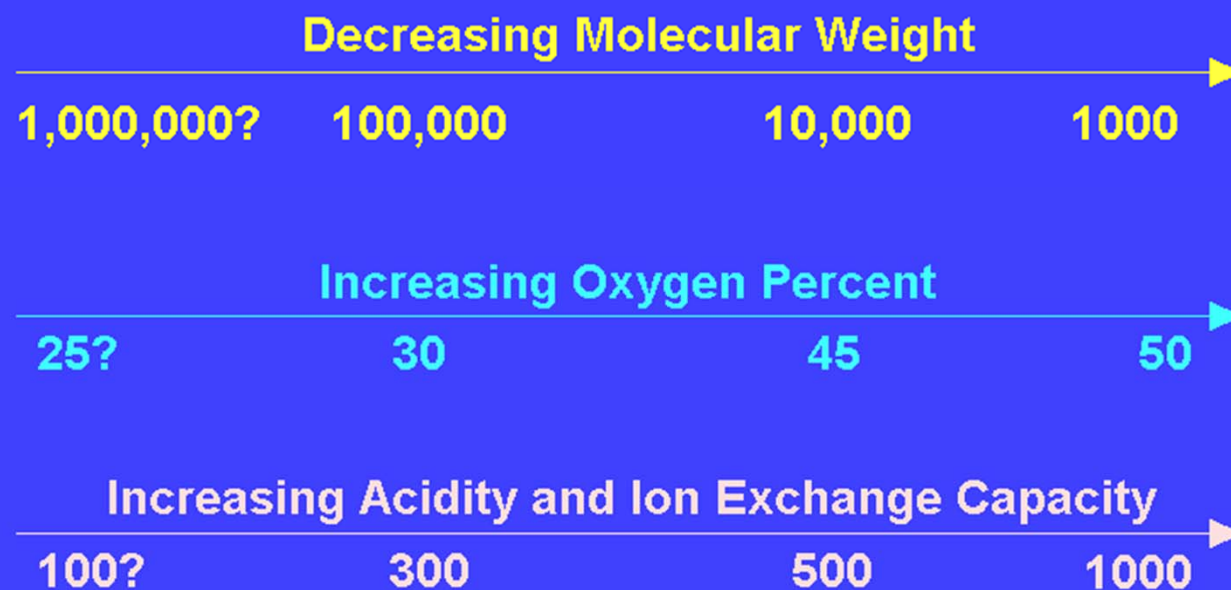
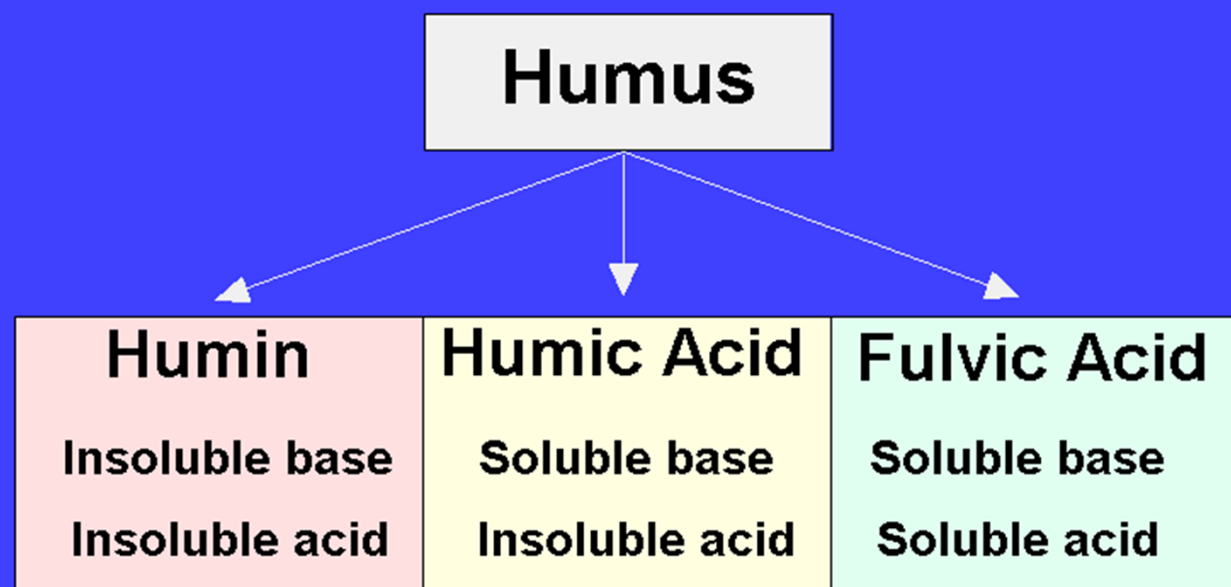
**Figure 5-22.**  
**Major carbon**  
**reservoirs and**  
**interactions**  
**between these**  
**reservoirs.**  
**Carbon**  
**concentrations**  
**are in grams**  
**of carbon.**  
**Data from**  
**Schidlowski**  
**(1988).**



# Humic Substances

- 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.
- Humic substances are found in soils, brown coal, fresh and marine waters, and marine and lacustrine sediments.

**Figure 5-23. Types of humic substances and general characteristics. Note that the distinction between the types of substances is based on their solubility in acids and bases. After Oades (1989).**



**Table 5-3. Elemental compositions, atomic ratios and atomic weights for soil humic and fulvic acids**

	Humic Acids	Fulvic Acids
Carbon (wt. %)	53.6 - 58.7	40.7 - 50.6
Hydrogen (wt. %)	3.2 - 6.2	3.8 - 7.0
Nitrogen (wt. %)	0.8 - 5.5	0.9 - 3.3
Oxygen (wt. %)	32.8 - 38.3	39.7 - 49.8
Sulfur (wt.%)	0.1 - 1.5	0.1 - 3.6
Mol. Wt. (Daltons)	2000 - 5000	500 - 2000
H/C (atomic)	~0.8	~1.3
O/C (atomic)	~0.5	~0.8

**Table 5-4. Composition 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	$10^3 - 10^6$	$500 - 10^4$	$<10^4$	$10^3 - 10^6$	$<10^3$	-

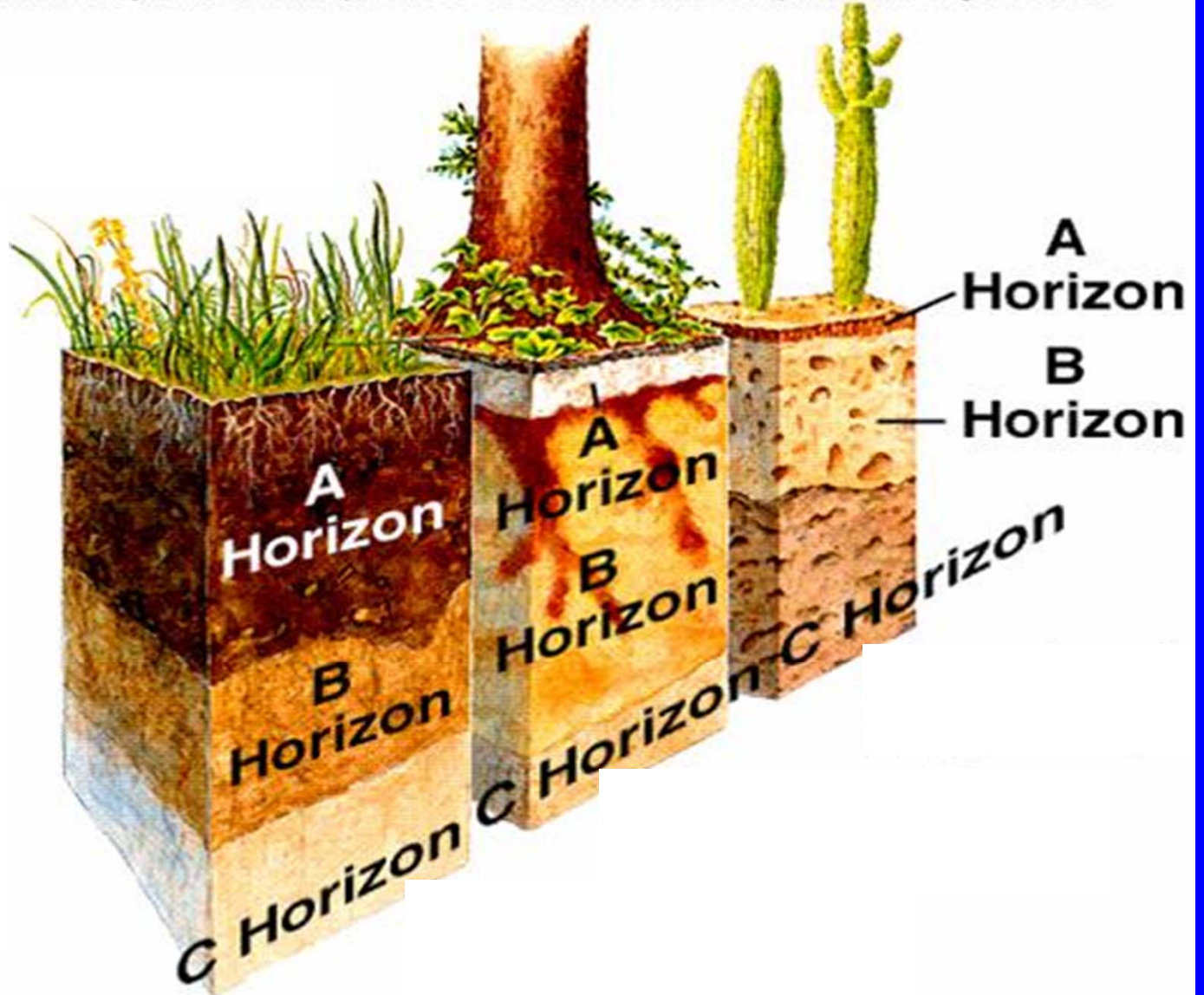
# Soil and Maine Organic matter

- **Soil:** is 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 environmental conditions.

# التربة Pedosphere

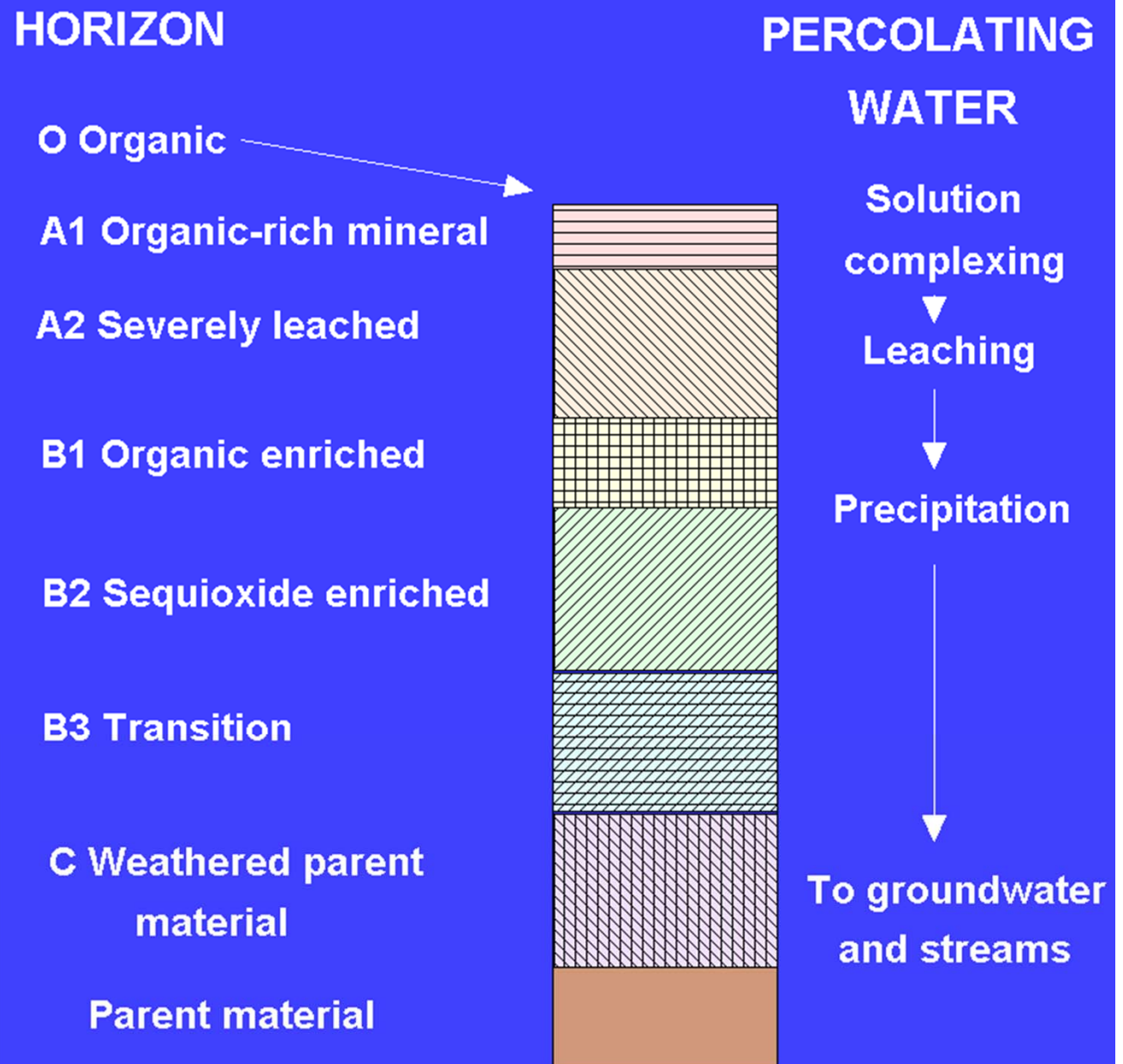
Enger/Smith, *Environmental Science, A Study of Interrelationships*, 6th ed. ©1998 The McGraw-Hill Companies, Inc. All rights reserved.

يعلو النطاق الصخري  
طبقة رقيقة من الفتات  
الصخري الناتج عن  
التجوية والتعرية التي  
تتعرض اليها صخور  
القشرة الارضية

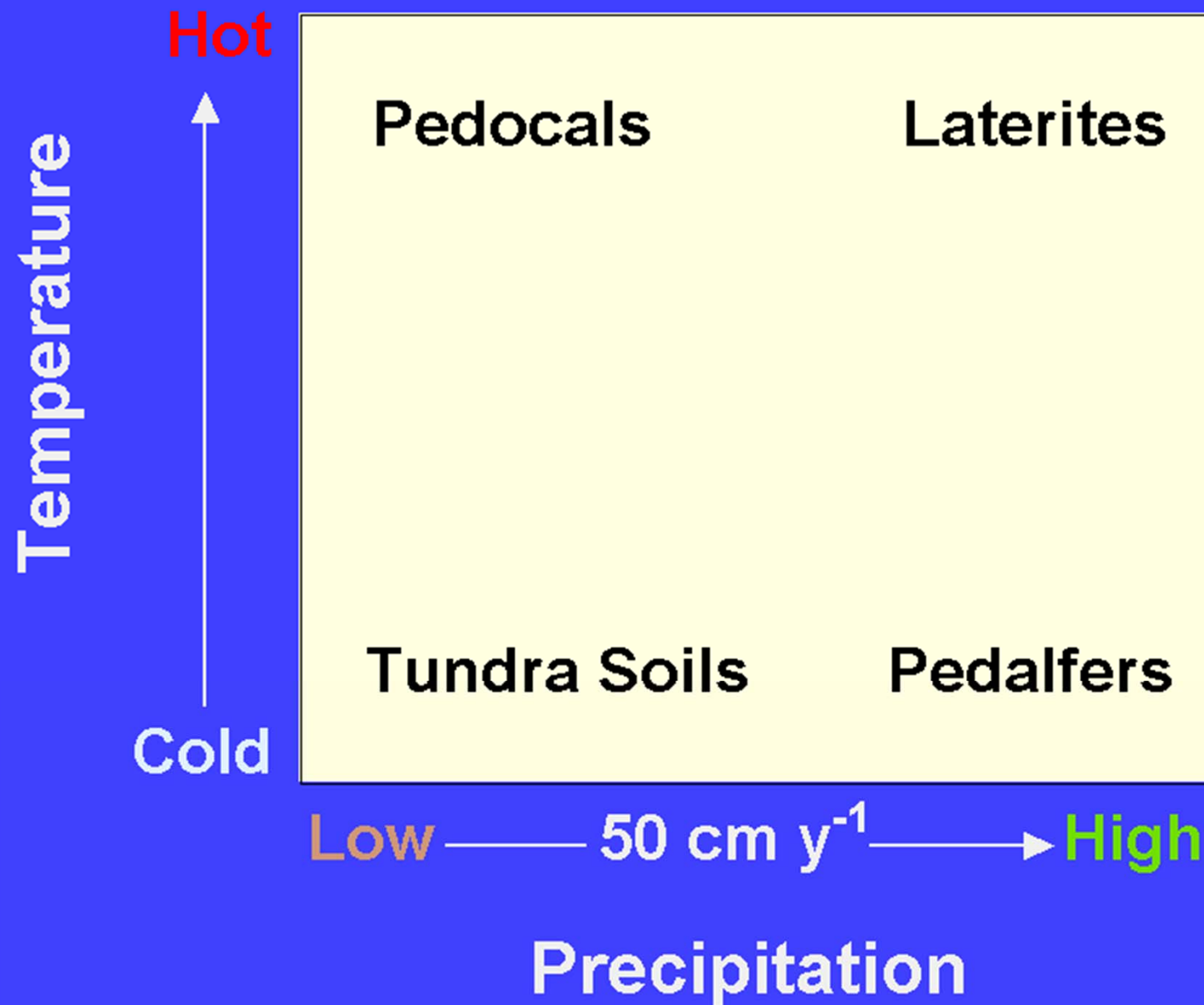




**Figure 5-24.**  
**Generalized soil profile for a**  
**spodosol. After**  
**Stevenson (1985).**  
**From HUMUS**  
**CHEMISTRY,**  
**GENESIS,**  
**COMPOSITION,**  
**REACTIONS by**  
**Stevenson.**  
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**Figure 5-25. Soil types as a function of the climate variables temperature and precipitation.**

**Table 5-5. Soil Classification**

Soil type	Characteristics and climatic conditions
Oxisols	Extensive alteration of silicate minerals to form clays, such as kaolinite, and iron oxides; wet equatorial regions
Calcisols	Precipitation of calcium carbonate as nodules and layers; hot dry regions
Gypsisols	Calcium sulfate forms in soil as gypsum or anhydrite; very arid regions
Gleysols	Waterlogged soils with poor drainage and reducing conditions; temperate and polar regions
Argillisols	Layers and grain coating of clay are common; wet mid-latitude regions
Spodosols	Grain coatings of organic material and iron oxides; wet mid-latitude regions
Vertisols	Poorly developed layering but strong vertical structures due to repeated desiccation of expandable clays; relatively dry regions
Histisols	High concentrations of organic material forming peat layers; moist temperate regions and occasionally humid equatorial regions
Protosols	Poorly developed soils; most common in polar regions but can occur anywhere

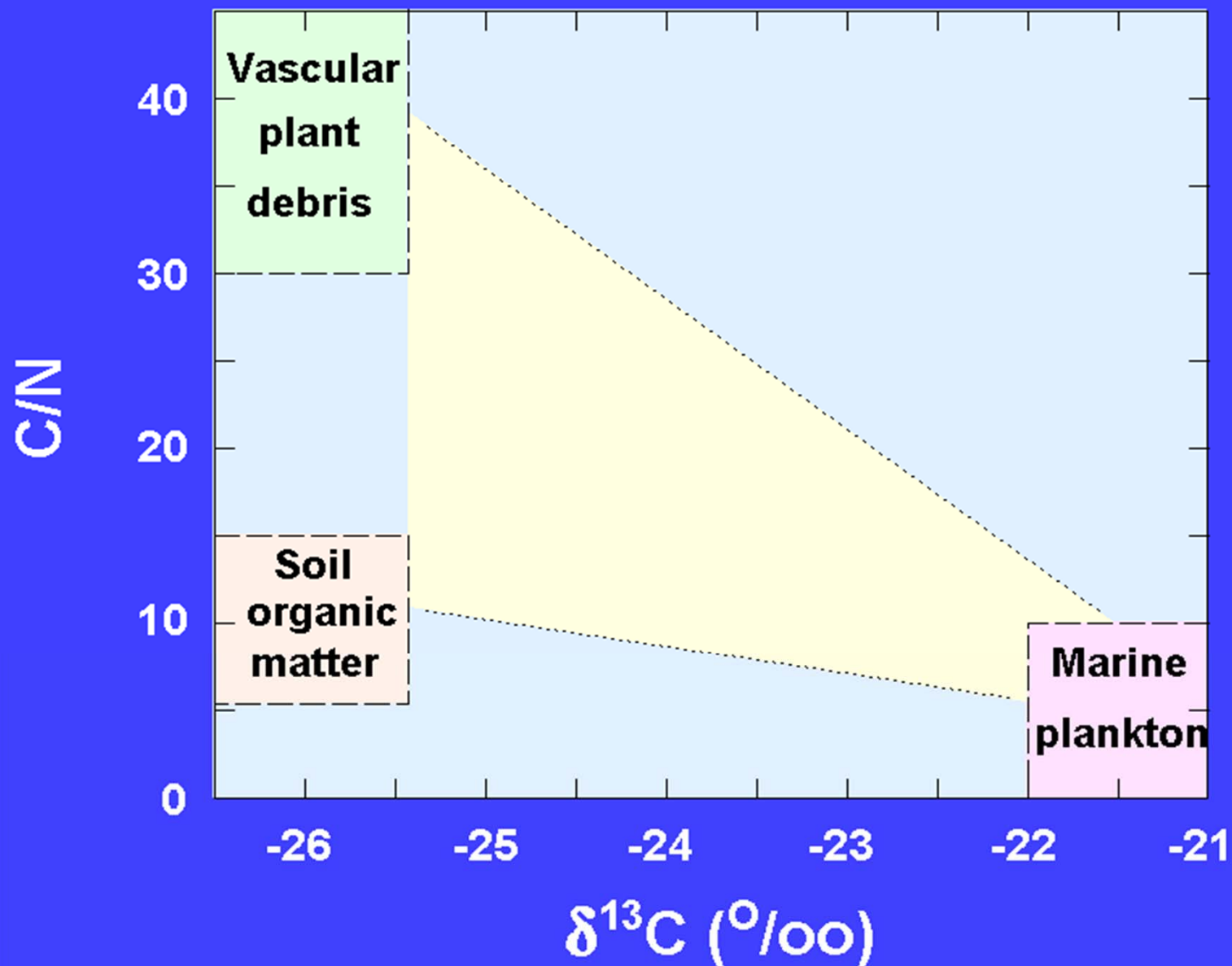
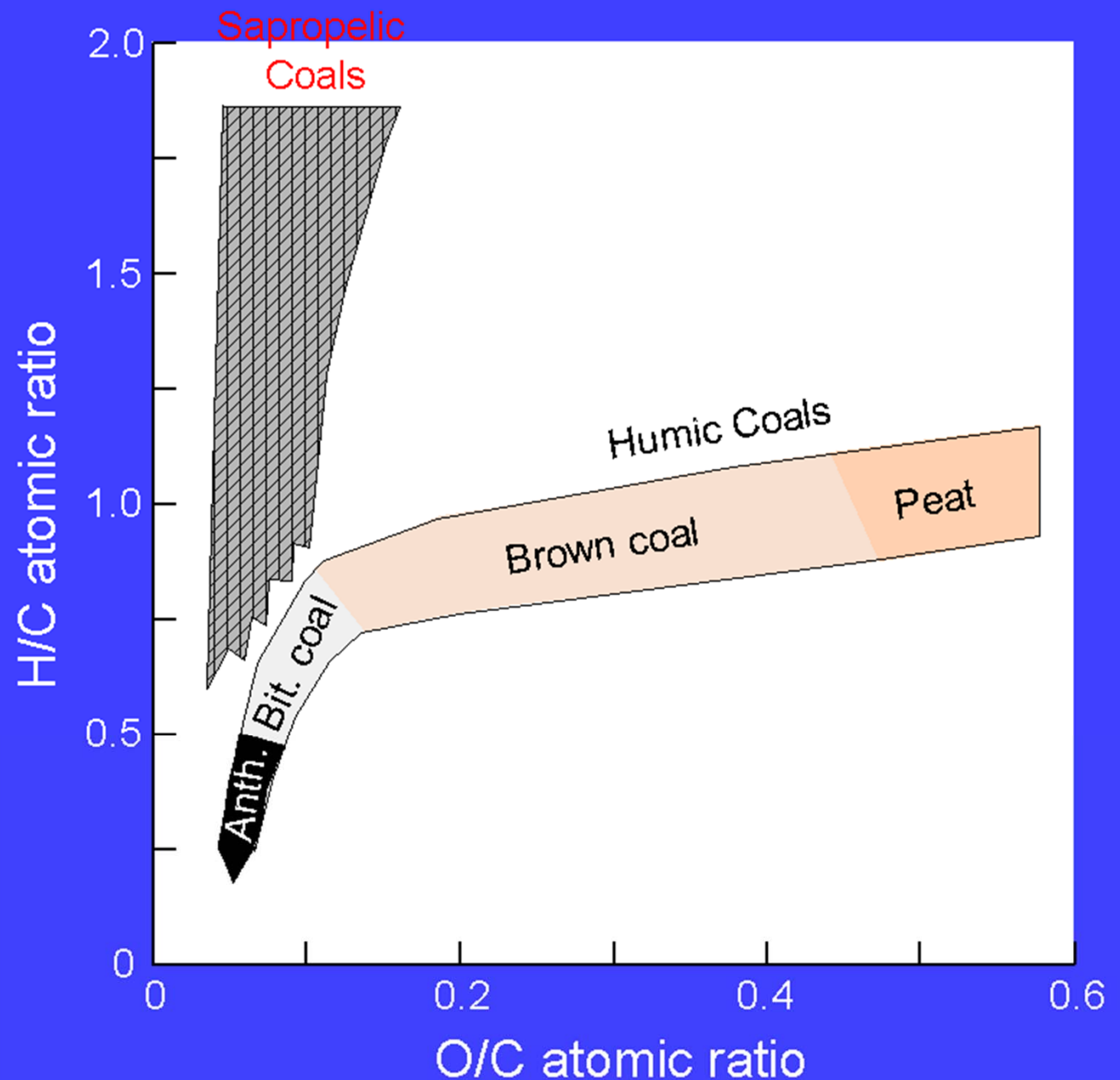


Figure 5-26. Atomic C/N versus  $\delta^{13}\text{C}$  for various reservoirs of organic carbon. Mixtures of the three end members lie within the field defined by the dashed lines. Modified from Hedges and Oakes (1997).

**Figure 5-27. Van Krevelen (1963) diagram indicating the changes in hydrogen, oxygen, and carbon during the coalification process. After Killops and Killops (1993).**



**Table 5-6. Concentration ranges in coal for some elements of environmental interest**

Element	Concentration range (ppm)	Element	Concentration range (ppm)
Sc	0.6 - 10.3	As	0.7 - 31
V	6 - 109	Se	0.4 - 3.3
Cr	2.6 - 25.4	Sb	0.1 - 7.3
Co	1.1 - 24.1	W	0.2 - 1.3
Ni	2 - 50	Pb	3 - 20
Cu	6 - 54	Th	0.5 - 3.7
Zn	3 - 65	U	0.2 - 3.8

# Petroleum

- **Petroleum is any hydrocarbon rich fluid (liquid or gas) derived from kerogen by increases in pressure and temperature**
- **Kerogen: is a polymeric organic material that occurs in sedimentary rocks in the form of finely disseminated organic macerals (the preserved remains of plant materials)**

# الهيدروكربونات الصلبة

تشكل الهيدروكربونات الصلبة وفي مقدمتها الفحم الحجري ما قيمته 92% من احتياط الوقود الاحفوري. وعلى العكس من النفط يتكون الفحم الحجري من **بقايا نباتات** عاشت على اليابسة وجرى دفنها لاحقا في الرسوبيات والصخور.

تحتوي النباتات على:

الهيدروكربونات الصلبة

الاصماغ

الشمع

الجنين ( هي مادة عضوية تشكل مع السليلوز قوام الخشب)

- ومن المواد الهيدروكربونية الصلبة أيضا الخث Peat وهو مادة غير متماسكة من بقايا النباتات تحتوي على 60% كربون.

## تكون الفحم

بقايا النباتات ← الخث ← اللجنيت Lignite ←  
الانثراسيت Anthracite ← الجرافيت

## وجود الفحم

تشير الدراسات الميدانية الى وجود الفحم الحجري في الصخور الرسوبية يصاحبه في ذلك وجود صخور مثل الغضار والرمل والحجر الجيري. ومعظم الطبقات الفحمية عدسية الشكل تعكس شكل المستنقع الذي تكونت فيه وتبلغ سماكته من سنتيمترات الى حوالي 3م.



# الهيدروكربونات السائلة

- تعتبر النباتات البحرية، وحيدة الخلية، التي تعيش على طول الارصفة القارية والمسماة العوالق البحرية والبكتيريا كذلك المصادر الرئيسية للمواد العضوية في المحيطات. ومعظم المادة العضوية التي تتجمع مع مرور الايام على قاع المحيط محصورة في الطين الذي يتحول ببطء الى غضار Shale وخلال هذا التحول يجري تحويل المادة العضوية الى نفط وغاز طبيعي وهذان المنتجان هما الحالتان اللتان يوجد عليهما النفط ويتم بعد ذلك استخلاص مكونات النفط بعملية التقطير والتي تسمى احيانا تكسير Cracking اي تكسير المواد الهيدروكربونية في مصافي النفط الى بنزين وديزل.....

# تكوين النفط وهجرته

- تعلم ان الرسوبيات التي تتجمع فيها المواد العضوية في ايامنا الحالية غنية بالمعادن الطينية وان هذه الرسوبيات ستتحول بدورها الى غضار Shale ولكن معظم الصخور الحاوية على النفط اما صخور رملية او صخور جيرية فما سبب ذلك؟

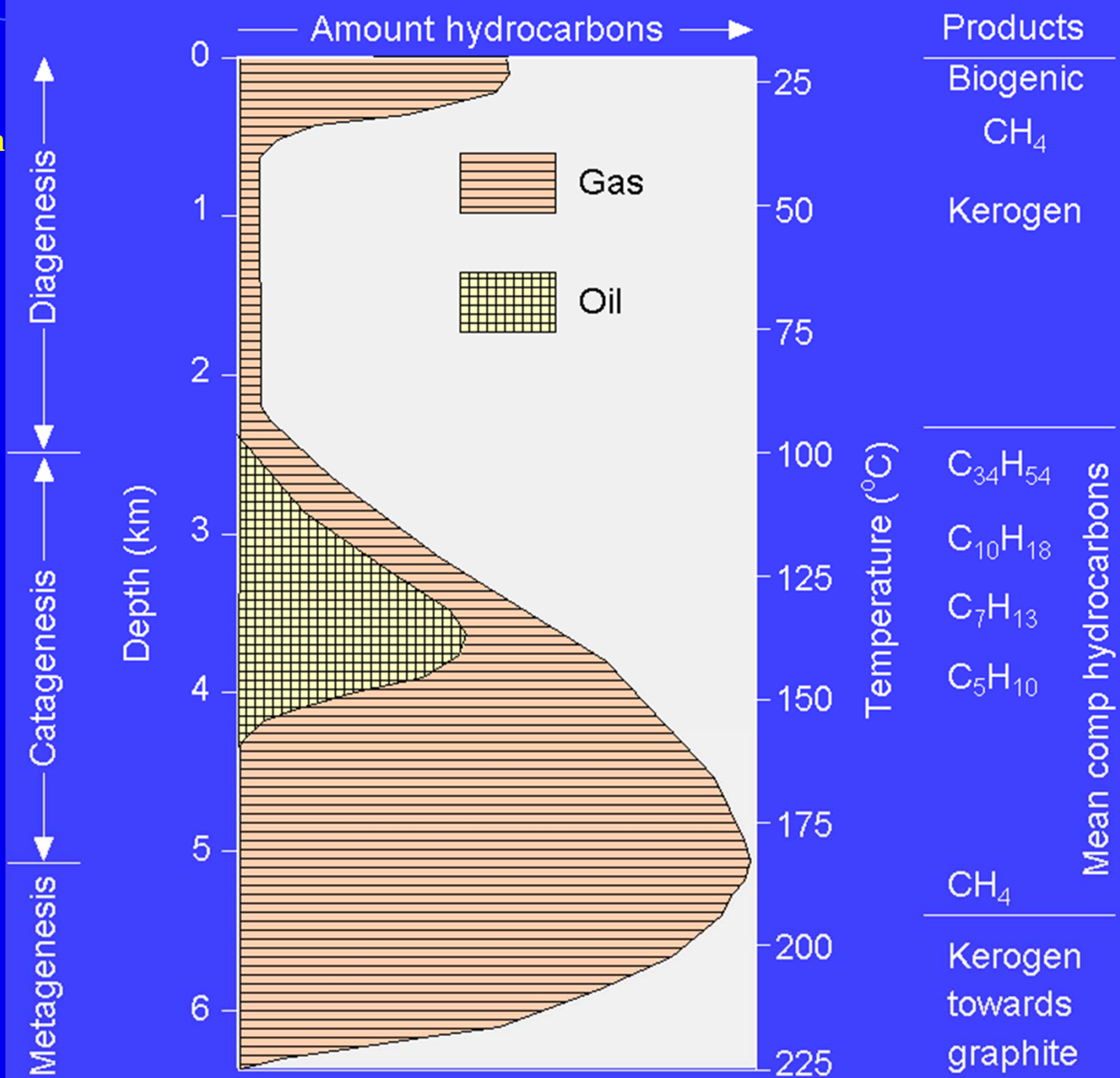
لقد لاحظ العلماء الجيولوجيون ومنذ عهد بعيد ان النفط يتكون في بيئة معينة اي في نوع ما من الرسوبيات ويهاجر بعد فترة الى نوع اخر منها. ومع مرور الزمن تبدأ قطرات الزيت والغاز بالتجمع الى بعضها بعضا ثم يجري عصرها بعيدا عن مكان تكونها. ولكي تتمكن القطرات المتولدة من الهجرة لا بد لها ان تصادف طبقات صخرية تسمح لها بالارتحال الى اعلى حيث الضغط الاقل وبالتالي فان هجرة النفط تتطلب صخورا ذا مسامية ونفاذية عاليتين ايضا

يسمى التكوين ذو المسامية العالية والنفاذية العاليتين والذي يمكن ان

يتجمع النفط خزاناً صخرياً **Reservoir Rock**.

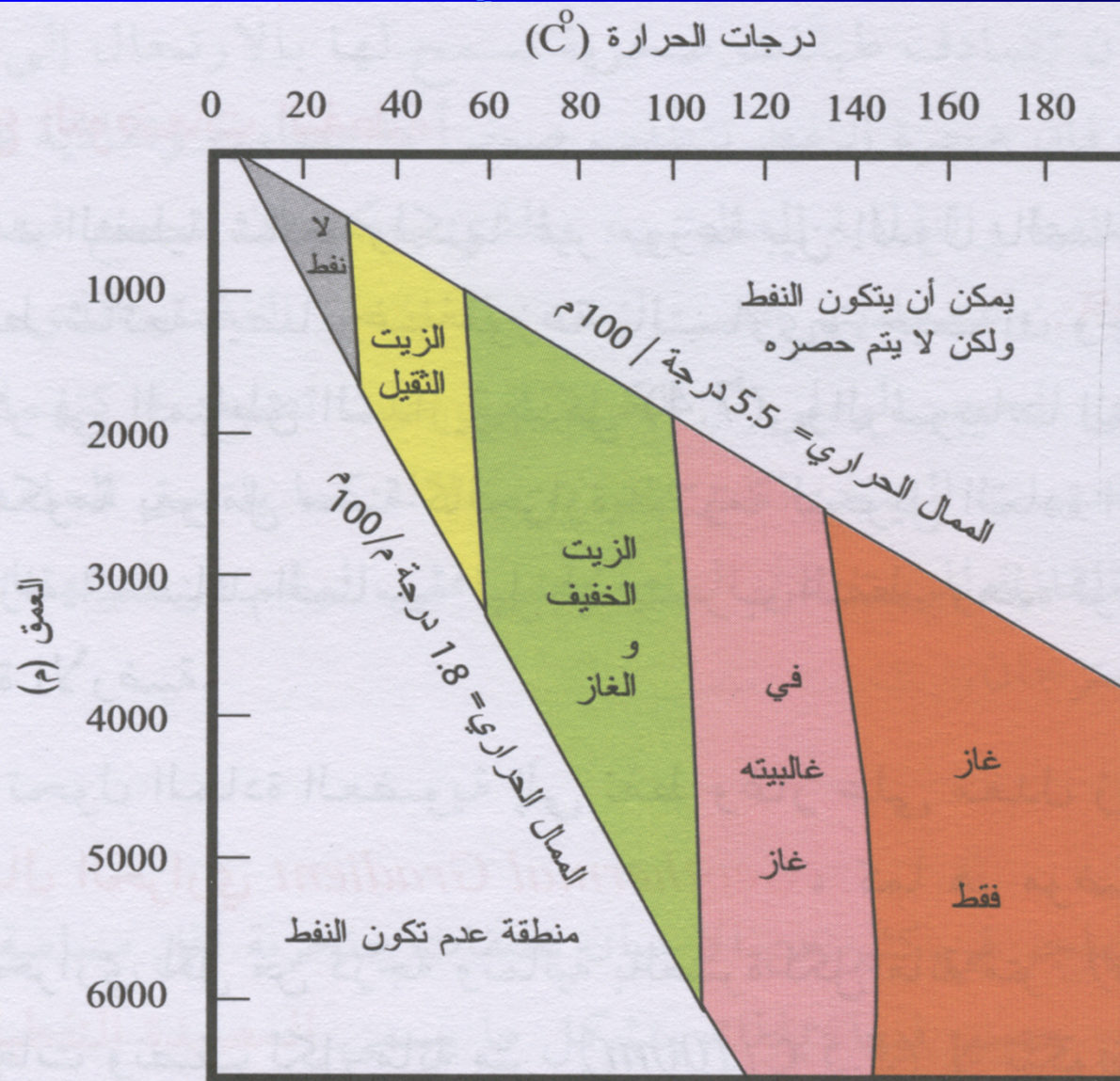
- و عندما يتم عصر الزيت والغاز من الغضار الذي جرى تكوينهما فيه ينتقلان بعد ذلك الى الحجر الرملي او الكربوناتي حيث تصبح حركتهما اكثر سهولة وعادة لا يلتصق النفط بحبيبات الصخر الذي يمر من خلاله كما يلتصق الماء لذلك تجري في الطبيعة عملية فصل تلقائية للزيت عن الماء

**Figure 5-28. Schematic representation of production of petroleum from a typical reservoir rock assuming an average geothermal gradient. Note the narrow P-T range over which oil is produced (called the *petroleum window*). With increasing temperature, the size of the mean hydrocarbon molecule decreases. During catagenesis, hydrocarbon chains break off and are expelled from the kerogen. During metagenesis, only methane is released. Modified from Killops and Killops (1993).**





# الممال الحراري Geothermal Gradient



الشكل 8.4: نافذة النفط، حيث تبين العمق والحرارة اللازمة لتكون النفط والغاز وحصره

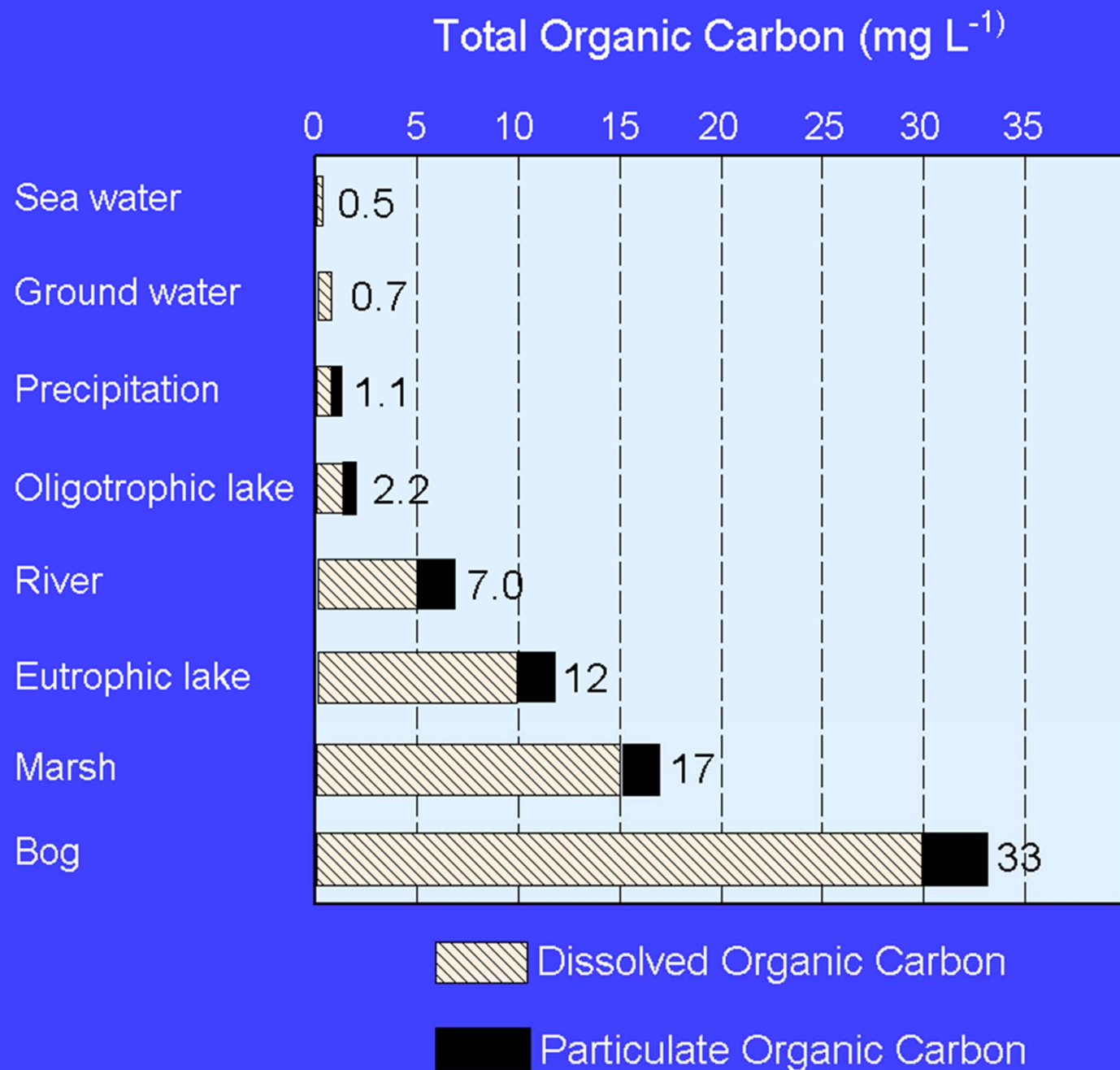
**Table 5-7. Elemental composition of crude oil**

Element	Abundance
	<i>In wt. %</i>
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
	<i>In ppm</i>
Ni	0.3-200
V	0.3-1000

# Natural Carbon inputs to surface and ground waters

- DOC
- POC
- TOC
  
- Sources of Carbon
  - Allochthonous
  - Autochthonous

**Figure 5-29.**  
**Average organic carbon**  
**concentrations for**  
**various aquatic**  
**systems. Note that**  
**the actual range in**  
**TOC can be**  
**substantial and**  
**depends on a**  
**variety of factors.**  
**See text. Taken**  
**from Thurman**  
**(1985a).**



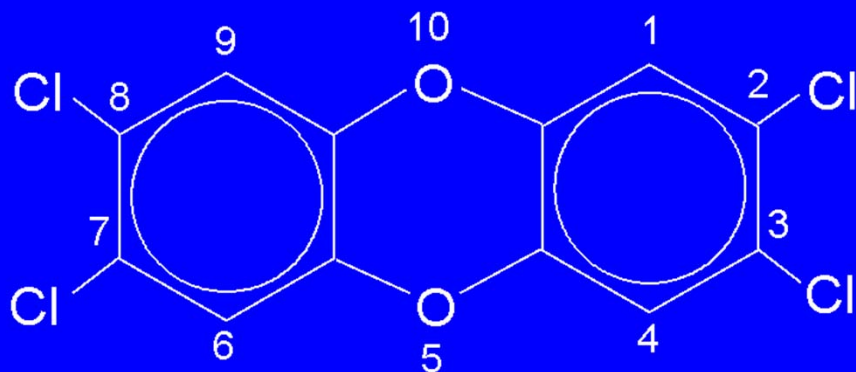


**Table 5-8. Median concentrations of organic carbon in various types of aquifers**

Aquifer	DOC (mg C L <sup>-1</sup> )
Sand and gravel	0.7
Limestone	0.7
Sandstone	0.7
Igneous	0.5
Oil shale	3
Humic colored	10
Petroleum associated	100

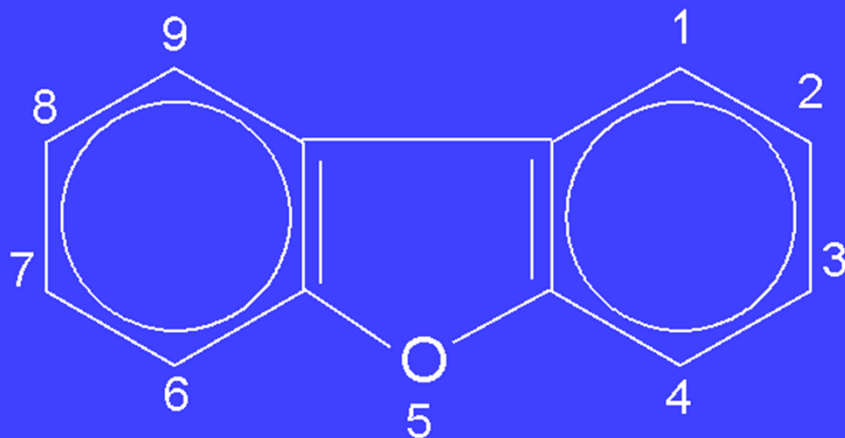
**Table 5-9. Data for selected pesticides**

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



**Figure 5-16.** Structure of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The rings are numbered as shown.

## Dibenzofuran



**Figure 5-30.** Basic structure of dibenzofuran. Positions 1 through 4 and 6 through 9 have attached hydrogens that can be replaced by chlorines in chlorodibenzofurans.

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

Dioxin or furan	TEQ
2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin	1
1,2,3,7,8-pentachlorodibenzo- <i>p</i> -dioxin	0.5
1,2,3,4,7,8-hexachlorodibenzo- <i>p</i> -dioxin	0.1
1,2,3,7,8,9-hexachlorodibenzo- <i>p</i> -dioxin	0.1
1,2,3,6,7,8-hexachlorodibenzo- <i>p</i> -dioxin	0.1
1,2,3,4,6,7,8-heptachlorodibenzo- <i>p</i> -dioxin	0.01
octachlorodibenzo- <i>p</i> -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

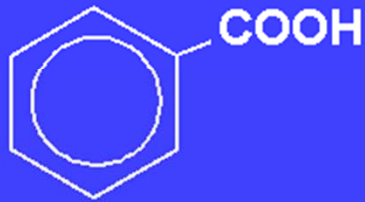
**Table 5-11. Solubility of BTEX aromatic hydrocarbons in water**

BTEX hydrocarbon	Solubility in distilled water (ppm)	Solubility in sea water (ppm)	Reference
Benzene	1696	201	1
Toluene	580	50	1
Ethylbenzene	161	111	2
<i>o</i> -xylene	171	130	2
<i>m</i> -xylene	148	106	2
<i>p</i> -xylene	156	111	2

**Table 5-12. Common DNAPLs**

Halogenated Volatiles	Nonhalogenated Semivolatiles
Chlorobenzene	2-Methyl naphthalene
1,2-Dichloropropane	<i>o</i> -Cresol
1,1-Dichloroethane	<i>p</i> -Cresol
1,1-Dichloroethylene	2,4-Dimethylphenol
1,2-Dichloroethane	<i>m</i> -Cresol
<i>trans</i> -1,2-Dichloroethylene	Phenol
<i>cis</i> -1,2-Dichloroethylene	Naphthalene
1,1,1-Trichloroethane	Benzo[ <i>a</i> ]anthracene
Methylene chloride	Fluorene
1,1,2-Trichloroethane	Acenaphthene
Trichloroethylene	Anthracene
Chloroform	Dibenzo[ <i>a,h</i> ]anthracene
Carbon tetrachloride	Fluoranthene
1,1,2,2-Tetrachloroethane	Pyrene
Tetrachloroethylene	Chrysene
Ethylene dibromide	2,4-Dinitrophenol
Halogenated Semivolatiles	Miscellaneous
1,4-Dichlorobenzene	Coal Tar
1,2-Dichlorobenzene	Creosote
Aroclor 1242, 1254, 1260	
Chlordane	
Dieldrin	
2,3,4,5-Tetrachlorophenol	
Pentachlorophenol	

**Figure 5-31.** Structures of some common organic acids and their dissociation constants,  $pK_a$ . Oxalic and sigma-phthalic acid have two dissociations constants because both acids have two-step dissociations. After Drever (1997).

Acid	Structure	$pK_a$
Acetic	$CH_3COOH$	4.9
Lactic	$  \begin{array}{c}  CH_3-CH-COOH \\    \\  OH  \end{array}  $	3.1
Oxalic	$  \begin{array}{c}  COOH \\    \\  COOH  \end{array}  $	1.2, 4.2
Benzoic		4.2
$\sigma$ -Phthalic		2.9, 5.5

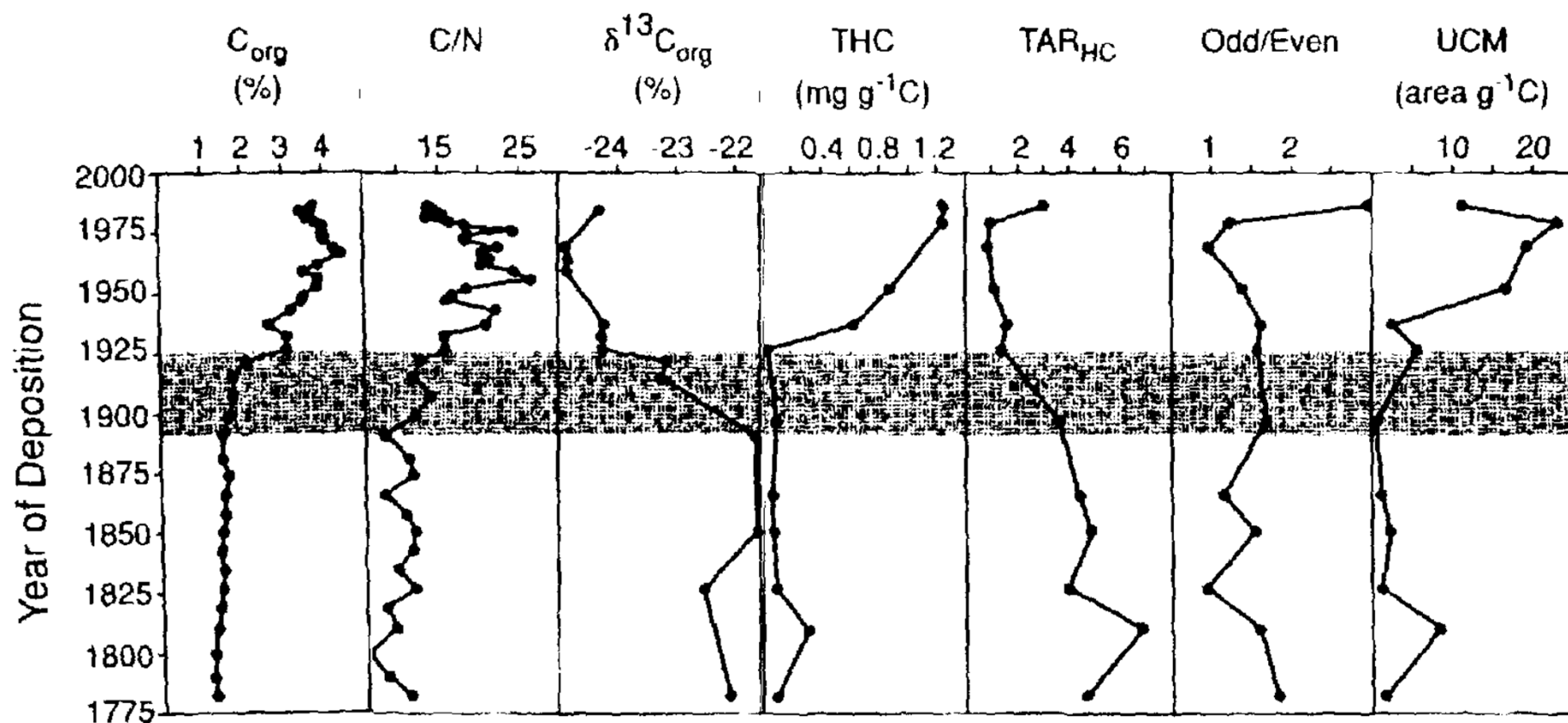
**Table 5-13.  $K_{oc}$  and Henry's Law constants for selected organic chemicals**

Compound	$\log K_{oc}$	H (unitless)
DDT	5.18	0.00213
Hexachlorobutadiene	4.46	186.797
1,2-Dichlorobenzene	3.23	0.07889
Lindane	3.11	0.00333
Napthalene	3.11	0.04701
Ethylbenzene	3.04	0.26282
m-Xylene	2.99	0.43736
o-Xylene	2.92	0.20846
4-Chloro-m-cresol	2.69	0.00010
Tetrachloroethene	2.56	1.05865
Toluene	2.48	0.26037
Benzene	1.92	0.22849
2,4-D	1.78	7.7E-9
Dichlorodifluoromethane	1.76	121.39765
Bromobenzene	2.18	0.07848

**Table 5-14. Half-lives for selected organic chemicals**

Compound	Half-life in days			
	Aerobic decomposition		Anaerobic decomposition	
	Minimum	Maximum	Minimum	Maximum
Cresol(s)	<1	29	10	49
Phenol	<1	4	8	28
Napthalene	1	20	25	258
Toluene	4	22	56	210
Benzene	5	16	112	720
Xylene(s)	7	28	180	360
Methyl parathion	15	70	1	7
Aldecarb	20	361	62	635
Lindane	31	413	6	31
Dieldrin	175	1080	1	7
Tetrachloroethene	180	360	98	1653
Chlordane	238	1386	1	7
DDT	730	5708	16	100





**Figure 5-C3-1. Organic carbon concentrations ( $C_{org}$ ), organic matter C/N ratios, delta  $^{13}C_{org}$ , total extractable hydrocarbons (THC), concentration ratios of terrigenous/aquatic *n*-alkanes (TAR<sub>HC</sub>), odd/even *n*-alkanes and unresolved complex mixture (UCM) relative to sediment age. Shaded area represents time of greatest environmental change as determined from the sediment record. Modified from Tenzer et al. (1999).**

# HENRY'S CONSTANT

The vapor pressure is only a measure of the volatility of a pure compound.

The volatility of an organic compound in an aqueous phase also depends on the solubility of that compound.

The important parameter describing this situation is the partitioning coefficient.

*Partitioning coefficient* - the ratio of the abundances of a given compound in two phases in equilibrium.

*Henry's Law constant* - the partitioning coefficient between a gas phase and liquid water.

# HENRY'S CONSTANT

The ratio of the abundance of the compound in air to the abundance of the compound in the aqueous phase at equilibrium.

The general definition of the Henry's constant is

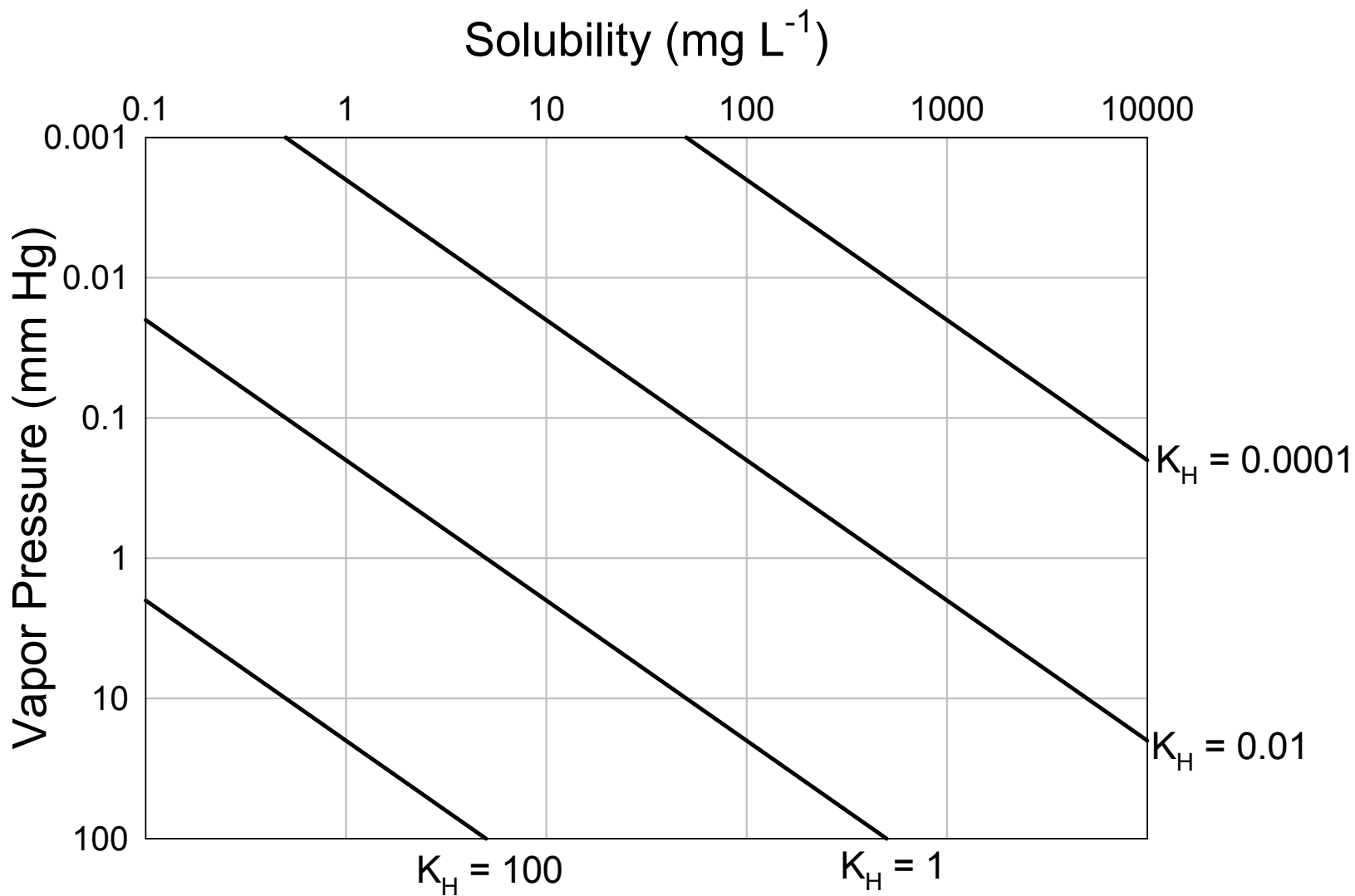
$$K_H = \frac{P_i}{C_w} \left( \text{atm L mol}^{-1} \right)$$

$P_i$  = Partial Pressure of the compound  
 $C_w$  = Molarity of the compound in aqueous solution

An alternate way to define the Henry's constant is

$$K_H = \frac{C_A}{C_w} \left( \text{mol L}_A^{-1} \text{ mol}^{-1} \text{ L}_w \right)$$

Henry's constant can be directly measured, or it can be estimated from the vapor pressure and solubility of the compound of interest.



Compounds most likely to partition into the gas phase (highest  $K_H$ ) are those with high vapor pressure and low solubility.

# OCTANOL-WATER PARTITIONING COEFFICIENT

The octanol-water partitioning coefficient,  $K_{ow}$ , describes the partitioning of an organic compound between immiscible octanol and water. It is defined as

$$K_{ow} = \frac{C_s}{C_w} \left( \text{mol L}_s^{-1} \text{ mol}^{-1} \text{ L}_w \right)$$

**Nonpolar organics** prefer octanol ( $K_{ow}$  high); **polar organics** prefer water ( $K_{ow}$  low).

The value of  $K_{ow}$  is useful in the estimation of other parameters. For example, water solubility is related by

$$\log K_{ow} = 7.30 - 0.747 \log S$$

- ⌘ **Octanol** is a straight chain fatty alcohol with eight carbon atoms and the molecular formula  $\text{CH}_3(\text{CH}_2)_7\text{OH}$ . Although the term *octanol* usually refers exclusively to the primary alcohol 1-octanol, there are other less common isomers of octanol such as the secondary alcohol, 2-octanol.
- ⌘ Octanol occurs naturally in the form of esters in some essential oils. The primary use of octanol is in the manufacture of various esters (both synthetic and naturally occurring), such as octyl acetate, which are used in perfumery and flavors.
- ⌘ **Water/Octanol Partitioning**
- ⌘ Octanol and water are immiscible. The distribution of a compound between water and octanol is used to calculate the partition coefficient (logP) of that molecule. It has been shown that water/octanol partitioning is a good approximation of the partitioning between the cytosol and lipid membranes of living systems.
- ⌘ Retrieved from "<http://en.wikipedia.org/wiki/Octanol>"

# ADSORPTION OF DISSOLVED ORGANIC COMPOUNDS

The value of  $K_{ow}$  can be used to estimate adsorption behavior.

Hydrophobic organic compounds do not interact electrically with surfaces of charged particles; they are most strongly adsorbed to neutral solid organic matter.

The partitioning coefficient between solid organic matter and water is

$$K_{oc} = \frac{C_{ad} (\text{g solute adsorbed/g soil organic carbon})}{C_w (\text{g solute/m}^3 \text{ solution})}$$

The value of  $K_{ow}$  has been related to  $K_{oc}$  by several relations of the type:

$$\log K_{oc} = -0.21 + \log K_{ow}$$

(Karickhoff et al., 1979)

$$\log K_{oc} = 0.49 + 0.72 \log K_{ow}$$

(Schwarzenbach and Westall, 1981)

Values of  $K_d$  can also be calculated from  $K_{oc}$  if the weight fraction of organic carbon ( $f_{oc}$ ) is taken into account:

$$K_d = K_{oc} f_{oc}$$



# PARTITIONING OF ORGANIC COMPOUNDS

How organic contaminants partition among the solid, liquid and gas phases in natural waters is crucial to predicting how far they will migrate and in selecting remediation techniques.

To determine the partitioning, one calculates the mass of the compound in one cm<sup>3</sup> of soil containing both water and air in its pore spaces.

For the solids  $C_s = K_d C_w$

where  $C_s$  is the concentration adsorbed to the soil,  $K_d$  is the distribution coefficient (cm<sup>3</sup> g<sup>-1</sup>),  $C_w$  is the concentration in the aqueous phase.

We can estimate  $K_d$  from the relation

$$K_d = 0.6 f_{oc} K_{ow}$$

Once  $C_s$  is determined for the compound, the mass of the compound  $M_s$  in a 1-cm<sup>3</sup> volume of soil is given by

$$M_s = C_s \rho_b$$

where  $\rho_b$  is the bulk soil density.

To calculate the mass of organic matter in water requires knowledge of the porosity and the volumetric water saturation.

The mass of water is given as

$$M_w = C_w n_w$$

where  $n_w$  is the water-filled porosity (the product of the porosity and the volumetric water saturation).

The concentration of the organic compound in the gaseous phase is given by

$$C_a = C_w K_H$$

and the mass of the compound in air by

$$M_a = C_a n_a$$

where  $n_a$  is the air-filled porosity.

## PARTITIONING OF ORGANIC COMPOUNDS (2% ORGANIC MATTER)

Compound	Air	Water	Solids
1,1,1-Trichloroethane $K_{ow} = 300$	5%	5%	90%
1,1,1-Trichloroethane $K_{ow} = 147.9$	6%	6%	88%
Trichloroethene 20°C	1.6%	4.6%	93.8%
Trichloroethene 90°C	30%	7%	63%
Acetone	0.07%	85%	15%

## PARTITIONING OF ORGANIC COMPOUNDS (1% ORGANIC MATTER)

Compound	Air	Water	Solids
1,1,1-Trichloroethane $K_{ow} = 300$	26%	23%	51%
1,1,1-Trichloroethane $K_{ow} = 147.9$	35%	31%	34%
Trichloroethene 20°C	14%	35%	52%
Trichloroethene 90°C	73%	16%	11%
Acetone	0.07%	99%	1%

# PARTITIONING OF ORGANIC COMPOUNDS

In a soil with **high organic matter** content, 1,1,1-TCA is partitioned almost entirely in the solid phases (difficult to remove contaminant).

In a soil with **low organic matter** content, 1,1,1-TCA is not as strongly partitioned into the solid phases and would be easier to remove.

Acetone is strongly partitioned into the aqueous phase

- ☒ More mobile and may migrate far from source
- ☒ Can be removed by pump-and-treat methods

# PROPERTIES OF SOME COMMON GROUND WATER CONTAMINANTS

Compound	BP (°C)	Density (25°C)	Water solubility (mg L <sup>-1</sup> ) (25°C)	Vapor Pressure (mm Hg) (10°C)	K <sub>H</sub> (25°C)	K <sub>ow</sub>
Methylene chloride	40	1.3182	20,000	260.9	0.105	17.78
Acetone	56.3	0.7899	∞	121.7	0.000842	1.74
Carbon Tetrachloride	76.8	1.5833	800	58.3	0.807	676.1
Benzene	80.1	0.88	1770	47.8	0.22	134.9
Trichloro- ethene	87.3	1.4578	1100	37.6	0.397	195
Tetra- chloroethene	121.3	1.613	150	400	0.928	400
2-Butanone	79.6	0.7994	26,800	314.3	0.001	1.82