Chapter 5 Carbon Chemistry

Scientists practicing in the environmental field are constantly faced with the problem of organic contaminants. Hence, a familiarity with the nomenclature and basic principles of organic chemistry is essential. This is a vast and complex field, as illustrated by the fact that more than 9 million carbon-based compounds have been identified. Only the rudiments of organic chemistry will be covered here, with particular emphasis on those organic compounds that are environmentally important. Additional topics involving organic chemistry are considered in Chapters 8 (atmospheric environment), 9 (freshwater environment), and 10 (marine environment). Although the naming of organic compounds may seem a dry topic, it is useful to be able to relate the names of compounds to their structure. For this reason, the chapter starts with a discussion of the basic nomenclature for organic compounds.

BASIC STRUCTURES AND NAMING OF ORGANIC COMPOUNDS

Organic compounds are primarily composed of carbon and hydrogen atoms. Other elements—e.g., oxygen, nitrogen, sulfur, phosphorous, and the halogens—may also occur in organic compounds. The fundamental building block of organic compounds is the carbon-carbon bond. The bonding between carbon atoms is covalent. ***Single bonds*** are formed when *one pair of electrons is shared between two carbon atoms.* ***Double bonds*** involve the *sharing of two pairs of electrons,* and ***triple bonds*** the *sharing of three pairs of electrons. If multiple bonds occur between carbon atoms, the compound is* referred to as ***unsaturated.*** *If there are only single bonds between the carbon atoms, the compound is* ***saturated.*** The carbon atoms are joined together to form chains, branched structures, or rings. *A* ***functional group*** is *an atom or a group of atoms that can be attached to the carbon atoms.* In most cases, a functional group contains at least one noncarbon atom. Also important is the order in which the functional groups are attached and the geometric position of the attached groups. All of this variability means that the naming of organic molecules is not an easy task.

Organic compounds have been named in a variety of ways, which, for the nonspecialist, introduces additional complexity. Organic compounds are often identified by trade names, common names, or acronyms that bear no relationship to the actual chemistry of the compound. ***Systematic names*** *contain structural information,* and the International Union of Pure and Applied Chemistry (IUPAC) naming system will be described in this section. All organic compounds listed in the Chemical Abstracts System (CAS) are given a unique number. In order to search for a particular compound in Chemical Abstracts, one must know the CAS number of the compound.

Formulas

The three-dimensional geometry of an organic molecule is important because it partly determines the properties of the molecule. ***Structural formulas*** *show the orientation of the atoms in a molecule in either two or three dimensions.* ***Condensed structural formulas*** are used to save space and *are written in terms of carbon units.* ***Molecular formulas*** *give the numbers of each type of atom in the molecule.* As one example of the types of formulas, consider the compound dichloromethane. The molecular formula is CH_2C1_2. Because this molecule contains only one carbon atom, the condensed structural formula would be the same. The two- and three-dimensional structural formulas are illustrated in Figure 5–1. Figure 5–2 illustrates the relationship between the condensed structural formula and the structural formula for butane. Note that in the condensed structural formula the H subscript indicates the number of hydrogen atoms attached to each carbon atom.

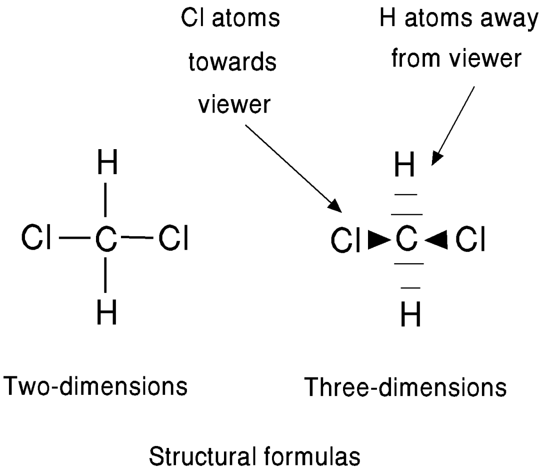


Figure 5–1 Two- and three-dimensional structural formulas for dichloromethane, CH_2C1_2. In a two-dimensional representation, single, normal-weight lines are used to connect atoms. In a three-dimensional representation, broken lines indicate bonds extending away from the viewer and arrows indicate bonds extending toward the viewer.

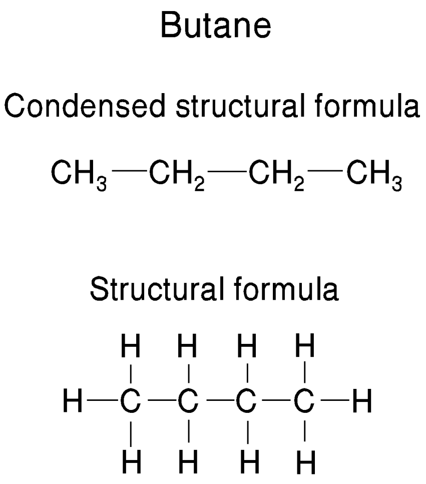


Figure 5–2 Relationship between the condensed structural formula and the structural formula of butane.

Isomers

Isomers are *compounds with the same molecular formula but different structural formulas.* Isomers are analogous to the polymorphs of inorganic chemistry. The two isomers of C_4H_{10} are illustrated in Figure 5–3. Note that in this case we are using condensed structural formulas.

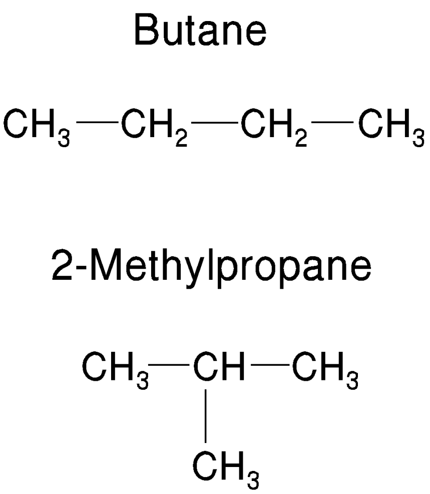


Figure 5–3 Isomers of C_4H_{10}. Both butane and 2-methlypropane have the same number of C and H atoms, but 2-methylpropane has a branched chain.

If the carbon atoms have double bonds, another type of isomer, called a *geometric* isomer, is possible. The presence of the double bond prevents free rotation between the two carbon atoms. If hydrogen atoms are replaced by substituent groups, there are two possible arrangements for these substituent groups. The two groups may occur on the same side of the double bond, the "cis" orientation, or they may occur on opposite sides of the double bond, the "trans" orientation. The physical and chemical properties of these two isomers are different. Thus, the distinction is important. As an example of the two types of geometric isomers, the condensed structural formulas for *cis*-2-butene and *trans*-2-butene are shown in Figure 5–4.

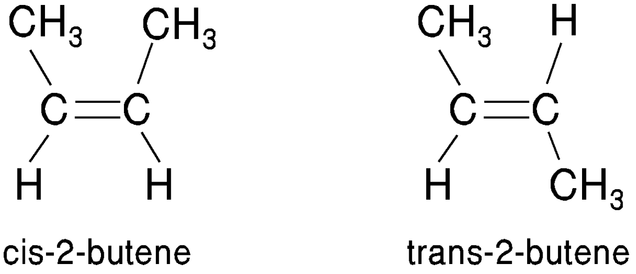


Figure 5–4 Examples of geometric isomers, *cis*-2-butene and *trans*-2-butene. In the first isomer, the two substituent groups are on the same side of the double bond. In the second isomer, the two substituent groups are on opposite sides of the double bond.

Hydrocarbons

Hydrocarbons contain only carbon and hydrogen and are the most common group of organic compounds. The major types of hydrocarbons are alkanes, alkenes, alkynes, and aromatic (or aryl) compounds. In ***alkanes*** the *C atoms have single bonds and occur as straight or branched chains and as rings.* ***Alkenes*** have a *double bond between two of the carbons,* and ***alkynes*** have a *triple bond between two of the carbons.* The type of bonding, single versus multiple, affects the *reactivity* of the molecule. Alkanes, because of their strong single carbon bond, tend to be chemically nonreactive except at high temperatures, such as those found during combustion. Alkanes can undergo ***substitution reactions*** in which *one or more hydrogens are replaced by atoms of another element.* For example, consider the photochemical reaction shown in Figure 5–5. In this reaction one of the hydrogen atoms in methane is replaced by chlorine. Hence, this is a substitution reaction. Alkenes and alkynes, because they have double and triple carbon bonds (they are unsaturated compounds), are chemically more reactive. For these types of compounds,

addition reactions, *in which some of the electrons in the unsaturated bonds are used to bind with additional atoms,* are common. Thus, atoms are added to the original organic molecule. An example of this type of reaction is the addition of hydrogen to ethylene to produce ethane (Figure 5–6).

$Cl_2 + UV \rightarrow Cl^{\cdot} + Cl^{\cdot}$ (Cl$^{\cdot}$ is a free radical)

$Cl^{\cdot} + CH_4 \rightarrow HCl + CH_3^{\cdot}$ (methyl radical)

$CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$ (chloromethane)

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

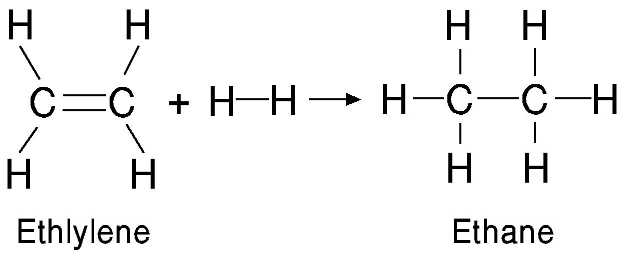


Figure 5–6 Example of an addition reaction in which hydrogen is added to ethylene to produce ethane (a hydrogenation reaction).

Naming and Types of Hydrocarbon Compounds

Alkanes Many organic compounds can be derived from alkanes, so it is useful to know the names of the more common alkanes and how these names are derived. The naming process is relatively straightforward and is done according to the following rules:

1. The name of the compound is based on the longest continuous chain of carbon atoms. The root name indicates the number of carbon atoms in the chain, and the suffix *ane* is added to the root name (Table 5–1). For example, a chain with three carbon atoms is propane.

Table 5–1 Prefixes for the Number of Carbon Atoms

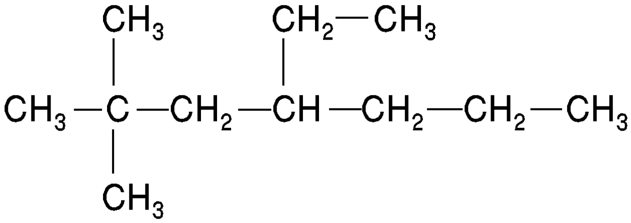
# C	Prefix	# C	Prefix	# C	Prefix
1	Meth	11	Undec	21	Henicos
2	Eth	12	Dodec	22	Docos
3	Prop	13	Tridec	23	Tricos
4	But	14	Tetradec	24	Tetracos
5	Pent	15	Pentadec	25	Pentacos
6	Hex	16	Hexadec	26	Hexacos
7	Hept	17	Heptadec	27	Heptacos
8	Oct	18	Octadec	28	Octacos
9	Non	19	Nonadec	29	Nonacos
10	Dec	20	Eicos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

2. The carbon atoms in the longest continuous chain are numbered sequentially from one end. If substituent groups are added to the chain, the numbering starts at the end of the chain that will give the lowest numbers for the substituent groups.

3. All groups attached to the longest continuous chain are identified by the number of the carbon atom to which they are attached and the name of the substituent group. If the substituent group is derived from an alkane, it is named by removing the terminal *ane* and replacing it with *yl*. For example, methane → methyl group. If two or more groups are present, their names are listed in alphabetical order.

4. A prefix is used to denote multiple substitutions by the same kind of group. This prefix is ignored when deciding the alphabetical order (rule 3).

As an example, consider the naming of the alkane shown in Figure 5–7. The longest continuous chain consists of seven carbon atoms; hence, the root name is heptane. The chain is numbered from the left because this will give the lowest numbers for the substituent groups. There are two types of substituent groups: CH_3– is methyl (one carbon atom is methane, substitute *yl* for *ane* to get methyl) and CH_2–CH_3– is ethyl. There are two methyl groups; hence we will use the prefix *di* to give dimethyl. Ethyl is earlier in the alphabet than methyl and will be listed first. The methyl groups are attached to the second carbon, and the ethyl group is attached to the fourth carbon. The complete name for this compound is 4-ethyl-2,2-dimethylheptane, where “4-ethyl” indicates that the ethyl group is attached to the fourth carbon, “2,2-dimethyr indicates that both methyl groups are attached to the second carbon, “di” indicates two methyl groups, and “heptane” indicates that the longest continuous chain is heptane (i.e., it has seven carbon atoms). At first glance this may seem to be a complicated name, but when considered in light of the rules, the name accurately represents the structural formula of the hydrocarbon.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_2-CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

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

Alkenes and Alkynes Because of the presence of double or triple bonds, the naming of alkenes and alkynes is somewhat more complicated than the naming of alkanes, but the rules are still relatively straightforward. Suffixes are used to designate double *(ene)* or triple *(yne)* bonds, and prefixes are used to locate the bonds. The initial phase of the naming process is similar to that for the alkanes. The rules are as follows:

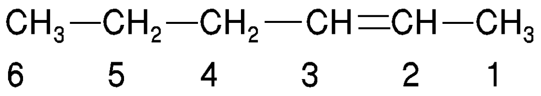
1. Find the longest chain containing the double and/or triple bonds. The stem name is based on the number of carbon atoms, as is the case for the alkanes. A prefix number is used to indicate the position of the carbon atom immediately before the double or triple bond, and a suffix *(ene* or *yne)* is used to indicate whether the compound is an alkene or alkyne.
2. The chain is numbered so that the double/triple bond will have the lowest location number. If both types of bonds are present, the double bond takes precedence in establishing the start of the numbering sequence.
3. If more than one double bond is present, the location numbers are indicated first and the ending is given as *diene, triene,* etc. If a triple bond is also present, the double bonds are designated in the main stem, dropping the *e,* and the triple bond is designated by an extra suffix.

4. Unsaturated substituents are named by using the prefix of the chain after replacing the terminal *e* with *yl*. For example, propene becomes propenyl.

The following examples illustrate the application of these rules to the naming of alkenes and alkynes.

EXAMPLE 5–1 Given the condensed structural formula shown in Figure 5–8, name the compound.

The double bond is located toward the right end of the chain, so we number from right to left. There is only one double bond and no triple bonds, so the suffix for the stem name is *ene*. The chain consists of six carbons, giving a stem name of hexene. The double bond starts with the second carbon atom, so the locator number is 2. The complete name of the compound is 2-hexene. If the compound contained a single triple bond, rather than a single double bond, the name would be 2-hexyne.

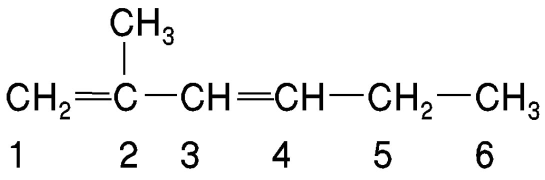


$$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{CH_2}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{CH_3}$$

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

EXAMPLE 5–2 Given the condensed structural formula shown in Figure 5–9, name the compound.

The first double bond is located toward the left end of the chain, so we number from left to right. There are two double bonds, so the suffix for the stem name is *diene*, and there are six carbons, giving a stem name of hexdiene. The double bonds begin with carbon atoms 1 and 3, the location numbers. There is one methyl group attached to carbon 2. The complete name of the compound is 2-methyl-1,3-hexdiene.

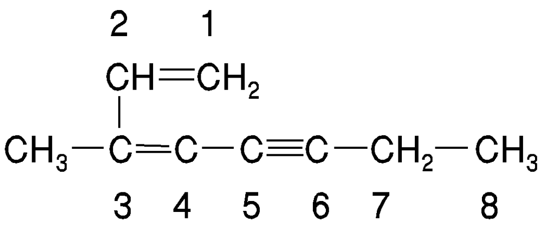


$$\underset{1}{CH_2}=\underset{2}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{3}{CH}=\underset{4}{CH}-\underset{5}{CH_2}-\underset{6}{CH_3}$$

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

EXAMPLE 5–3 Given the condensed structural formula shown in Figure 5–10, name the compound.

We start numbering with the double bond closest to the end of the chain. There are two double bonds and one triple bond in the chain, and there are eight carbon atoms, so the stem name becomes l,3-octdien-5–yne. Note that the *e* is dropped from *diene.* “Oct” indicates there are eight carbons, and “dien” indicates that there are two double bonds. The 1,3 indicates the positions of the double bonds, and the “5–yne” indicates the position of the triple bond (the fact that it’s a triple bond is indicated by the “yne” suffix). The substituent group is a methyl group, and this group is attached to the third carbon atom. The complete name of the compound is 3-methyl-1,3-octdien-5–yne.



$$CH_3-\overset{\overset{CH=CH_2}{|}}{C}=C-C\equiv C-CH_2-CH_3$$

Figure 5–10 Condensed structural formula for 3-methyl-1,3-octdien-5-yne.

Cyclic Hydrocarbons In cyclic hydrocarbons the carbon atoms are arranged in a ring. The cyclic hydrocarbons do not form flat structures like aromatic hydrocarbons and are thus distinguished from them. For simple rings, without attached substituent groups, the prefix *cyclo* is used to distinguish a ring structure. For example, cyclohexane would consist of six singly bonded carbon atoms in a ring structure, cyclohexene would consist of six carbon atoms with one double bond in a ring structure, and cyclohexyne would consist of six carbon atoms with one triple bond in a ring structure. If substituent groups are attached, the carbon atoms are numbered so as to give the substituents the lowest possible location numbers. If a double bond is present, the numbering of the carbon atoms starts with the double bond.

Aromatic (Aryl) Hydrocarbons The basic building block of the aromatic hydrocarbons is the benzene ring, which consists of six carbon atoms and six hydrogen atoms. It was originally thought that the ring consisted of alternating single and double bonds, but it was eventually realized that the ring has six identical bonds, neither single nor double. Modern representations of the benzene ring show it as a hexagon enclosing a circle, indicating that it consists of a ring of delocalized (π) electrons. Thus, one can find two different symbols (Figure 5–11) for the benzene ring in the literature. In the IUPAC system, the benzene-ring carbon atoms are numbered from 1 to 6, starting with one substituent and continuing either clockwise or counterclockwise so that the lowest number for each substituent is obtained. Benzene derivatives are also identified in the literature by specific names based on long usage or on the basis of the ortho-, meta-, and para-system. An example of a name based on long usage is *xylene*, which is used for a benzene ring with two attached methyl groups. In the ortho-, meta-, para-system, the positions are defined relative to a particular constituent with ortho- (*o*) one carbon atom removed from the constituent, meta- (*m*) two carbon atoms removed, and para- (*p*) three carbon atoms removed. An example of this naming convention, for a benzene ring with attached methyl groups, is shown in Figure 5–12. Aromatic hydrocarbons are characterized by their low H:C atomic ratio, relatively strong C-C bonds, a tendency to undergo substitution reactions, and the delocalization of π electrons over several carbon atoms, which adds substantial stability to the ring structure.

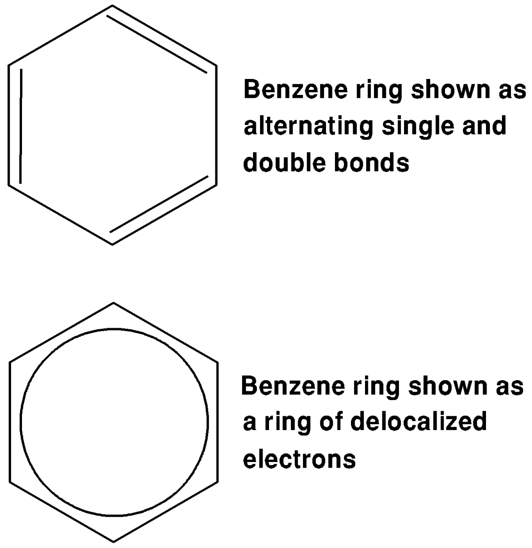


Figure 5–11 Representations of the benzene ring found in the literature.

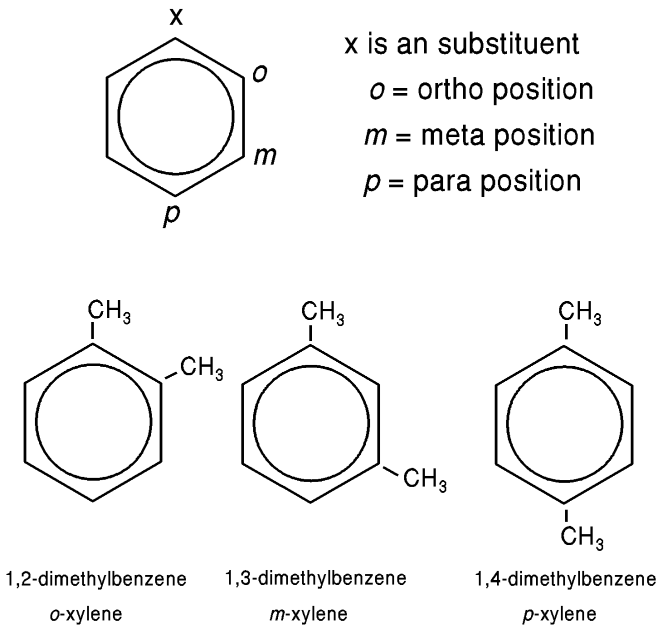


Figure 5–12 Illustration of the naming conventions for the benzene ring using attached methyl groups. Note that while not shown on the diagram, the other sites are occupied by hydrogen atoms.

Polycyclic Aromatic Hydrocarbons (PAH) This important group of compounds consists of two or more fused benzene rings, which form a planar structure (Figure 5–13). These compounds are formed by the incomplete combustion of other hydrocarbons. Because there are many partial combustion and pyrolysis processes that favor the production of PAHs, they are widely distributed in the environment. Some PAHs are precursors to cancer-causing metabolites and are of significant environmental interest. For example, benzo[a]pyrene is a particularly potent carcinogen.

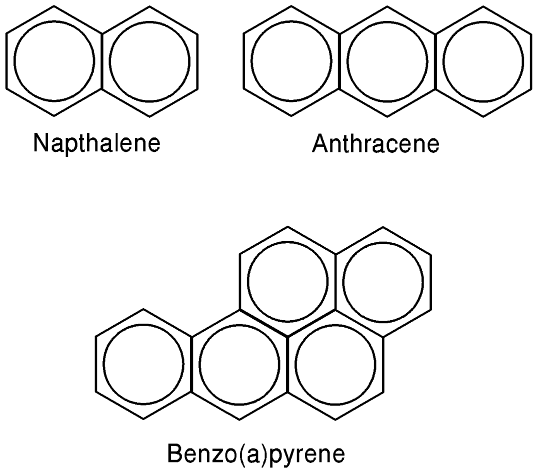


Figure 5–13 Examples of polycyclic aromatic hydrocarbons (PAHs) including the known carcinogen benzo(a)pyrene. Where the benzene rings do not share edges, hydrogen atoms are attached to the carbon atoms.

Functional Groups

So far, we have considered the basic structures of organic molecules that consist only of carbon and hydrogen. However, organic molecules can contain other elements, such as oxygen, nitrogen, and the halogens (F, Cl, Br). These atoms occur in functional groups that are attached to the main carbon skeleton and lead to the great diversity in properties noted for the organic compounds. ***Functional groups*** *consist of specific bonding configurations of atoms in organic molecules and usually, but not always, contain at least one element other than carbon or hydrogen.* Note that two carbon atoms connected by either a double bond or a triple bond can also be considered a functional group. The functional groups of most interest in environmental geochemistry are carboxylic acid (COOH), hydroxyl (OH), aldehyde (COH), amine (NH_2), nitro compounds (NO, NO_2), sulfonic acids (SOOOH), and organohalides (Cl, F, Br). Examples of compounds containing these different types of functional groups are shown in Figure 5–14.

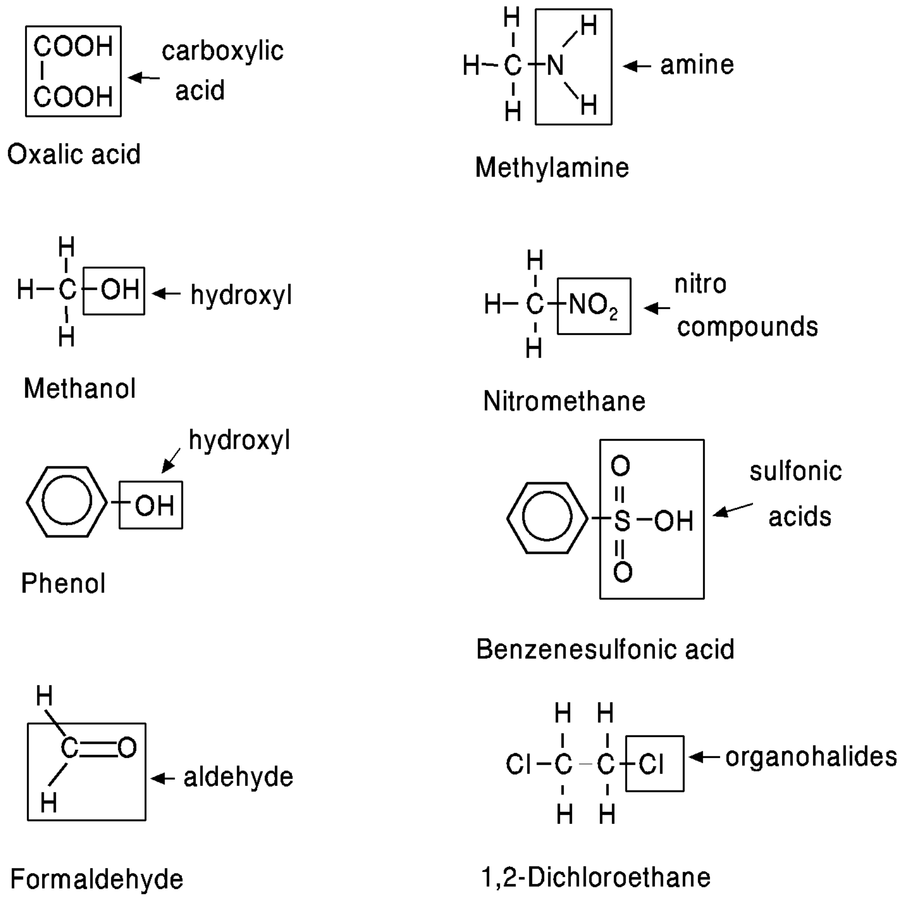


Figure 5–14 Examples of important functional groups. For each molecule the functional group is enclosed in a box and the name of the group is indicated by the arrow. The name of the compound is listed under each molecule.

Organohalide Compounds

This particular group contains some of the most useful, most toxic, and most environmentally sensitive organic compounds. The chlorofluorocarbons (CFCs) that have achieved notoriety for their effect on stratospheric ozone are organohalides, as are DDT, PCB, and dioxins. The fundamental structures are the same as those described in the preceding sections on hydrocarbons except that each molecule contains at least one atom of F, Cl, Br, or I. Thus, we can have saturated, unsaturated, cyclic, and aromatic halides, each of which starts with the basic hydrocarbon structure. The naming is relatively straightforward in that the halogen atoms are listed as substituents using prefixes such as fluoro (for F), chloro (for Cl), bromo (for Br), and iodo (for I).

As an example, consider the naming of the compound 1,2-dichloroethane (shown in Figure 5–14). This is a halogenated hydrocarbon because it contains two chlorine atoms that have replaced two hydrogen atoms. The basic hydrocarbon structure is a straight chain consisting of two carbon atoms; hence the root name is ethane. There are two substituent chlorine atoms, giving the prefix dichloro (di = two, chloro = Cl). One chlorine atom is attached to each carbon atom, Thus, they are in positions 1 and 2. We now have the complete name for the compound, 1,2-dichloroethane. If more than one type of halogen atom appears in the molecule, then multiple halogen prefixes are used. The numbers of each type of halogen atom are indicated by a prefix added to the halogen prefix (sometimes used, mono = 1, di = 2, tri = 3, tetra = 4, penta = 5, hexa = 6, etc.). For example, a compound having the formula CCl_2F_2 (this is a methane molecule in which all the hydrogen atoms have been replaced by halogen atoms) would be named dichlorodifluoromethane. This is a rather long name, but it does accurately describe the chemical formula. For unsaturated chains, naming is done in a similar way. For example, a compound having the condensed structural formula CH_2-CCl_2 would be named 1,1-dichloroethene. The root chain is ethene (two carbon atoms doubly bonded), and there are two chlorine atoms (dichloro) attached to the first carbon atom. A similar practice is followed for the aromatic hydrocarbons. For example, consider a benzene ring with two attached chlorine atoms, one in position 1 and the other in position 3. The name of this compound would be 1, 3-dichlorobenzene. The root structure is the benzene ring, and the two chorine atoms (dichloro) are attached to carbon atoms 1 and 3. A listing of representative halogenated hydrocarbons is given in Table 5–2.

Table 5–2 Examples of Halogenated Hydrocarbons

Name	Formula	Name	Formula
Chloromethane	CH_3Cl	1,1,2,2-Tetrachloroethane	$Cl_2CH–CHCl_2$
Bromomethane	CH_3Br	1,1,1,2-Tetrachloroethane	$Cl_3C–CH_2Cl$
Dichloromethane	CH_2Cl_2	Pentachloroethane	$Cl_3C–CHCl_2$
Trichloromethane	$CHCl_3$	Hexachloroethane	$Cl_3C–CCl3$
Tetrachloromethane	CCl_4	2-Chloropropane	$CH_3–CHCl–CH_3$
Bromodichloromethane	$CHCl_2Br$	1,2-Dibromo-3-chloropropane	$BrCH_2–BrCH–$
Trichlorofluoromethane	CCl_3F	Chloroethene	$CH_2=CHCl$
Chlorodifluoromethane	$CHClF_2$	1,1-Dichloroethene	$CH_2=CCl_2$

Dichlorodifluoromethane	CCl_2F_2	Trichloroethene	$ClCH{=}CCl_2$
Chloroethane	$CH_3–CH_2Cl$	Tetrachloroethene	$Cl_2C{=}CCl_2$
1,2-Dichloroethane	$ClCH_2–CH_2Cl$	1 -Chloropropene	$ClCH{=}CH–CH_3$
1,1,1 -Trichloroethane	$CH3-CCl_3$	1,3-Dichloropropene	$ClCH{=}CH–CH_2Cl$

Polychlorinated biphenyls (PCBs) *consist of two benzene rings joined by a single bond with attached chlorine atoms.* Both benzene rings have five available carbon atoms that can bond to the substituted chlorine atoms. For these molecules the root name is biphenyl and the positions of the substituents are indicated, for example, by 2 and 2′ (2 indicating the first ring and 2′ the second ring), etc. The standard prefixes are used to indicate the type and number of each of the substituent atoms. PCB compounds have very high chemical, thermal, and biological stability; low vapor pressures; and high dielectric constants. For this reason, they have wide industrial applications. However, because of their high stability, PCBs accumulate in the environment and subsequently in the fatty tissues of birds and fish. They are viewed as a significant environmental and health hazard and are no longer manufactured in the United States.

The ***chlorinated phenols***, particularly pentachlorophenol and the trichlorophenol isomers, are significant hazardous wastes. These compounds have been widely used as wood preservatives. With reference to Figure 5–14, a phenol is a benzene ring that has an attached OH functional group. In pentachlorophenol all the hydrogens attached to the benzene ring have been replaced. At one site the OH functional group is attached to the benzene ring, and at the other five sites chlorine atoms are attached to the ring. In the case of trichlorophenol, three of the five hydrogen atoms have been replaced by chlorine atoms.

DDT (dichlorodiphenyltrichloroethane) is a halogenated insecticide that was once widely used. It is known as a “hard pesticide” because of its persistence in the environment. This persistence was seen as a plus because after application the pesticide remained active for a relatively long period of time and did not have to be reapplied. It also has a low toxicitiy in mammalian systems. However, as Carson (1962) so eloquently described in her book *Silent Spring*, the unforeseen hazards, due to biomagnification, to other biosystems were significant. DDT breaks down to DDD (dichlorodiphenyldichloroethane) and DDE (dichlorodiphenyldichloroethene). DDE has been shown to be hazardous to male animals and affects reproduction. Because of these problems, the use of DDT has been banned in the United States and many other countries. The structure of DDT is shown in Figure 5–15.

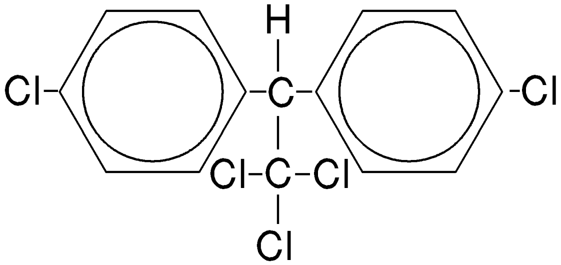


Figure 5–15 Structure of DDT. The molecule consists of two benzene rings joined by a chlorinated ethane group. Each ring has a Cl atom substituting for a H atom. The IUPAC name for this molecule would be dichlorodiphenyltrichloroethane.

Dioxins are a byproduct of pesticide manufacture and are often found as residues in pesticides. They can also be produced by the incomplete combustion of PCBs during waste incineration. The dioxins have a high thermal stability and do not decompose until the temperature exceeds 700°C. Of this group of compounds the most hazardous is TCDD (Figure 5–16), often referred to simply as *dioxin.* For some animals, this compound is one of the most toxic of all synthetic substances. The basic structure of dioxin is two benzene rings connected by an oxygen-containing cyclical hydrocarbon. The benzene rings have from one to eight chlorine atoms substituting for hydrogen atoms, giving a total of 75 possible chlorinated derivatives.

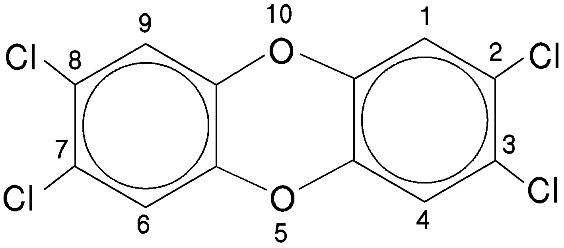


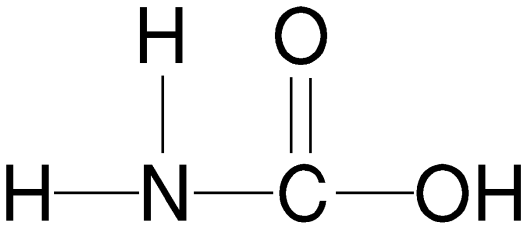
Figure 5–16 Structure of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The rings are numbered as shown. Note that the chlorine atoms occur in positions 2, 3, 7, and 8. The tetra prefix indicates that there are four chlorine atoms.

Organooxygen Compounds

These compounds have an oxygen-containing functional group. Some of these chemicals are hazardous and/or toxic. *Alcohols* contain a hydroxyl functional group attached to an alkane. They are named by changing the *e* ending of the alkane to *ol*—hence, methanol (Figure 5–14). *Phenols* (aromatic alcohols) are benzene rings in which one hydrogen is replaced with an OH functional group (Figure 5–14). *Ketones* contain a carbonyl group (C=O) that occurs in the alkane molecule bonded to two other carbon atoms. In the IUPAC system, the ketones are named by changing the *e* ending of the alkane to *one.* However, because of common usage, older names are often retained. For example, propanone is usually referred to as acetone. *Carboxylic acids* are organic acids that contain a hydroxyl group attached to a carbonyl group (the carboxylic acid functional group –COOH). The acids of alkanes are named by replacing the *e* of the root alkane with *oic acid.* For example, propane with a substituent carboxylic acid group would be called *propanoic* acid. *Ethers* consist of two carbon groups connected by an oxygen. In traditional naming schemes, if the two groups are the same, then the group name is only used once with the word *ether* added. If the two groups are different, then both groups are named. For example, CH_3-O-CH_3 is dimethyl ether and CH_3-O-CH_2-CH_3 is ethyl methyl ether (the alkane on the left of the oxygen is a methyl group and the alkane on the right of the oxygen is an ethyl group). In the IUPAC system, the naming of ethers is different. One group (the smaller if the groups are of different size) is combined with the oxygen to form a substituent, and the other group becomes the root name of the compound. An *oxy* ending is added to the group serving as the substituent. For example, methane becomes methoxy and phenol becomes phenoxy. For the examples given, in the IUPAC system methyl ether ; methoxymethane and ethyl methyl ether ; methoxyethane.

Organonitrogen Compounds

Nitrogen occurs in a number of functional groups in organic compounds. Nitrogen can form single, double, or triple covalent bonds, and nitrogen functional groups are found as substituents on alkanes, alkenes, alkynes, and aromatic hydrocarbons. Two important classes of organonitrogen compounds are the amino acids and amines. *Amino acids* are characterized by the presence of an amino group (NH_2, Figure 5–14). *Amines* can be considered as derivatives of ammonia (NH_3), in which one or more of the hydrogen atoms are replaced by alkyl groups (functional groups derived from alkanes are referred to as *alkyl* groups) or an aromatic ring. The naming of the organonitrogen compounds will not be discussed here, but a few examples will be given. *TNT* (2,4,6-trinitrotoluene) consists of a benzene ring with one attached methyl group (this is usually called *toluene* from long usage) and three NO_2 functional groups. *Carbamates* are extensively used as pesticides and herbicides. These are complex organic molecules derived from carbamic acid (Figure 5–17). The resulting carbamate is combined with methyl and other functional groups, and aromatic or heterocyclic compounds, to produce a wide variety of pesticides and herbicides. The carbamates are referred to as *soft pesticides* because they quickly break down in the natural environment. They are, however, neurotoxins and at high concentrations are toxic to mammals. *Aminocarboxylic acids* ($-CH_2CO_2H$ groups bonded to nitrogen atoms) form a variety of organonitrogen compounds that are chelating agents. An example is the monohydrate of trisodium nitrilotriacetate (NTA) that is used as a substitute for phosphate detergent and in metal plating formulations. When released to the environment, this chelating agent can mobilize heavy metals.



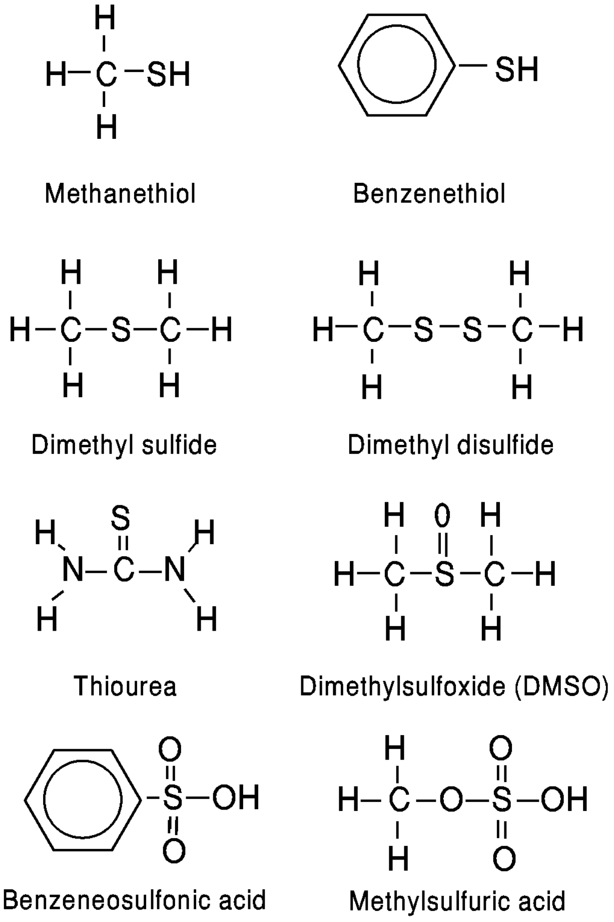
$$\mathrm{H-\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH}$$

Figure 5–1 7 Carbamic acid.

Organosulfur Compounds

Sulfur can occur in a number of oxidation states (−2, +4, +6), leading to a variety of organic sulfur compounds. There are three major groups of organosulfur compounds: (1) compounds that contain a functional group in which oxygen is replaced by sulfur, (2) compounds that contain a functional group consisting of sulfur and oxygen (Figure 5–14), and (3) sulfur heterocyclics. Examples of the various types of sulfur compounds are shown in Figure 5–18. *Thiols* (called *mercaptans* in the older literature) are analogous to alcohols in which the oxygen atom has been replaced by sulfur (R-SH, R is the root molecule). *Sulfides* contain a single sulfur atom that connects hydrocarbon groups (e.g., dimethyl sulfide), and *disulfides* contain two sulfur atoms joined by a single bond (e.g., dimethyl disulfide). *Thiourea* compounds contain both sulfur and nitrogen. One example is

1-napthylthiourea (ANTU), which is an excellent rodenticide. *Sulfoxides* and *sulfones* contain both sulfur and oxygen. Sulfoxides are analogous to ketones, in which the carbonyl carbon has been replaced by sulfur. In sulfones, sulfur has six bonds, four with oxygen and two with carbon. *Sulfonic acids and salts* are organic derivatives of sulfurous acid (H_2SO_3), and *sulfates* are organic derivatives of inorganic sulfuric acid (H_2SO_4).



Methanethiol Benzenethiol

Dimethyl sulfide Dimethyl disulfide

Thiourea Dimethylsulfoxide (DMSO)

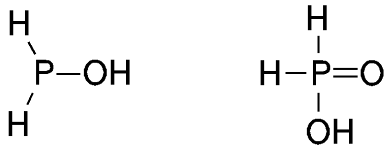
Benzeneosulfonic acid Methylsulfuric acid

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.

Organophosphorus Compounds

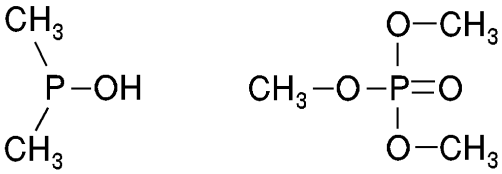
Phosphorus can occur in organic compounds in either the trivalent (3+) or pentavalent (5+) oxidation state. Compounds containing trivalent phosphorus are indicated by the suffix *ous* (acid) or *ite*; compounds containing pentavalent phosphorus are indicated by the suffix *ic* (acid) or *ate*.

Organophosphorus compounds can also be distinguished on the basis of their linkages, i.e., number of P-C bonds relative to the number of P-O-C linkages. Compounds that contain only P-C linkages can be viewed as having been derived from phosphine (PH_3) or phosphane (PH_5). Note the *ine* and *ane* suffixes, indicating the trivalent and pentavalent oxidation states, respectively. In the naming of organophosphorus compounds, the prefix (*phosph*) indicates that the compound contains phosphorus atoms, the center part of the name indicates the number of hydroxyl groups ("in" = 1, "on" =, 2 and "or" = 3), and the suffix indicates the oxidation state of the phosphorus. Many of the important nerve gases and insecticides belong to this class of organic compounds. Examples of various types of organophosphorus compounds are shown in Figure 5–19. Phosphinous acid contains phosphorus in the trivalent state and has one hydroxyl group. Parsing the name, "phosph" indicates a phosphorus compound, "in" indicates one hydroxyl group, and "ous" indicates a trivalent phosphorus atom. Phosphinic acid has an "ic" suffix, indicating that the phosphorus is pentavalent. Dimethyl-phosphinous acid has two methyl groups ("dimethyl"), one hydroxyl group ("in"), and phosphorus in the trivalent state ("ous"). Trimethyl phosphate has three methyl groups ("trimethyl"), and no hydroxyl groups, and the phosphorus is in the pentavalent oxidation state ("ate").



Phosphinous acid

Phosphinic acid



Dimethylphosphinic acid

Trimethyl phosphate

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

Esters

Esters are a special group of compounds formed by a condensation reaction involving carboxylic acids and alcohols. Esters are named by listing the alcohol portion with a *yl* ending and, separated by a space, the acid portion with an *oate* ending. Consider the reaction shown in Figure 5–20 in which methanol (an alcohol) and butanoic acid (a carboxylic acid) are combined. The resulting compound is methyl butanoate (methyl is the alcohol portion of the ester and butanoate is the carboxylic acid portion of the ester). In the condensation reaction, H_2O is expelled.

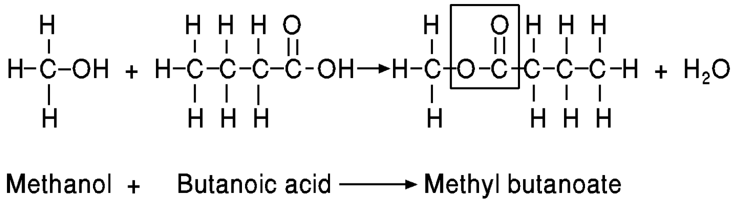


Figure 5–20 Condensation reaction between an alcohol (methanol) and a carboxylic acid (butanoic acid) to form an ester (methyl butanoate). Note that water is expelled during this reaction. The ester functional group is enclosed by the box.

Polymers

The last group of organic compounds that are of environmental interest are the polymers. Synthetic polymers have a variety of uses and are widely dispersed in the environment. Many are resistant to degradation, and these materials have become an important component of landfills. During combustion, some of these polymers can release toxic gases. ***Polymers*** are *high-molecular-weight compounds that are composed of a large number of simple repeating units (called monomers).* The conversion process from monomer to polymer is known as *polymerization.* The monomers are linked together to form straight or branching chains. The polymer may contain only a single monomer (homopolymer) or two or more different monomers (copolymers). Some of the common monomers are shown in Figure 5–21. Typical polymers formed from these monomers are Polyvinylchloride (water and sewer pipes), polyethylene (plastic bags and milk bottles), polypropylene (impact-resistant plastics), polyacrylonitrile (carpets), polystyrene (foam insulation), and polyte-trafluoroethylene (Teflon coatings).

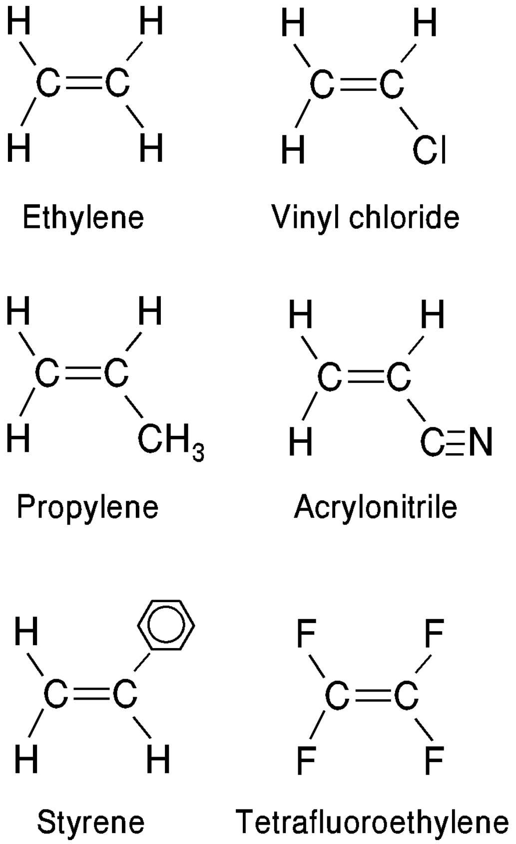


Figure 5–21 Examples of monomers used to build the common synthetic polymers. See text for examples of the uses of each synthetic polymer.

CARBON COMPOUNDS IN THE ENVIRONMENT

Carbon-based compounds, both of natural and anthropogenic origin, are widely dispersed in the environment. All known life is carbon based and, hence, carbon is the most important element in the biosphere. In Chapter 8 we will consider the impact of carbon-based compounds—notably, CO_2, CH_4, and chlororluorocarbons—on the atmosphere. In this chapter we will emphasize the role of carbon in the hydrosphere and geosphere, and we will look at the interactions between synthetic carbon-based compounds and the biosphere, atmosphere, hydrosphere, and geosphere.

Natural Sources

The ultimate source of all carbon at the earth's surface is the mantle of the earth. This carbon (usually referred to as *primordial carbon*) was released to the atmosphere during volcanic processes that led to the partial degassing of the mantle. This release of carbon is the initial step in the carbon cycle (Figure 5–22). Atmospheric carbon (in the form of CO_2) is removed either by photosynthetic processes or by dissolution in fresh and marine (by far the most important) waters.

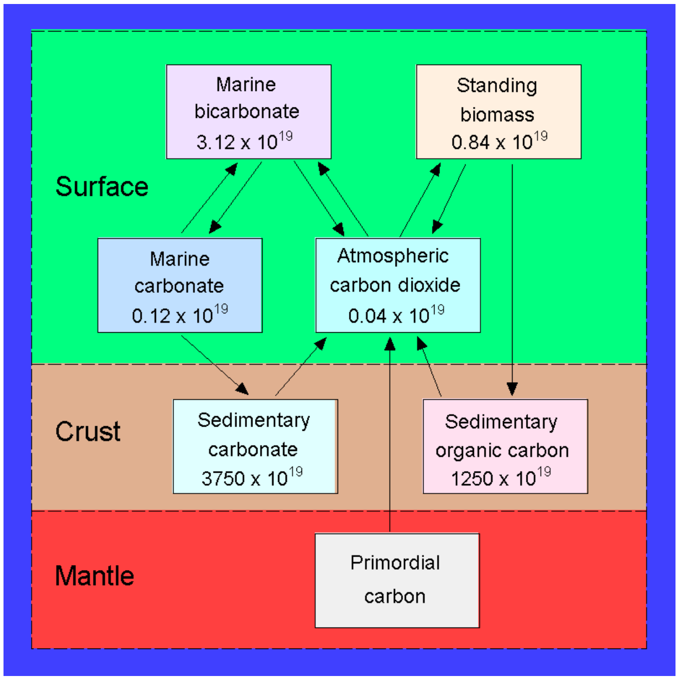


Figure 5–22 Major carbon reservoirs and interactions between these reservoirs. Carbon concentrations are in grams of carbon. Data from Schidlowski (1988).

Photosynthesis is often represented by the following simplified reaction:

$$6CO_2 + 6H_2O \xrightarrow[\text{sunlight}]{\text{chlorophyll}} C_6H_{12}O_6 + 6O_2$$

where $C_6H_{12}O_6$ is a sugar molecule. During cellular respiration, this process is reversed and sugars and oxygen are consumed while CO_2 and water are released. The production of biomass via photosynthesis is referred to as *primary* production, and photosynthetic organisms are primary producers. Note that a minor source of primary production is the sulfur-reducing bacteria. The biomass produced by the primary producers is subsequently consumed by higher-trophic-level organisms (consumers). The cycling of organic matter in the surface environment is complex and will not be considered in detail here. However, the excretions of organisms and the breakdown of biomass through decay and decomposition releases carbon to the surficial environment (i.e., soil, streams, groundwater). Much of this carbon is recycled to produce new organic matter, but some of it is transferred to the sedimentary environment. The other major reservoir for surficial carbon is the ocean. Given the pH (~8.2) of ocean water, the bulk of the dissolved carbon occurs as bicarbonate ion. Carbon is ultimately removed from the ocean as carbonate shell material and is preserved in the carbonate sediments.

Killops and Killops (1993) suggest that a useful way to look at the cycling of organic carbon is to define two subcycles: geochemical and biochemical. The geochemical subcycle contains the bulk of the carbon, 99.95%, and this carbon is found in the sedimentary rocks both as organic carbon (peat, coal, petroleum) and as sedimentary carbonate. This cycle operates on a time scale of millions of years. The biochemical subcycle consists of DOC (dissolved organic carbon), POC (particulate organic carbon), biota biomass, and soil organics and operates on a time scale of tens of years. These two cycles are linked by a two-way flux, which represents the transfer of organic carbon between sedimentary rocks and the surface environment. It would normally be expected that this transfer would approximate a steady state, but given the current significant use of fossil fuel, the cycle is not in balance. More carbon is currently transferred to the surficial environment than is returned to the sedimentary rocks.

In these various cycles, organic carbon is released to the environment. For example, the excretion of urea by organisms contributes organonitrogen compounds to streams and lakes. This is a natural addition (nonanthropogenic). However, if this release is due to large concentrations of animals being raised as livestock, then the release is often considered anthropogenic. Similarly, petroleum released to the environment by natural oil seeps is not considered anthropogenic, but petroleum released during an oil spill *is* considered anthropogenic. PAHs are considered to be a significant air pollutant produced during the incomplete combustion of fossil fuels. They are generated under conditions of local oxygen deficiency and can be viewed as pyrolysis products. Interestingly, PAHs are found in the sedimentary record and are apparently the result of wildfires initiated by lightning strikes. They can also be caused by igneous intrusions that locally heat coal and wood to sufficiently high temperatures to cause incomplete combustion. Chemically, there is no difference between these types of releases and anthropogenic releases.

Anthropogenic Sources

A vast number of organic chemicals have been synthesized for various uses. Among these are a wide variety of compounds used as pesticides, insecticides, and herbicides. Many of these have a significant environmental impact. Other organic compounds have various uses in industrial processes. Because most of these organic compounds have not previously existed in the natural environment, their impact can be significant. In addition, there are releases of organic compounds that are naturally present, but in amounts far above those normally encountered (e.g., oil spills, leakage from underground storage tanks, etc.). In terms of environmental impact, anthropogenic releases of organic compounds are typically the most serious and require the greatest expenditure of effort for cleanup and remediation.

HUMIC SUBSTANCES

Humic substances can be defined as "*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*'' (Aiken et al., 1985). Humic substances are found in soils, brown coal, fresh and marine waters, and marine and lacustrine sediments. There are three types of humic substances: humin, humic acid, and fulvic acid (Figure 5–23). ***Humin*** is *that fraction of the humic material that is insoluble in water at all pH values.* ***Humic acid*** is *soluble in water at pH values greater than 2,* and ***fulvic acid*** 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 two environments.

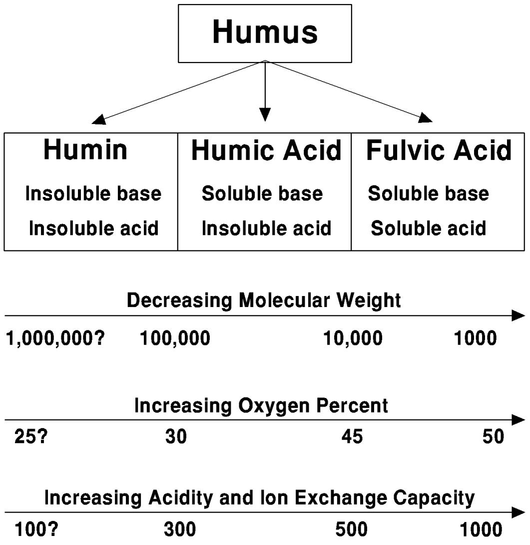


Figure 5–23 Types of humic substances and general characteristics. Note that the distinction between the types of substances is based on their solubility in acids and bases. After Oades (1989).

Attempts to structurally characterize humic substances have generally proven unsuccessful. However, compositional information can be obtained from elemental and functional group analysis. Chemical compositions for soil humic and fulvic acids and characteristic elemental ratios are given in Table 5–3.

Table 5–3 Elemental Compositions, Atomic Ratios, and Atomic Weights for Soil Humic and Fulvic Acids[1]

	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[2])	2000–5000	500–2000
H/C (atomic)	~0.8	~1.3
O/C (atomic)	~0.5	~0.8

[1] Sources of data: Schnitzer (1978), Thurman (1985a), Killops and Killops (1993). [2] The dalton is a unit of molecular weight. The unit is defined so that the weight of ^{12}C = 12.000 daltons.

The character of the humic substances varies as a function of the chemical environment, i.e., soil vs. freshwater vs. marine. Some of these differences are summarized in Table 5–4 (p. 142). Of note is the higher aromatic content of soil humic substances compared to marine humic substances, which suggests that humic substances from these two environments may be differentiated on the basis of their aromaticity. The H/C atomic ratio is of significance in that it is an indirect indicator of the relative proportion of aliphatic to aromatic compounds. An increase in aromatic compounds is marked by a decrease in the H/C ratio. Also of note is the lower molecular weight of freshwater humic substances compared to soil humic substances.

Table 5–4 Composition of Humic Substances in Various Environments*

	Soil	Groundwater	Surface water	Lake sediments	Seawater	Marine sediments
Aromatic hydrocarbon	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	—

*Sources of data: Hatcher et al. (1980), Harvey and Boran (1985), Ishiwatari (1985), Killops and Killops (1993), Malcolm (1985), Thurman (1985b).

Humic and fulvic acids are macromolecules that consist of flexible extended chains with only limited branching and cross-linking. These chains form the backbone of the macromolecule to which smaller molecules are attached. Humic substances form stable complexes with polyvalent (metal) cations. These complexes are important in the mobilization and transport of metal ions. This ability to form complexes with metal ions is due to the high abundance of oxygen-containing functional groups. Infrared spectroscopy studies have shown that COOH groups play a predominant role in the complexing of metal ions by fulvic and humic acids. There is some evidence to suggest that OH, C==O, and NH_2 groups may also play a role. In general, the maximum amount of any metal ion that can be complexed by humic or fulvic acid is approximately equal to the content of acidic functional groups (in particular, COOH). For most humic substances, the amount of metal cation that can be complexed falls in the range 1.5 to 5.0 meq g^{-1} of humic substance. Factors that affect the actual amount of metal ion bound to humic substances are the pH, ionic strength of the solution, and the functional group content. At any particular pH and ionic strength, the trivalent cations are bound in greater amounts than the divalent cations. For any particular metal cation, stability constants tend to increase with pH and then at some point begin to decrease with increasing pH. Increasing ionic strength of the solution leads to a decrease in the stability constants for all metal-humic complexes. Case Studies 5–1 and 5–2 explore the relationships between humic substances and the mobility of various trace metals.

CASE STUDY 5–1 Chemical and Physical Characteristics of Heavy Metals in Humus in the Vicinity of the Base Metal Smelter at Flin Flon, Manitoba, Canada

Henderson et al. (1998) investigated the distribution of heavy metals in humus from the area surrounding the Cu-Zn smelter at Flin Flon. Concentrations of a variety of trace metals were found to diminish with distance from the smelter, and background values were reached at 70–104 km from the smelter. For example, Zn samples collected within 5 km of the smelter have concentrations 94X background, 40X background at 10 km, 16X background at 20 km, 5X background at 40 km, and 1.6X background at 80 km, a logarithmic variation with distance. Sequential extraction analysis was used to determine the occurrence of the trace metals in the humus: soluble organics (humic and fulvic acid complexes), labile phases in the insoluble residue (humin), and nonlabile phases in the insoluble residue (mineral matter). For the smelter-derived elements, Zn, Pb, Cd, and Cu were found to correlate with the soluble organic phase, and As and Hg were correlated with the nonlabile insoluble residue. In the insoluble residue, the concentration of Zn increased in the labile fraction with distance from the smelter. This was ascribed to a decrease in the particulate component with increasing distance from the smelter and secondary processes, such as weathering and alteration, becoming relatively more important. In the case of Hg, the nonlabile component of the insoluble residue contained greater than 95% of the total Hg, indicating that this element largely occurs with mineral components and is relatively insoluble in the natural environment. Investigation of a soil horizon revealed that more than 70% of the Zn was found in the soluble organic and labile fractions, indicating that this element would be readily mobile in the soil horizon, but only 16% of the Hg was found in these fractions. Thus, the association of Zn with humic substances leads to a high mobility for this element in the natural environment.

Source: Henderson et al. (1998).

CASE STUDY 5–2 Transport of Long-Lived Radionuclides

Amano et al. (1999) investigated the transport from soil to rivers of long-lived radionuclides produced during the Chernobyl nuclear reactor accident. Previous studies had suggested that up to 90% of the total radionuclides in streams draining the Chernobyl area were transported to the streams as dissolved fractions in runoff components. The various radionuclides were separated from soil samples using sequential selective extraction, resulting in three fractions: humin plus insolubles, free fulvic acid, and free humic acid. The bulk of the DOC was composed of compounds with molecular weight less than 10,000 Da (daltons). Most of the Pu (79%) and Am (68%) were found in molecular weight fractions greater than

10,000 Da (fulvic acid fractions), and most of the Cs (85%) and Sr (63%) were found in molecular weight fractions less than 10,000 Da (humic acid fractions). The distribution of the radionuclides was essentially the same for soil water (pH = 4.7) and river water (pH = 7.5), indicating that pH had little effect on the transport of these radionuclides. The authors concluded that the transuranic elements were associated with dissolved humic substances in both soil and river water and that they were concentrated in the higher-molecular-weight fraction. Complexation of the radionuclides with humic and fulvic acids was responsible for their mobility in the surface environment.

Source: Amano et al. (1999).

SOIL AND MARINE ORGANIC MATTER

In this section we will briefly consider some of the fundamental differences between organic matter found in soils and organic matter found in marine sediments. A more complete discussion of this topic can be found in Hedges and Oades (1997).

Soil Organic Matter

Soil can be defined as "*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*" (Loughnan, 1969). Most soils exhibit well-developed soil horizons, as illustrated in Figure 5–24 for a spodosol. This type of soil forms in response to strong leaching and acidity and is typical of soils found in temperate regions. The O horizon is rich in accumulated plant material. The underlying A1 horizon contains organic matter, and the A2 horizon is a leached zone. The B1 horizon is a zone of net accumulation of organic material; the B2 horizon is a zone of net accumulation of metal oxyhydroxides. The B3 horizon is a transition zone to the C horizon, which consists of weathered rock unaffected by the processes of soil formation.

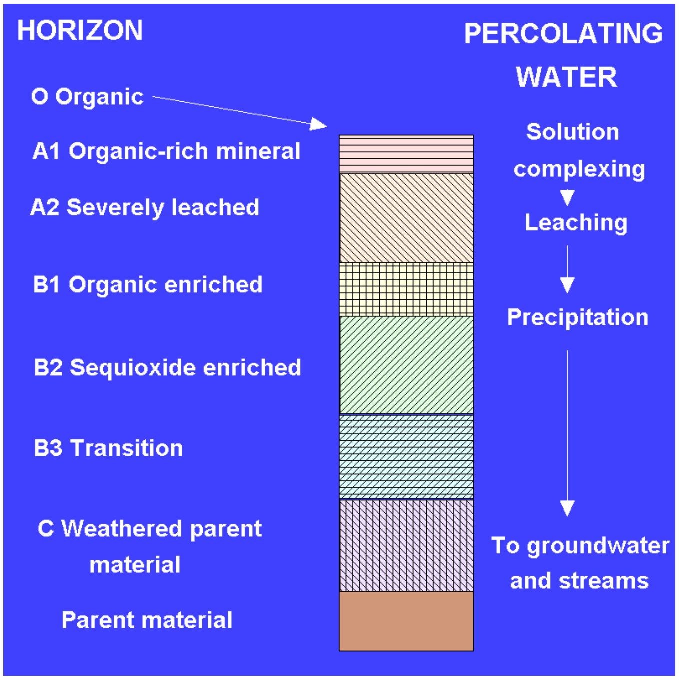


Figure 5–24 Generalized soil profile for a spodosol. After Stevenson (1985). From HUMUS CHEMISTRY, GENESIS, COMPOSITION, REACTIONS by Stevenson. Copyright © 1994. This material is used by permission of John Wiley & Sons, Inc.

The major determining factor in soil formation is climate, and the two most important variables are temperature and precipitation. Although the bedrock that is weathered to form the soil is of secondary importance, it should be noted that lithology does exert a fundamental influence; i.e., soils produced from the weathering of quartz sandstone cannot be rich in calcium, and those produced from the weathering of limestone cannot be rich in silica. A simple classification of soils as a function of climate is shown in Figure 5–25. With reference to Figure 5–25, ***pedalfers*** are *soils that are high in Al and Fe and are found in humid regions*, ***pedocals*** are *soils that are high in Ca and are found in deserts or semiarid regions*, ***latentes*** are *highly leached soils that largely consist of iron and aluminum oxides and are found in the tropics*, and ***tundra soils*** are *found in cold, dry climates*. Table 5–5 gives a modern classification of soil types.

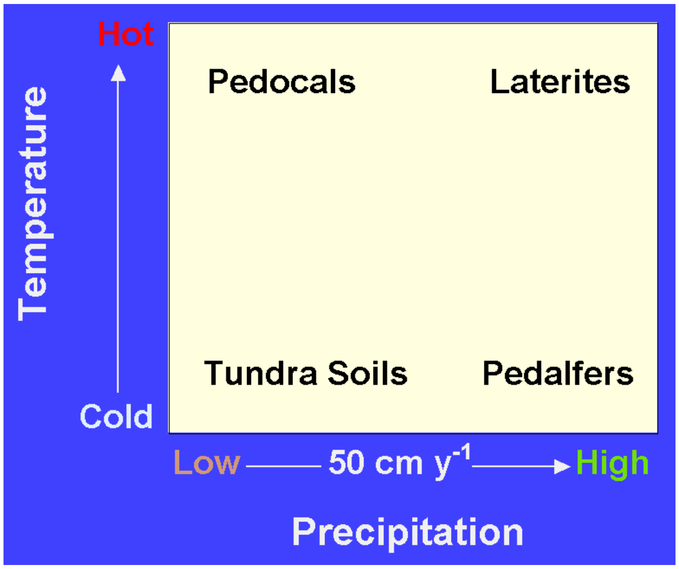


Figure 5–25 Soil types as a function of the climate variables temperature and precipitation.

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 midlatitude regions
Spodosols	Grain coatings of organic material and iron oxides; wet midlatitude 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

*Modified from Nichols (1999).

Soils are a dynamic mixture of mineral particles, organic material, organisms, water, and air.

Porosity varies from 30 to 60%, with 50% porosity being an average value. The pore spaces are filled with either water or air and the water/air ratio is continuously changing. Temperature changes can be significant on a daily or monthly basis. pH values range from 4.0 to 8.5. The major input of organic matter to soils is litterfall or root invasion by vascular plants. These sources have high C/N ratios (wood, 175–400; tree leaves, 20-50; grasses and herbaceous plants, 25–80) (Hedges and Oades, 1997). Herbivores and detritivores feed on the plant parts. The total microbial biomass accounts for 2-3% of the soil organic matter. This microbial biomass is composed of bacteria, actinomycetes, and fungi. These organisms are nitrogen-rich, with C/N ratios ranging from about 5 (bacteria dominant) to 15 (fungi dominant). Thus, two distinct types of organic matter are found at the earth's surface, organic matter associated with vascular plants, which has high C/N ratios, and organic matter associated with microbial biomass, which has low C/N ratios (see Figure 5–26).

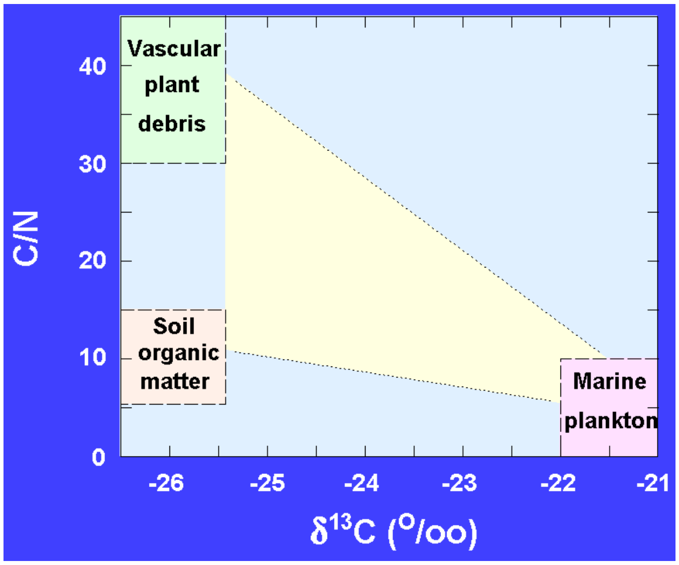


Figure 5–26 Atomic C/N versus δ^{13}C for various reservoirs of organic carbon. Mixtures of the three end members will lie within the field defined by the dashed lines. Modified from Hedges and Oades (1997).

Marine Organic Matter

The marine sedimentary environment differs from the soil environment in a number of important ways. Marine sediments tend to have greater porosity than soils, with the porosity of fine-grained sediments ranging from 70 to 90% at the surface and from 50 to 60% at depths on the order of a meter or more. The pH of the pore waters varies between 7 and 8, a much narrower range than that shown by soils. Surface layers are oxic, but with increasing depth the pore waters become anoxic.

Vascular plants are essentially absent from the ocean, and the major source of organic material is phytoplankton. C/N ratios in phytoplankton are around 6. Bacteria are the primary decomposers. In terms of carbon isotopes (see Chapter 6), marine plankton tend to be isotopically heavier than either vascular plants or soil organic matter. Thus, it is possible to distinguish the sources of organic carbon on the basis of their C/N ratios and $\delta^{13}C$ values (Figure 5–26). Case Study 5–3 describes how various chemical and isotopic signatures can be used to determine the sources of organic matter in a freshwater system.

CASE STUDY 5–3 Using Sedimentary Organic Matter to Record Environmental Changes in a River-Lake Ecosystem

Lake George is located in the St. Marys River system, which flows from Lake Superior to Lake Huron. The lake acts as a trap for sediments transported by the river. Previous work showed that sediments accumulated in Lake George at a relatively high rate of 0.5 cm y^{-1} and that the sediments were not disturbed by mixing. The region around the St. Marys River was clear-cut for lumber in the late 1800s and industrialization began in the 1900s with the construction of paper mills, steel mills, and tanneries. In 1986, a 64-cm sediment core was collected by a SCUBA diver from the northern end of the lake. This core was used by Tenzer et al. (1999) to document the impact of anthropogenic activities on the watershed of the St. Marys River.

The sediment core was divided into 1-cm sections for the top 20 cm and into 2-cm sections for the lower part of the core. The chronology of the layers was determined by ^{210}Pb geochronology and confirmed by comparing the calculated age for the bomb fallout maximum with the ^{137}Cs peak in the core (see Chapter 6). The geochronology indicated that the deposition rate decreased from 0.265 g cm^{-2} y^{-1} for the top part of the core to 0.165 g cm^{-2} y^{-1} for pre-1950 deposition.

The authors determined total organic carbon (TOC), total nitrogen (TN), $\delta^{13}C$, the concentrations of total C^{16}-C^{36} *n*-alkanes (THC, total extractable hydrocarbons), and several other parameters. The results of some of the analyses are shown graphically in Figure 5–C3-1. Starting from the present, TOC increases until about 1970 and then begins to decrease. The biggest change occurs around 1925, and from about 1920 on TOC is uniform and relatively low. The C/N ratio shows a similar pattern, with C/N maxima roughly corresponding to TOC maxima. Similar to TOC, C/N shows low and relatively constant ratios prior to 1920. $\delta^{13}C$ values become less negative with time, and the maximum negative value corresponds with the TOC and C/N maxima. Typical Great Lakes plankton have a C/N ratio of about 7 compared to C/N ratios from 17 to 42 for leaves and needles of vascular plants from the St. Marys water shed. Vascular plants had $\delta^{13}C$ values between –25.1‰ and –29.8‰; organic material produced by algae were inferred to have $\delta^{13}C = -22‰$. The increased C/N ratios and more negative $\delta^{13}C$ values were interpreted to reflect the increased contribution of land-derived organic matter that accompanied industrial development along the St. Marys River. The decrease in C/N ratios and increase in $\delta^{13}C$ after 1970 reflect a decrease in anthropogenic inputs following the United States-Canada Great Lakes Water Quality Agreement of 1972. Assuming end-member $\delta^{13}C$ values of −22‰ for pristine (algae) organic matter and –28‰ for average vascular plant material, and average $\delta^{13}C = -24.6‰$ for sediments deposited around 1970, gives an approximately 40% greater contribution of land plant material to the sediments relative to 1900.

Hydrocarbons are particularly useful in determining the source of organic carbon. Aquatic algae and photosynthetic bacteria are dominated by C_{17} *n*-alkanes; the waxy coatings of vascular plants are dominated by C_{27} to C_{31} *n*-alkanes. The terrigenous/aquatic ratio, $(TAR_{HC}) = (C_{27} + C_{29} + C_{31})/ (C_{15} + C_{17} + C_{21})$, and variations in this ratio are interpreted to indicate changes in the land-derived component of the organic matter. Petroleum hydrocarbons can be distinguished from biological hydrocarbons on the basis of two characteristics: (1) odd-carbon chain lengths are not dominant in petroleum hydrocarbons (biogenic *n*-alkanes have odd/even ratios = 5 to 10, while petroleum *n*-alkanes have odd/even ratios ~ 1), and (2) a more diverse range of molecular structures results in an *unresolved complex mixture* (UCM) that cannot be separated by high-resolution gas chromatography. During the 1900s, the change with time of TAR_{HC} suggests that vascular plants were a less important component of the organic carbon, an observation at variance with other lines of evidence. The authors suggest that this is because the short-chain hydrocarbons were better preserved in the younger sediments. The odd/even ratio = 1 and UCM is at a maximum around 1970, indicating a significant input of petroleum-derived hydrocarbons. Changes in these values in more recent sediments indicate a reduction in anthropogenic inputs.

Source: Tenzer et al. (1999).

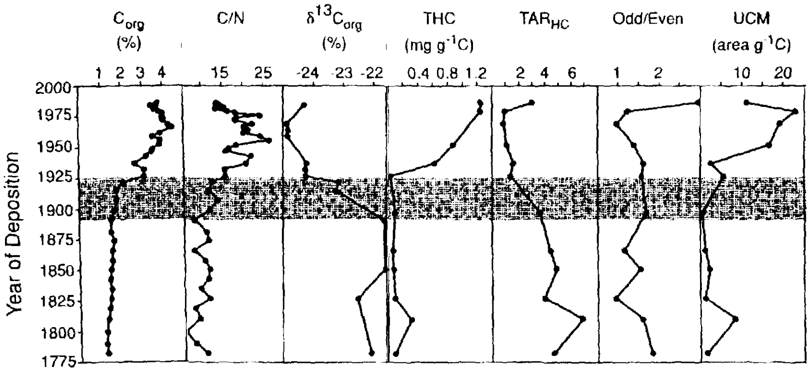


Figure 5–C3–1 Organic carbon concentrations (C_{org}), organic matter C/N ratios, $\delta^{13}C_{org}$, total extractable hydrocarbons (THC), concentration ratios of terrigenous/aquatic *n*-alkanes (TAR_{HC}), odd/even *n*-alkanes and unresolved complex mixture (UCM) relative to sediment age. Shaded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

FOSSIL FUELS

Coals

Coals are classified as ***humic coals*** if they are *derived from humic substances via a peat stage* and as ***sapropelic coals*** if they are *formed from fairly fine-grained organic muds in quiet, oxygen-deficient shallow waters.* The humic coals are lustrous, dark-brown to black, exhibit stratification, and often contain the remains of woody tissue. The sapropelic coals are dull, unstratified, and contain allochthonous organic and mineral matter. The sapropelic coals are subdivided into can-nel and boghead coals. The conversion of organic matter to coal involves two stages: biochemical and geochemical. The biochemical phase involves biological processes; the geochemical stage involves physicochemical processes due to increasing pressure and temperature. These processes lead to a release of volatiles, primarily methane, water, and carbon dioxide; the elimination of oxygen-containing functional groups; and an increase in the percent of aromatic units. These changes are illustrated in Figure 5–27, which shows the relative increase in carbon with increasing degree of coalification.

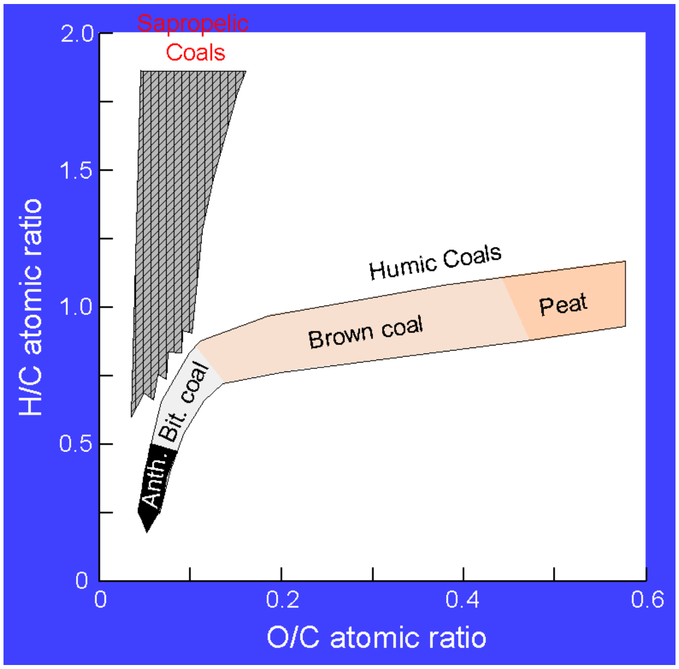


Figure 5–27 van Krevelen (1963) diagram indicating the changes in hydrogen, oxygen, and carbon content during the coalification process. After Killops and Killops (1993).

Of major environmental interest is the metal, sulfur, and fly ash content of coals. Metals that were incorporated in the original organic material tend to remain during the coalification process. Thus, coal is often high in a number of trace elements of environmental concern. Lyons et al. (1989) determined the concentrations of trace elements in a variety of coals, ranging from high-volatile bituminous coals to meta-anthracites. Concentration ranges determined for elements of environmental interest are given in Table 5–6.

Lyons et al. (1989) also investigated the distribution of these trace elements between organic and inorganic (i.e., mineral) components of the coal. For the elements listed in Table 5–6, they concluded that As, Co, Cu, Ni, Sc, and Th generally showed an inorganic association, whereas Cr, Sb, U, V, W, and Zn generally showed an organic association. Se and Pb did not correlate with either association. Metals associated with inorganic components would presumably remain with the fly ash and could be successfully removed from the effluent stream by electrostatic precipitation of the fly ash. Metals associated with organic components would be released to the effluent stream during combustion and dispersed into the atmosphere. These associations would be expected to vary on a coal-by-coal basis, so it is necessary to determine the distribution of elements in a particular coal in order to determine the potential trace metal contribution of this coal to the atmosphere during combustion (see Case Study 5–4).

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

*From Lyons et al. (1989).

CASE STUDY 5–4 Distribution of Metals and Other Elements in Coals

A number of studies have been carried out on the distribution of metals and other elements in coal. Several of these are cited in this case study to indicate the variability of these elemental associations in coal. Christanis et al. (1998) found that in the Philippi peat of eastern Macedonia, Greece, Ge, Mo, Pb, Se, Ta, Tl, U, and W were correlated with organic content and the other trace elements were correlated with mineral phases. For lignites from central Anatolia, Turkey, Querol et al. (1997) found that Mn, B, Be, Ge, Y, Zr, Nb, Hf, W, and U showed positive correlation with organic matter and Mn, U, Th, Sc, Ge, and HREE showed positive correlation with phosphate, suggesting that apatite or another phosphate mineral is the major host. Co, Mo, Ta, Pb, and IREE showed positive correlation with both Fe and S, indicating that Fe-sulfide minerals are the hosts for these elements. As and V had mixed affinities. For United Kingdom coal fields, Spears and Zheng (1999) found that Rb, Cr, Th, Ce, Zr, Y, Ga, La, Ta, Nb, and V were associated with the clay minerals; As, Mo, Sb, Tl, Se, Bi, and Pb with pyrite; Sr and Ba with phosphate minerals. Germanium was the only element that had a major organic association. For medium- to high-volatile bituminous coals from Nova Scotia, Canada, Mukhopadhyay et al. (1998) found that most lithophile elements, including B, Cr, U, V, and the REE, were associated with the clay minerals; Cu, Pb, and Zn with the sulfide minerals; and Cl, Ca, As, and Mn with organic matter. Of note is the marked variability of the element associations. Major factors affecting trace element concentrations are the abundance and sources of detrital minerals, the presence of volcanic material, and seawater or brine incursions into the basins of deposition.

Sulfur occurs in coal either combined with organic molecules or as physically separate sulfide minerals (of which pyrite is the most common). Sulfur occurs in reduced form (S^-, S^{2-}) because the organic-rich depositional environment is reducing (see Chapter 4). If Fe^{2+} (or other metal ions) is present, it will combine with the reduced sulfur to produce minerals such as marcasite (FeS) and pyrite (FeS_2). If there is a low abundance of metal ions, free hydrogen sulfide (H_2S) and polysulfides $(HS_4^-, HS_5^-, S_4^{2-}, S_5^{2-})$ are formed. These species can combine with various organic molecules to form a variety of sulfur-containing compounds. In terms of "cleaning up" coal, the way in which sulfur occurs in the coal is of key importance. If the sulfur occurs in separate sulfide minerals, then in principle it can be physically separated by flotation techniques. If the sulfur is bound to organic molecules, there is no effective way to remove the sulfur before burning the coal.

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 macerais (the preserved remains of plant material).* Four types of kerogen (I, II, III, and IV) have been distinguished on the basis of H/C and O/C atomic ratios, types of organic molecules (aliphatics versus aromat-ics), functional groups, and other criteria. Type II kerogen is the most common precursor for petroleum. Type I has the highest petroleum-forming potential but is present in low abundance. Type IV kerogen is not a petroleum precursor. Kerogen is converted to petroleum through a series of reactions starting in the ***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)* and ending at temperatures of about 225°C. These reactions result in the expulsion of CO_2 and CH_4 and a reduction in the size of the hydrocarbon molecules. The hydrocarbon formation process for a typical source rock is schematically illustrated in Figure 5–28 (p. 148). Note that natural gas is generated throughout the P-T range, but the formation of oil is confined to a narrow P-T range. Thus, the thermal history of a basin is an important factor in terms of its oil-producing capability. Also note the reduction in the size of the mean hydrocarbon molecule with increasing temperature.

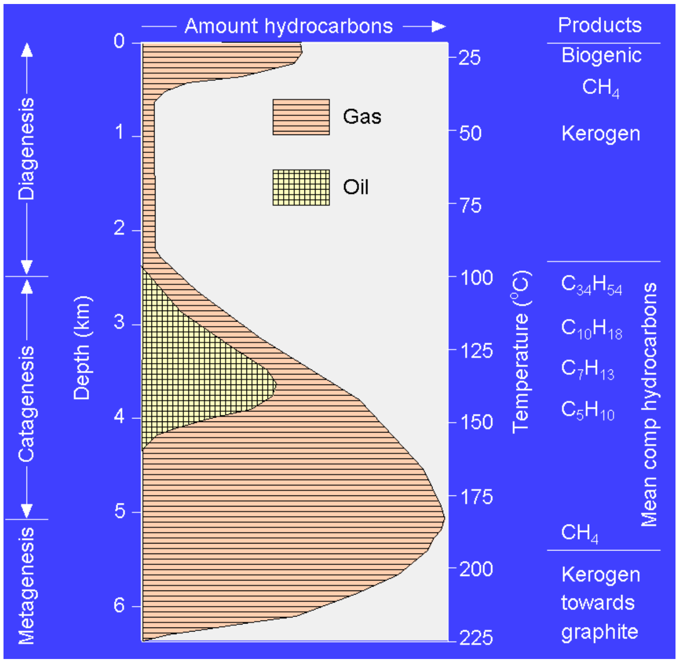


Figure 5–28 Schematic representation of production of petroleum from a typical reservoir rock assuming an average geothermal gradient. Note the narrow P-T range over which oil is produced (called the *oil window*). With increasing temperature, the size of the mean hydrocarbon molecule decreases. During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

The elemental composition of crude oil is given in Table 5–7. Nitrogen, sulfur, and oxygen are often associated with the resins and asphaltenes (fragments of polymeric material with molecular weight > 500) and are referred to as *polar NSO compounds.* Trace metals, such as nickel and vanadium, are also associated with polar NSO compounds. Note the range in sulfur and nitrogen concentrations in crude oil. These are important elements because the SO_2 and NO_X gases produced during combustion are precursors to the sulfuric and nitric acids of acid rain. *Crude oil that is low in sulfur* is referred to as ***sweet***, and *crude oil that is high in sulfur* is referred to as ***sour.***

As might be anticipated, sweet crude is of lesser abundance, and hence more costly, so that reducing sulfur emissions through fuel substitution incurs additional cost. The *average oil* contains 57% aliphatic hydrocarbons, 29% aromatic hydrocarbons, and 14% resins and asphaltenes. Sulfur, as thiophenic compounds, accounts for 2% of the aromatic hydrocarbon fraction (Killops and Killops, 1993). Crude oils can be classified according to the relative amounts of acyclic (normal and branched) alkanes, cycloalkanes, and aromatic hydrocarbons plus NSO compounds (Tissot and Welte, 1984). The main classes of normal crude oils, according to the classification of Tissot and Welte (1984), are (1) paraffinic oils containing mainly acyclic alkanes and < 1% suflur, (2) paraffinic-naphthenic oils containing mainly acyclic alkanes and cycloalkanes and < 1 % sulfur, and (3) aromatic-intermediate oils containing < 50% aromatic hydrocarbons and > 1 % sulfur. Class 1 crude oil is derived from terrestrial organic matter, class 2 from terrestrial or marine organic matter, and class 3 from marine organic matter.

Table 5–7 Elemental Composition of Crude Oil*

Element	Abundance
	In 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 *In ppm*
Ni	0.3−200
V	0.3−1000

*From Baker (1964), Hodgson (1954), Levorsen (1967).

NATURAL CARBON INPUTS TO SURFACE AND GROUND WATERS

Carbon in water is generally reported as dissolved organic carbon (DOC), particulate organic carbon (POC), or total organic carbon (TOC). ***DOC*** is *the carbon remaining in a water sample* *after it has passed through a 0.45–μm filter.* By convention, any material that passes through a 0.45–μm filter is considered to be in solution. ***POC*** is *the particulate matter retained by a 0.45–μm filter*. ***TOC*** is the *total carbon content of the sample* **(*DOC* + *POC*)**. All of these measurements are made by converting the organic matter to CO_2 and then measuring the amount of CO_2 produced. The distinction between DOC and POC is considered significant because carbon that occurs in the dissolved state is chemically more reactive than carbon that occurs as plant and animal organic matter and as organic coatings on silt and clay.

The sources of the carbon can either be ***allochthonous*** *(from outside the aquatic system)* or ***autochthonous*** *(from within the aquatic system).* The two allochthonous sources are soil and plant material, and a major difference between these two sources is the much longer decomposition time for the soil organic material (> 100 years). Leaching experiments on fresh plant litter using distilled water have shown that a significant proportion (25–40%) of the plant organic matter can be solubilized in 24 hours. This material is similar to fulvic acid but differs from soil and aquatic fulvic acids in that it has a lower carboxy lie acid content and a higher percentage of carbohydrates. A number of studies have shown that plant material is a major contributor to the DOC of streams, a conclusion largely based on the young ^{14}C age of the DOC. Because stream fulvic acid differs from plant leachates, it is generally assumed that rapid oxidation of the plant material in the upper soil layers results in an increase in carboxyl content and a decrease in carbohydrate content. Autochthonous organic carbon is largely derived from algae, either as direct excretions or by the bacterial and chemical breakdown of POC. The relative significance of these two types of inputs, allochthonous vs. autochthonous, depends on the size of the body of water. In streams and small lakes, allochthonous sources are dominant, whereas in large lakes, and notably the ocean, autochthonous sources become dominant.

The concentration of dissolved and particulate organic carbon varies with the aquatic environment. For example, both sea-water and groundwater have low organic carbon concentrations (Figure 5–29) and insignificant particulate organic carbon. At the other extreme are marsh and bog waters, which have both high total organic carbon and significant particulate organic carbon (Figure 5–29). The primary source of sea-water carbon is photosynthetic activity, which is confined to the top 200 meters of the ocean. Hence, surface waters have higher carbon content than deep waters. Coastal waters also have higher carbon content due to land inputs. Groundwater has generally low carbon content because organic carbon is used as a food supply by heterotrophic microbes and converted to CO2 (in aerobic groundwater) or CH4 (in anaerobic groundwater) and is also adsorbed onto grain surfaces, where it is chemically and biochemically degraded to CO2. However, the carbon content of any particular aquifer can be very different from the average depending on the type of aquifer (Table 5–8). Marsh and bog waters have the highest organic carbon concentrations for the obvious reason that they are in contact with an organic-rich environment. Stream organic carbon content varies as a function of both the climate (which determines biological productivity) and the stream discharge. In general, the DOC content of a stream first increases during increased flow and then declines. The increase is due to the initial flushing of organic carbon from the soil into the stream, and the decline reflects the subsequent dilution effect of the increased stream flow. Stream POC shows a logarithmic correlation with the sediment concentration. The difference in carbon content between oligotrophic and eutrophic lakes (Figure 5–29) is directly related to the much higher biological productivity of the eutrophic lake. Precipitation carbon content is, on average, 1.1 mg L–1. However, precipitation samples collected within the canopy zone of a forest, or as drip from the canopy, have higher carbon contents. This is due to the washing of carbon from the leaves and limbs of the canopy. From this discussion it is clear that a number of factors control the concentration of organic carbon in aquatic systems. A more detailed discussion of this topic can be found in Thurman (1985a).

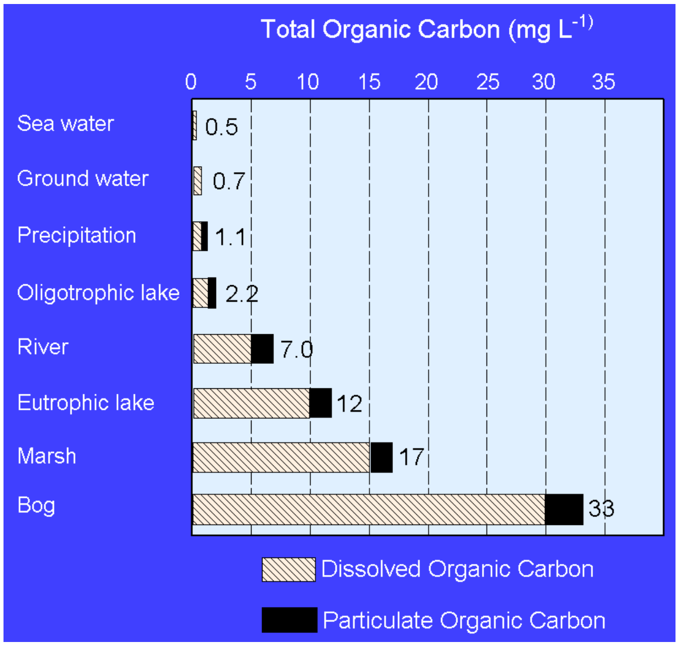


Figure 5–29 Average organic carbon concentrations for various aquatic systems. Note that the actual range in TOC can be substantial and depends on a variety of factors. See text. Taken from

Thurman (1985a).

Table 5–8 Median Concentrations of Organic Carbon in Various Types of Aquifers*

Aquifer	DOC (mg CL^{-1})
Sand and gravel	0.7
Limestone	0.7
Sandstone	0.7
Igneous	0.5
Oil shale	3
Humic colored	10
Petroleum associated	100

*Data from Leenheer et al. (1974) and Feder and Lee (1981).

ANTHROPOGENIC CARBON INPUTS TO SURFACE AND GROUND WATERS

A tremendous variety of organic chemicals occur in surface and ground waters. In this section we will look at some of these inputs and their impact and remediation. This will not be an exhaustive discussion and the student should access the literature for a broader perspective.

Organic Carbon

The TOC of surface and ground waters is an important parameter, and at high concentrations organic carbon can be considered a pollutant. The oxidation of organic matter leads to the extraction of dissolved oxygen from the water. This process can be represented by the following simple reaction:

$$\mathrm{CH_2O_{(aq)}\ [carbohydrate] + O_{2\,(aq)} \rightarrow CO_{2\,(g)} + H_2O_{(aq)}}$$

If there is a significant amount of organic matter, the oxygen may be totally depleted in the water column, leading to anoxic conditions. This is what happens during eutrophication, when excessive production of organic matter leads to essentially total depletion of dissolved oxygen. As an example of eutrophication, consider a lake surrounded by homes, each having its own septic system. If phosphorus is present in the effluent (phosphate detergents are used by the homeowners), this phosphorus can enter the lake. For any biological system there is a limiting factor that controls productivity, and this limiting factor is often a nutrient element (N, K, P). If in the case of the lake phosphorus is the limiting element, the addition of the sewage effluent to the lake will result in increased production of plant material. The subsequent decay of this plant material leads to oxygen depletion and a reduction, or elimination, of fish and other oxygen users in the lake ecosystem. The lake "dies" from *overnourishment* ***(eutrophication).*** *The capacity of the organic matter in a sample of natural water to consume oxygen* is referred to as the ***biological (or biochemical) oxygen demand (BOD).*** BOD is measured experimentally by holding a sealed water sample at 25°C for 5 days and measuring the change in oxygen content (mg L^{-1}). For unpolluted surface waters in the United States, the median BOD is 0.7 mg L^{-1} O_2. This is much less than the saturation O_2 value at 25°C of 8.7 mg L^{-1}. Under anaerobic (oxygen-free) conditions, organic matter will decompose if the appropriate bacteria are present. This decomposition can be represented by the following simple equation:

$$2\mathrm{CH_2O}\ [\text{organic matter}] \rightarrow \mathrm{CH_4}\ [\text{methane}] + \mathrm{CO_2}$$

This is a reducing environment and elements and compounds occur in their reduced state (see Chapter 4). Also note that methane gas is released, a common product of anaerobic decay of organic material both in natural waters and sanitary landfills.

Pesticides

Pesticides are used to control the growth of unwanted organisms. They can be divided into three types depending on their purpose: ***insecticides***, which *control insects;* ***herbicides***, which *control plant growth*; and ***fungicides***, which *control the growth of various types of fungus.* Pesticides are often divided into two groups, *hard* and *soft.* ***Hard pesticides*** are *typically organochlorine compounds that are persistent in the environment but have a low toxicity in mammalian systems.* ***Soft pesticides***, *typically organophosphorus compounds and carbamates, have a short residence time in the environment but are often highly toxic* (Table 5–9). Toxicity is usually expressed as LD_{50}, *the amount of the chemical per unit of body mass required to produce death in 50% of an exposed animal population.* This measurement is specific to a particular group of animals, often rats and guinea pigs, and there is some debate about the universal application of this measure to other animal populations. However, on a relative basis it can be used to rank the toxicity of various chemicals. The organochlorines have a low solubility in water (Table 5–9) but are much more soluble in organic solvents. This means that they are concentrated in the fatty tissue of animals. DDT is an example of an organochlorine insecticide. Because of its low mammalian toxicity and persistence in the environment, thus minimizing the number of repeat applications, it was considered an ideal pesticide. Many animals metabolize DDT by the elimination of HCl, forming a derivative called DDE (referred to as a *metabolite* of DDT). This metabolite is also persistent in the environment and can interfere with reproductive functions. In the case of some birds, this interference caused the birds to produce shells that were deficient in calcium carbonate and thus easily broken.

The tendency of a particular organic chemical in water to concentrate in the fatty tissue can be expressed as the bioconcentration factor (***BCF*****).** The BCF is based on the partitioning of a particular solute between water and fish. The BCF can be estimated using the following relationship (Kenaga and Goring, 1980):

$$\log \mathrm{BCF} = 0.935 \; * \; \log \; K_{\mathrm{ow}} - 1.495 \qquad (5\text{–}1)$$

where K_{ow} is the octanol/water partition coefficient, which is defined as follows:

$$K_{\mathrm{ow}} = [S]_{\mathrm{octano}} / [S]_{\mathrm{water}} \qquad (5\text{–}2)$$

where $[\mathrm{S}]_{\mathrm{octanol}}$ is the concentration of the chemical in the alcohol l-octanol and $[S]_{\mathrm{water}}$ is the concentration of the chemical in water. Because this is usually a large ratio, it is commonly reported as the log of the partition coefficient. K_{ow} values for some common pesticides are given in Table 5–9. The higher the K_{ow} value, the more strongly the chemical is partitioned into the fatty tissue. Chemicals with log K_{ow} values of 7 to 8 or greater tend to be strongly adsorbed to sediments and are thus unlikely to enter living tissue.

Because of their persistence and partitioning into fatty tissue, the concentration of organochlorine compounds increases as one moves higher in a food chain. This is called

Table 5–9 Data for Selected Pesticides[1]

Pesticide	Solubility in H_2O (mg kg^{-1})	LD_{50} (mg kg^{-1})	log K_{ow}	log BCF[2]
Hard				
HCB	0.0062	3,500−10,000	5.3	3.5
DDT	0.0034	115	3.9−6.2	2.2−4.3

Pesticide	Solubility in H_2O (mg kg^{-1})	LD_{50} (mg kg^{-1})	log K_{ow}	log BCF[2]
Toxaphene	n/a	85	2.9−3.3	1.2−1.6
Dieldrin	0.20	46	5.1−6.2	3.3−4.3
Mirex	0.20	700	5.8	3.9
Soft				
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

[1] From Baird (1995).

[2] BCF values calculated from the relationship of Kenaga and Goring (1980).

biomagnification. The efficiency of an ecological process is about 10%. In moving from one trophic level to another, only about 10% of the total biomass is transferred to the next trophic level, but effectively *all* of the pesticide is transferred to the next trophic level. As an example, consider the following simple coastal ocean food chain:

$$\underset{(0.05)}{\text{Plankton}} \rightarrow \underset{(0.5)}{\text{Minnows}} \rightarrow \underset{(5)}{\text{Needlefish}} \rightarrow \underset{(50)}{\text{Cormorants}}$$

The values in parentheses, assuming 10% efficiency, are the DDE concentrations in ppm. Relative to the plankton, there is a 1000X increase in DDE in the cormorants. The water may have significantly lower DDE concentrations than the plankton, so the total biological magnification from water to cormorant may be on the order of millions of times.

Dioxins, PCBs, and Dibenzofurans (DFs)

These compounds are all chlorinated hydrocarbons that have been shown to be toxic in animal experiments. The basic structure of dioxin and PCB has been described in the section on nomenclature. The basic furan ring contains five atoms, one is oxygen and the other four are carbon. In dibenzofuran, benzene rings are attached to each side of the furan ring (Figure 5–30). There are 75 different varieties of dioxins, called ***congeners***—*members of the same chemical family that differ only in the number and position of the same substituent.*

The toxicity of dioxin varies as a function of the number and location of the chlorine atoms. TCDD (Figure 5–16) is considered to be the most toxic dioxin. Note that in this molecule there are an intermediate number of Cl atoms and they are located at the positions farthest from the central ring. Dioxins with fewer or greater numbers of Cl, or with the Cl atoms located closer to the central ring, are found to be less toxic, and a fully chlorinated dioxin is virtually nontoxic. Dioxins are found as contaminants in herbicides and fungicides. Perhaps the most famous example of this contamination was "Agent Orange," used as a defoliant in Vietnam. Dioxin concentrations were around 10 ppm in Agent Orange, far above the values now found in herbicides (< 0.1 ppm). PCBs are chemically inert liquids, have low vapor pressures, high combustion temperatures, and are excellent electrical insulators. For this reason they were widely used as coolants for power transformers and capacitors. Other industrial uses were subsequently found. PCBs are virtually insoluble in water but very soluble in fatty or oily substances and thus tend to concentrate in fatty tissue. There are 209 congeners in the PCB family. Dibenzofurans are produced when PCBs are heated in the presence of oxygen. There are 135 dibenzofuran congeners. Furans with intermediate amounts of Cl have a toxicity similar to that of TCDD.

The relative toxicities of a number of dioxins and furans (compared to TCDD) are given in Table 5–10. Note the variation in toxicity with the numbers and positions of the Cl atoms. The ***toxicity equivalence factor (TEQ)*** for a mixture of dioxins and furans is *calculated on the basis of the relative abundance of each of the dioxins.*

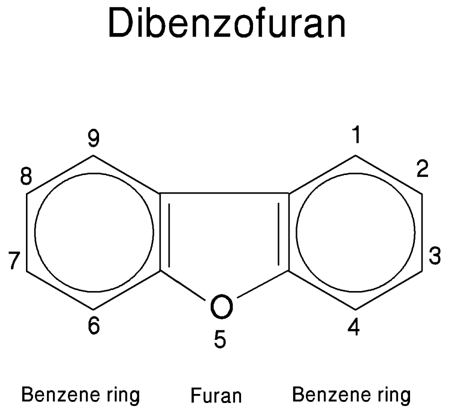


Figure 5–30 Basic structure of dibenzofuran. Positions 1 through 4 and 6 through 9 have attached hydrogens that can be replaced by chlorines in chlorodibenzofurans.

EXAMPLE 5–4 Suppose that an individual ingested 20 pg (picograms) of 2,3,7,8-tetra-chlorodibenzo-*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,

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

The individual has ingested a total of 260 pg of dioxin but this is equivalent to only 20.6 pg of TCDD. Thus, not only the total exposure to dioxins but the actual composition of the dioxins is important in determining the health or environmental hazard.

PAHs

Polycyclic aromatic hydrocarbons (PAHs) consist of fused benzene rings. Representative structures are shown in Figure 5–13. The only commercially produced PAH is napthalene, whose vapor is toxic to some insects. PAHs are common air pollutants and are the result of incomplete combustion, particularly of wood and coal. PAHs are found in creosote, which is used as a wood preservative. They can also be introduced into the aquatic environment through oil spills. Certain PAHs are known carcinogens and their distribution in the environment is of concern. In the aquatic environment they tend to be adsorbed on sediment particles because their solubility in H_2O is low. Like other hydrocarbons, they tend to concentrate in fatty tissue, and various aquatic organisms have relatively high burdens of PAHs. Case Study 5–5 describes the distribution and sources of PAHs found in Lake Erie sediments.

Table 5–10 Toxicity Equivalence 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
l,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

*From Baird (1995).

NAPLs

Nonaqueous-phase liquids (NAPLs) are *hydrocarbons that have very low solubility in water*. They can be very important contaminants in groundwater systems. The NAPLs are divided into two groups on the basis of density. ***LNAPLs (light nonaqueous-phase liquids)*** are *less dense than water and will float on the water table.* ***DNAPLs (dense nonaqueous-phase liquids)*** are *more dense than water and can sink deep into the saturated zone.*

CASE STUDY 5–5

Distribution of PAHs in Lake Erie Sediments

Smirnov et al. (1998) investigated the distribution of PAHs in the sediments of Lake Erie. Among the PAHs found in the sediments were anthracene, benz(a)anthracene and its isomers, and benzo(a)pyrene. Principal component analysis (PCA) revealed three distinct groups of sediments in terms of PAH content and δ^{13}C. These were identified as the City Zone (average TPAH = 4997 ng g^{-1}, δ^{13}C = −25.4‰), the South Zone (average TPAH = 1914 ng g^{-1} δ^{13}C = –26.2‰), and the North Zone (average TPAH = 764 ng g^{-1}, δ^{13}C = –27.0‰). The City Zone was interpreted to be the result of direct input of fluvial sediments from Detroit, Cleveland, and Buffalo. The South Zone represented a region of small isolated inputs, and the North Zone was essentially uncontaminated by fluvial inputs. The authors concluded that approximately 80% of the total PAHs in the sediments were deposited by direct fluvial input of contaminated material. The other 20% represented atmospheric deposition.

Source: Smirnov et al. (1998).

Table 5–11 Solubility of BTEX Aromatic Hydrocarbons in Water

BTEX hydrocarbon	Solubility in distilled water (ppm)	Solubility in seawater (ppm)	Reference
Benzene	1696	201	1
Toluene	580	50	1
Ethylbenzene	161	111	2
o-Xylene	171	130	2
m-Xylene	148	106	2
p-Xylene	156	111	2

[1] Keeley et al. (1988).

[2] Sutton and Calder (1975).

LNAPLs are predominantly petroleum and gasoline-related compounds that are less dense than water and hence float on the groundwater table. Thus, they are rapidly dispersed over a wide area and pose a significant environmental problem. Among these compounds are a group of aromatic compounds that are often referred to as BTEX (benzene, toluene, ethyl-benzene, and xylenes). The BTEX compounds have a high solubility in freshwater (Table 5–11) and are potentially serious health hazards. The solubility of BTEX compounds is much lower in seawater, a high-ionic-strength solution. Toluene [methylbenzene] consists of a benzene ring with one attached methyl group. Ethylbenzene consists of a benzene ring with one attached ethyl group. The xylenes—oxylene [1,2-dimethylbenzene], *m*-xylene [1,3-dimethylbenzene], and *p*-xylene [1,4-dimethylbenzene]—have two methyl groups attached at different positions on the benzene ring. The names in brackets are the corresponding IUPAC names. Of concern are those LNAPLs that have a relatively high solubility (benzene and toluene) in freshwater. These can enter the drinking water supply and pose a health hazard. For example, benzene is a known carcinogen.

DNAPLs are mostly halogenated hydrocarbons and commonly occur as contaminants in groundwater. Sources are facilities that use chlorinated solvents, manufacture pesticides, and treat wood. Spills of transformer oils are also an important source. Chlorinated aliphatic hydrocarbons, PAHs, and PCBs are the compounds of most concern because they are relatively soluble in water. DNAPLs commonly found in the environment are listed in Table 5–12. Because these compounds do penetrate the zone of saturation, they are widely dispersed in groundwater. They are also not readily biodegradable. Hence, DNAPL releases are generally of much greater environmental concern than LNAPL releases.

NAPL concentrations are affected by four processes: volatilization, hydrolysis, in situ biodegradation, and dissolution. ***Volatilization*** occurs when NAPLs come in contact with air. For any particular chemical, standard reference works give equilibrium vapor pressures. For example, for benzene the equilibrium vapor pressure is 0.10 atm. For a mixture of hydrocarbons, the vapor pressure for a particular compound is proportional to its relative molar abundance in the mixture. The volatility of organic compounds is utilized in the sparging remediation process. In this process large volumes of air are passed through the contaminated zone and the organic compounds volatilize into the air stream. ***Hydrolysis*** occurs when an organic compound reacts with water to form a derivative compound. This type of reaction is particularly important for the chlorinated hydrocarbons that are often found in DNAPLs. The reaction can be written

$$\text{R-X} + \text{H}_2\text{O} \rightarrow \text{R-OH} + \text{X}^- + \text{H}^+$$

where R-X is an organic compound and X is an attached halogen, carbon, phosphorous, or nitrogen group. The attached group is replaced by OH^-. ***Biodegradation*** is a biological process involving aerobic bacteria. The bacteria utilize dissolved oxygen to directly consume the organic compound. This process is particularly important for LNAPLs. ***Dissolution*** occurs when the organic compounds dissolve in water. The effectiveness of this process is directly related to the solubility of the particular organic compound and the volume of water through which it can be dispersed. Case Study 5–6 describes the natural attenuation of hydrocarbons in a groundwater system.

Table 5–12 Common DNAPLs*

Halogenated volatiles	Nonhalogenated semivolatiles
Chlorbenzene	2-Methyl naphthalene
1,2-Dichloropropane	*o*-Cresol

Halogenated volatiles	Nonhalogenated semivolatiles
1,1-Dichloroethane	*p*-Cresol
1,1 -Dichloroethylene	2,4-Dimethylphenol
1,2-Dichloroethane	*m*-Cresol
trans-1,2-Dichloroethylene	Phenol
cis-1,2-Dichloroethylene	Naphthalene
1,1,1 -Trichloroethane	Benzo[*a*]anthracene
Methylene chloride	Fluorene
1,1,2-Trichloroethane	Acenaphthene
Trichloroethylene	Anthracene
Chloroform	Dibenzo[*a,h*]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	

*From Bedient et al. (1994).

CASE STUDY 5–6 Natural Attenuation of Aromatic Hydrocarbons in Groundwater Near a Former Manufactured-Gas Plant

Manufactured-gas plants produced gas from either coal or oil. These plants disappeared with the advent of interstate gas distribution pipelines, but pollution associated with these plants still exists. Contaminants from these sites include trace elements, volatile organic compounds (VOCs), monoaromatic hydrocarbons (MAHs), and PAHs. Landmeyer et al. (1998) investigated the breakdown of organic pollutants in groundwater from one of these sites located in South Carolina. The transport of organic contaminants through the groundwater system is a function of the rate of groundwater flow and the rate of degradation. If degradation rates are relatively high compared to groundwater flow, transport of the organic contaminants will be limited.

Biodegradation rates are often determined by laboratory experiments in which a sample of aquifer material is spiked with ^{14}C-labeled compounds. In this study, the authors used ^{14}C-napthalene (a PAH), ^{14}C-benzene, and ^{14}C-toluene (MAHs). Experiments were carried out under both aerobic and anaerobic conditions. It should be noted that in a groundwater system contaminated with hydrocarbons, conditions are usually anaerobic. First-order biodegradation rate constants under aerobic conditions were toluene = $-0.84\ d^{-1}$, benzene = $-0.03\ d^{-1}$, and napthalene = $-0.88\ d^{-1}$. Under anaerobic conditions, the rate constants were toluene = $-0.002\ d^{-1}$, benzene = $-0.00014\ d^{-1}$, and napthalene = $-0.000046\ d^{-1}$. Under aerobic conditions, which are unlikely to be attained in the aquifer, the breakdown of all three aromatic hydrocarbons is rapid. Under anaerobic conditions, the breakdown is much slower.

The authors also determined the adsorption coefficients for toluene and napthalene [the partitioning of a contaminant between an aqueous phase (groundwater) and a solid phase (aquifer material)]. For napthalene, K_d = 137 L kg^{-1} and for toluene, K_d = 9.9 L kg^{-1}. The difference in the two partition coefficients indicates that napthalene would be retained in the solid phase relative to toluene as groundwater moved through the system.

In combination with a groundwater flow model for the site, these data were used to model the transport of both PAH and MAH contaminants. The model indicated that MAH concentrations would have reached a steady state before discharge to an adjacent surface-water body, but not naphthalene concentrations. Time-integrated measurements of actual benzene concentrations indicated steady-state conditions, but toluene and napthalene concentrations decreased with time, indicating an additional remediation process.

To understand the significance of these results the student should recognize that there is a continual leaching of PAHs and MAHs from the site into the groundwater system. The steady-state result for benzene indicates that benzene is degrading within the groundwater system at the same rate at which it is being added. The observed concentration decreases for toluene and napthalene with time indicate that these compounds are degrading at a rate faster than the rate of addition. If discharge from the site was stopped, natural processes would remove these various organic compounds from the groundwater.

Source: Landmeyer et al. (1998).

GEOCHEMICAL AND BIOCHEMICAL PROCESSES THAT CONTROL THE CONCENTRATION OF ORGANIC CHEMICALS IN WATER

In the previous sections we have considered the types of organic compounds, their distribution in the environment, and some of the factors that control their distribution and decomposition. Here we will look at the specific physical and biological processes that control the concentrations of carbon compounds in natural waters. These are important processes because they will determine the rate at which a contaminant is removed from the system, the rate at which it is dispersed through the system, and the techniques that can be used to remove the pollutant. Physical/chemical processes are sorption/partition, precipitation, volatilization, and oxidation-reduction. Biological processes are direct consumption by primary producers (i.e., photo- and chemosynthesis), decomposition by bacteria under aerobic or anaerobic conditions, and oxidation-reduction.

Sorption/Partition

Particles are present in natural systems, and dissolved organic carbon is partitioned between the aqueous phase and the particles. The particle mixture is complex, consisting of both the products of erosion and biological activity. The possibilities are a variety of silicate (usually dominated by the clays), carbonate, oxide, and sulfide minerals; organic particles; and organic and oxide coatings on pre-existing particles. Given the complexity of natural systems, it is usually best to experimentally determine the sorption/partition characteristics (Case Study 5–6). What is usually determined is the distribution coefficient, i.e., the amount adsorbed per unit mass of solid divided by the concentration of the substance in the aqueous phase. The amount adsorbed per unit mass may change with variations in absolute concentration. When this occurs, the adsorption process is represented by an adsorption isotherm. We will consider adsorption isotherms in Chapter 7. If the distribution of the substance is independent of concentration, we have the simple relationship

$$C_{\text{ads}} = K_{\text{d}} * C_{\text{soln}}$$

where C_{ads} is the concentration of the substance adsorbed by the particles, C_{soln} is the concentration of the substance in water, and K_{d} is the distribution coefficient.

EXAMPLE 5–5 In Case Study 5–6 it was found that the adsorption of napthalene onto sedimentary particles followed a linear relationship, with K_{d} = 137 L kg^{-1}. If the napthalene concentration in the groundwater was 3.2 mg L^{-1}, calculate the concentration of napthalene adsorbed onto the sedimentary particles in the aquifer.

$$C_{\text{ads}} = K_{\text{d}} \times C_{\text{soln}} = (137\text{ L kg}^{-1})(3.2\text{ mg L}^{-1}) = 438\text{ mg kg}^{-1} = 438\text{ ppm}$$

Assuming that 1 L of groundwater has a mass of 1 kg, the concentration of napthalene in the groundwater is 3.2 ppm compared to a concentration of 438 ppm for napthalene adsorbed onto the sedimentary particles.

In the case of organic acids and bases, pH plays an important role in the adsorption process. For acids, the pH of the solution has to be 2 units less than the pK_{a} for complete adsorption, and when the pH is 2 units greater than the pK_{a}, maximum desorption occurs. The desorption is related to the ionization of the organic acid, which is less at lower pH. In the case of bases, the opposite effect is observed, and bases do not adsorb in acid solutions because H^+ ions are combined with OH^- (protonation), leading to ionization of the base.

Because organic acids are important in the natural environment, we will briefly consider their properties. The equilibrium reaction for an organic acid, in this case one containing the carboxylic acid group, can be written

$$\text{RCOOH} \rightleftharpoons \text{H}^+ + \text{RCOO}^-$$

where R is the root molecule and COOH is carboxylic acid. The equilibrium constant for this reaction is written

$$K_a = \frac{[H^+][RCOO^-]}{[RCOOH]}$$

Analagous to pH, the equilibrium constant is often expressed as

$$pK_a = -\log_{10} K_a$$

For a given pK_a, as the solution becomes more acidic (lower pH equals higher H^+ concentration) the amount of dissociated acid decreases; i.e., $RCOO^-$ becomes smaller. At higher pH, more of the acid is dissociated. Adsorption is inversely related to the degree of dissociation, so increasing pH leads to a decrease in adsorption. Some common organic acids are illustrated in Figure 5–31 along with their pK_a's. Note that acids with more than one carboxylic acid group have multiple-step dissociations and, thus, have more than one pK_a value.

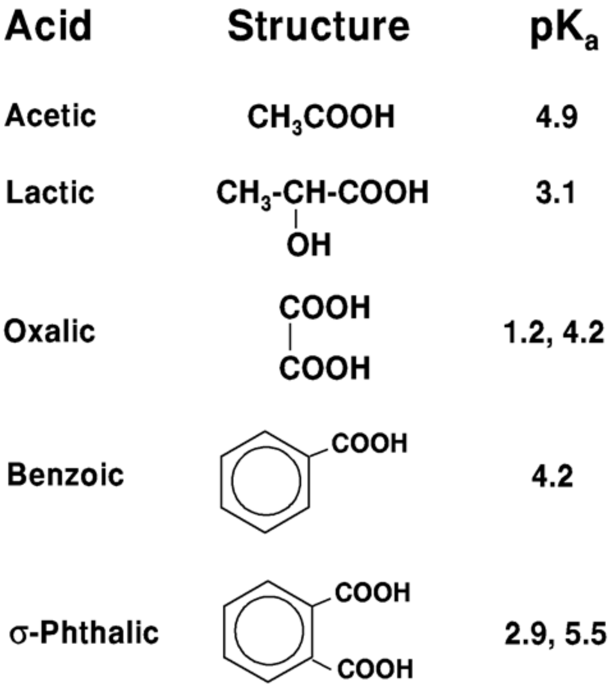


Figure 5–31 Structures of some common organic acids and their dissociation constants, pK_a. Oxalic and σ-phthalic acid have two dissociation constants because both acids have two-step dissociations. After Drever (1997).

In the case of the partitioning of an organic chemical between soil and water, the partition coefficient is often normalized to the organic carbon content of the soil. The relationship becomes

$$K_{oc} = K_d \times \frac{100}{\%oc} = \frac{\mu\text{g chemical/g organic carbon}}{\mu\text{g chemical/g water}} \qquad (5\text{–}3)$$

K_{oc} values for selected compounds are found in Table 5–13.

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

*Data from Hounslow (1995).

EXAMPLE 5–6 A field has been treated with DDT (obviously, not in the United States) and rainwater percolating down through the soil contains 3 ppb DDT. Organic carbon makes up 3% of the soil. Calculate the amount of DDT adsorbed per gram of soil. For DDT, log K_{oc} = 5.18 (Table 5–13).

$$\begin{aligned} C_{\text{ads}} &= K_{\text{oc}} * C_{\text{soln}} = (1.514\times10^{5})(3\text{ ng g}^{-1}) \\ &= 4.542\times10^{5}\text{ ng g}^{-1}\text{ C} = 454\mu\text{g g}^{-1}\text{ C} \end{aligned}$$

Only 3% of the soil is organic carbon, so the amount of DDT adsorbed per gram of soil is

$$454\times0.03 = 13.6\ \mu g\ \text{DDT g}^{-1}\text{ of soil} \equiv 13.6\text{ ppm} \quad ■$$

Precipitation

Precipitation of organic matter generally occurs when there is a significant change in the ionic strength of a solution, with an increase in ionic strength leading to decreased solubility. Recall from Chapter 2 that for neutral species increasing ionic strength leads to activity coefficients greater than 1 and a decrease in solubility. The most likely place for organic precipitation to occur is where freshwater meets seawater, for example, in an estuary.

Volatilization

Many organic compounds have low volatility; i.e., they do not readily go into the vapor state (evaporate). However, evaporation is an important process for a number of organic compounds of anthropogenic origin. These include the hydrocarbons, ketones, aldehydes, and esters. In general, low-molecular-weight nonpolar molecules have the greatest vapor pressures and are most easily evaporated. As common, everyday examples, nail polish remover (essentially acetone) and gasoline spills (when you overfill your gas tank) evaporate relatively quickly. The first example is a ketone and the second is a hydrocarbon.

The partitioning of an organic compound between liquid and vapor is often expressed in terms of a Henry's law constant, which is written

$$H_i = \text{Concentration in vapor state/Concentration in water} \qquad (5\text{–}4)$$

A number of different units have been used for this constant, including atm-liter $\text{g}-{}^{1}$, atmliter mol^{-1} atm (mole fraction)$^{-1}$, and a dimensionless unit. Note that the units depend on how the concentrations of the organic compound in the vapor and liquid are measured. For example, in the case of atm-liter g^{-1}, the concentration in the vapor is measured in atmospheres and the concentration in the liquid is measured in g L^{-1}. For the dimensionless unit, the concentrations in both the vapor and liquid phase are generally measured in mol L^{-1}. Dimensionless Henry's law constants for selected organic compounds are found in Table 5–13.

The volatility of organic compounds is important for one type of remediation called *sparging*. This technique is used to remove volatile organics, such as LNAPLs, from soil and groundwater. The process involves passing large volumes of air through the soil. The volatile organic compound partitions into the air and is exhausted from the site. You should recognize the practical difficulties of this type of remediation, in which the inter-connectivity of the pore space (permeability) is an important factor.

EXAMPLE 5–7 Benzene (a BTEX hydrocarbon) is released during an industrial accident and enters the groundwater system. The average concentration of benzene in the water is 1000 ppm. If the water is in contact with air, calculate the concentration of benzene in the air in mol L^{-1}. First convert 1000 mg kg^{-1} to mol L^{-1}. Assume that 1 kg of water is equivalent to a volume of 1 L. The molecular weight of benzene (C_6H_6) is 78.

$$1000 \times 10^{-3}\ \text{g L}^{-1}\ \text{benzene}/78\ \text{g mol}^{-1} = 1.28 \times 10^{-2}\ \text{mol L}^{-1}\ \text{benzene}$$

The Henry’s law constant for benzene is 0.22849 (Table 5–13).

$$C_\text{v} = H_i * C_\text{w} = (0.22849)(1.28 \times 10^{-2}\ \text{mol L}^{-1}) = 2.92 \times 10^{-3}\ \text{mol L}^{-1}$$

It is decided to remediate this spill by sparging. The goal is to reduce the benzene contamination to 10% of its original concentration in the groundwater. Assuming that we are dealing with an ideal situation, and that saturation of the vapor space is instantaneous, how many liters of air must we pass through the system for each liter of contaminated water? Note that the rate at which the concentration of benzene decreases with time is not constant; i.e., the concentration decrease is a first-order process (see Chapter 2). Using the dimensionless Henry’s law constant and setting 1 cycle = 1 liter of air,

$$\text{Cycles} = \ln(C_\text{f} / C_\text{i})(-H_i) = \ln(0.1/1)(-0.22849) = 10\ \text{cycles} = 10\ \text{liters of air}$$

If we decide to reduce the concentration to 1% of the original, we would need to pass 20 liters of air through the system per liter of water. Note that this calculation assumes an ideal situation. In the real world much larger volumes of air would be required.

Oxidation-Reduction

In Chapter 4 we considered the basic principles of electrochemistry. The abundance of organic matter in the natural environment is important in terms of decomposition reactions that deplete the waters in oxygen and, thus, lower the overall Eh. In addition, it has been shown that humic ($E° = 0.7$ V) and fulvic ($E° = 0.5$ V) acids can act as reducing agents.

Biological Processes

Particulate organic matter (POC) is removed from the water column by consumers and decomposers (bacteria and fungi). Dissolved organic carbon (DOC) is removed by microbial action. In both cases, microbial decomposition appears to be most important. The presence of sediment increases the rate of microbial decomposition. The rate of microbial decomposition is also related to the size of the organic molecule, with increasing size leading to decreasing rates of decomposition. Microbial decomposition under aerobic conditions can be represented by the following simple reaction:

$$\mathrm{CH_2O + O_2 \rightarrow CO_2 + H_2O + Energy}$$

This is the dominant reaction in the aerated portions of streams, lakes, and the ocean. Anaerobic decomposition can be represented by the following simple reaction:

$$\mathrm{CH_2O + A(oxidized) \rightarrow CO_2 + A(reduced)}$$

where A is an electron acceptor (an oxidizing agent, see Chapter 4). If A is an organic compound, then the product is an organic compound. Hence, during anaerobic decay a number of intermediate organic compounds are produced that contribute to the total DOC. The final products of anaerobic decay are usually CH_4 and CO_2. Other types of microbial actions involve transformations of organic compounds. For example, through microbial action an organohalide compound can be degraded by *dehalogenation,* in which a halogen atom is replaced by another atom or group, such as OH. Case Study 5–7 deals with the biodegradation of chlorinated and nonchlorinated organic contaminants.

Degradation Half-Life

A useful concept is that of ***degradation half-life,*** i.e., *the length of time it takes for 50% of an organic compound to be degraded.* Note that this is an exponential relationship just as in the case of radioactive decay (a first-order process). Thus, for each half-life the existing concentration is reduced by 50%. The half-life of organic compounds in soil and surface and ground water is a function of the initial concentration of the compound, the temperature, and whether the decomposition occurs under aerobic or anaerobic conditions.

CASE STUDY 5–7 Biotransformations of Organics in Soil Columns and an Infiltration Area

Bosma et al. (1996) investigated the biodegradation of chlorinated and nonchlorinated organic contaminants in sand sediments from the Rhine River and from a dune infiltration site at the Amsterdam municipal water works. Under aerobic conditions all the nonchlorinated compounds were transformed, but most of the chlorinated compounds were not transformed. This situation was reversed under anaerobic conditions in which the chlorinated compounds were transformed by reductive dechlorination (H replaces Cl), but of the nonchlorinated organic contaminants only toluene showed significant transformation. In all of the experiments the authors observed that there was a lag time before the transformations occurred. They interpreted these time delays to reflect the time required to increase the microbial population to a level where the transformations became measurable, or the time required to induce enzymes needed for the contaminant breakdown. In the anaerobic experiments the reductive dechlorination was slower at 4°C than at 20°C.

Source: Bosma et al. (1996).

CASE STUDY 5–8 Aerobic Biodegradation of Alkylated Aromatic Hydrocarbons

Budzinski et al. (1998) investigated the aerobic degradation of aromatic compounds using a bacterial community from marine sediments. The aromatic fraction was prepared from an Arabian light-crude residue. The experiments were conducted over a period of seven days and measurements were made at 1,2, 3, and 7 days. At the end of seven days, the napthalenes had completely degraded and there were significant reductions in the amounts of dibenzothiophenes and phenanthrenes. The degradation was found to follow first-order kinetics, and there were no differences between sulfur-containing aromatic compounds (dibenzothiophenes) and non-sulfur-containing aromatic com pounds (phenanthrenes). For the naphthalenes, $t_{1/2} \approx 17$ h; dibenzothiophenes, $t_{1/2} = 32-50$ h; and phenanthrenes, $t_{1/2} = 32-51$ h. Given these data, the nonalkylated aromatic compounds are degraded first. Among the alkylated aromatic compounds, there were important differences in biodegradation rates depending on the position of the alkyl substituents on the aromatic rings. Remember, alkyl groups are derived from al-kanes. The half-lives determined by these experiments indicate that all the aromatic compounds would degrade rapidly in marine sediments. For the aromatic hydrocarbon with the longest half-life (51 h), 99% of the hydrocarbon would be degraded after 14 days.

Source: Budzinski et al. (1998).

In general, the half-life increases with increasing concentration and decreases with increasing temperature. Half-lives are determined by experiment or by measuring changes with time in natural systems (Case Study 5–8).

EXAMPLE 5–8 Assume an organic contaminant is introduced into an aquifer. Right after the spill the concentration of the organic contaminant is 12 mg L^{-1}. A measurement made 20 days later reveals that the concentration of the contaminant has decreased to 1 mg L^{-1}. Assuming that this is a first-order reaction, what is the half-life for this particular organic contaminant?

$$C_\mathrm{i} = C_\mathrm{o} e^{-kt}$$

Rearranging this equation and solving for k gives

$$k = \ln C_\mathrm{o} / C_\mathrm{i} \times 1/t = \ln 12 \times 1/20\ \mathrm{d} = 0.124\ \mathrm{d}^{-1}$$

The half-life is the time it takes 50% of the organic contaminant to degrade; i.e., $C_\mathrm{o}/C_\mathrm{i} = 2$.

$$t_{1/2} = \ln 2 / k = 0.693/0.124\ \mathrm{d}^{-1} = 5.6\ \mathrm{d} \quad \blacksquare$$

Half-lives for various organic compounds can be found in the literature (Table 5–14). These values are often determined for a particular system and may not be appropriate for other systems. The data, however, do give us an idea of the relative rates at which various organic chemicals break down under aerobic and anaerobic conditions in the natural environment.

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

*Data from Hounslow (1995).

QUESTIONS AND PROBLEMS

1. What is the difference between a *saturated* and an *unsaturated* organic compound?

2. What is a *functional group*?

3. How do *molecular* and *structural* formulas differ?

4. What is an *isomer*?

5. Distinguish between *alkanes, alkenes,* and *alkynes.*

6. Give an example of a *substitution* reaction.

7. Give an example of an *addition* reaction.

8. What are the distinguishing characteristics of a *PAH*?

9. Distinguish between *hard* and *soft* pesticides.

10. Define *polymer*.

11. What is *primordial carbon*?

12. Compare and contrast the *geochemical* and *biochemical* carbon cycles.

13. Define *humic substances.*

14. Distinguish between *humin, humic acid, and fulvic acid.*

15. Define the terms *labile* and *nonlabile* as used in Case Study 5−1.

16. What role do humic and fulvic acids play in the mobility of radionuclides in the surface environment (Case Study 5−2)?

17. Define *soil.*

18. What are the major factors in soil formation?

19. How could you distinguish organic carbon from a marine source from organic carbon from a land source?

20. How can sulfur occur in coal, and why is this important in the context of the environmental impact of coal combustion?

21. Summarize the associations of trace metals in coal with mineral and organic fractions (Case Study 5–4).

22. What factors are important in the formation of petroleum, and how do these factors affect the final petroleum product?

23. Distinguish among *POC*, *DOC,* and *TOC.*

24. Distinguish between *allochthonous* and *autochthonous* sources of carbon.

25. What is *BOD,* and how is it determined?

26. What is LD_{50}, and what is its significance?

27. What is *BCF,* and how is it determined?

28. What are the major factors that determine the toxicity of a *dioxin*?

29. What are *NAPLs, LNAPLs,* and *DNAPLs*?

30. Name and describe the four processes that affect NAPL concentrations.

31. Discuss the relationship between pH and the adsorption of organic acids.

32. Why do dissolved organic compounds tend to precipitate when the ionic strength of a solution increases?

33. What are the factors that favor high vapor pressures for organic compounds?

34. What is *sparging*, and why is the volatility of an organic compound important when using this process?

35. What is *BTEX*?

36. The famous Woburn toxics case (A *Civil Action)* involved the transport of various chlorinated hydrocarbons via the groundwater system to two water supply wells. Referring to Case Study 5–**7,** what variables in the groundwater system are important in the breakdown of chlorinated hydrocarbons?

37. Define *degradation half-life.*

38. Draw the structural formula for the benzene ring (remember the ring consists of six carbon atoms and six hydrogen atoms). Given this structure, and charge balance considerations, why was the carbon bonding in the benzene ring once thought to consist of alternating single and double bonds?

39. Draw the structural formula for 2-methylbutane.

40. Draw the structural formula for 2,5–dimethylhexane, and write the molecular formula.

41. Draw the structural formula for 3-ethyl-2-methylpentane, and write the molecular formula.

42. Draw the structural formula for 1,4-dimethylcyclohexane, and write the molecular formula.

43. Write the condensed structural formula for 2,4-octadiene.

44. Write the condensed structural formula for 2-ethyl-l,3-hexadiene.

45. Write the condensed structural formula for 2-methyl-l-penten-3-yne.

46. Draw the structural formula for 1,2-dichlorobenzene.

47. Draw the structural formula for 1,1-dichloroethylene.

48. Draw the structural formula for 1,2,3,6,9-pentachlorodibenzo-*p*-dioxin.

49. Draw the structural formula for methylamine.

50. Name the compound illustrated in Figure 5–P50.

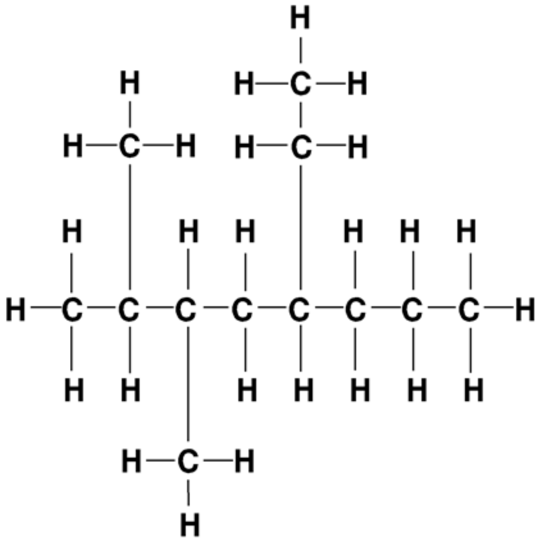


Figure 5–P50 Structural formula for problem 50.

51. A chemical analysis of dissolved organic carbon (DOC) in a water sample yields the following:

Partial Water Analysis	
Carbon (wt%)	45.0
Hydrogen (wt%)	6.0
Oxygen (wt%)	46.0
Molecular weight (daltons)	800

a. Calculate the atomic H/C and O/C ratios.

b. Is the DOC fulvic or humic acid? List the criteria used to make the identification.

c. Is this a saltwater or freshwater sample? List the criteria used to make the identification.

52. Keil et al. (1994) analyzed organic material extracted from the Columbia River, the Columbia River estuary, and the continental shelf sediments off Washington. The sediments were separated into sand, silt, and clay size fractions. Bulk sediment analyses were also done. A partial listing of their data is given here.

Data for Columbia River and Continental Shelf Sediments				
Location	Size	C (wt%)	N (wt%)	δ^{13}C‰
Columbia River sedimentary plume	Bulk	1.34	0.12	−22.5
	Clay	3.48	0.43	−22.9
	Sand	32.1	0.77	−25.6
Columbia River estuary				
suspended sediment	Silt	3.93	0.37	−26.0
Midshelf	Bulk	1.02	0.09	−22.5
	Clay	3.99	0.47	−23.1
	Sand	25.8	0.80	−24.7
Continental slope	Bulk	2.70	0.26	−22.0
	Clay	3.21	0.38	−22.1
	Sand	0.27	0.01	−23.7

a. Calculate the atomic C/N ratio for each sample.

b. Plot the data on a copy of Figure 5–26. Indicate the type of material you are plotting, i.e., bulk, clay, silt, or sand, and use different symbols to indicate each environment.

c. Calculate the relative percentage of vascular plant debris, soil organic matter, and marine plankton in each sample. The problem is solved graphically using the lever rule. (See the section in Chapter 6 dealing with mixing diagrams.)

d. What conclusions can you draw about the source of the organic material in the different sediment size fractions?

53. A harbor is currently the site of an oil refinery, and a number of ships enter the harbor to unload crude oil and to load gasoline. A sediment core was obtained from the floor of the harbor. Using the dating techniques discussed in Chapter 6, the ages of the various layers in the core were determined. The organic material in the sediment was analyzed and the ratio of odd chain lengths to even chain lengths was determined for the alkanes. Also determined was the unresolved complex mixture (UCM), which represents molecular structures that cannot be resolved with high-resolution gas chromatography. Some of these data are listed here. You will need to refer to Case Study 5–3 in order to answer these questions.

Data for Harbor Sediments		
Age of Sediment layer	Odd/even	UCM (area g^{-1} C)
1990	5	2
1980	3	4
1970	1	20
1960	5	1
1950	5	1
1940	5	1

a. When did the oil refinery first begin to operate? Why did you select this date?

b. What might have happened around 1970? Why?

c. What has happened since 1970? List some reasons for the changes observed in the chemical data after 1970.

54. The following chemical data were obtained for four coal samples. Plot the data on the van Krevelen diagram (Figure 5–27), and classify each of the samples.

Data for Some Coal Samples				
Sample	1	2	3	4
C (wt%)	55.44	72.95	84.24	93.50
H (wt%)	5.60	5.24	5.55	2.81
O (wt%)	36.56	20.50	8.67	2.72

55. For Carbaryl (a carbamate), log K_{ow} = 2.81 (Karickhoff, 1981; note that this paper tabulates K_{ow} values for a number of organic compounds). Calculate the BCF for this insecticide.

56. An individual has the following dioxin exposure: 10 pg 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin, 40 pg l,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin, 120 pg 2,3,4,7,8-pen-tachlorodibenzofuran, and 200 pg 1,2,3,4,6,7,8-heptachlorodibenzofuran. Calculate the TEQ for this exposure.

57. In Case Study 5−6, the first-order rate constant for the breakdown of toluene under aerobic conditions was -0.84 d^{-1}, and under anaerobic conditions the rate constant was -0.002 d^{-1}. Calculate the time required to degrade 90% of the toluene under aerobic and anaerobic conditions.

58. In Case Study 5–6 it was found that the adsorption of toluene onto sedimentary particles followed a linear relationship, with K_d = 9.9 L kg^{-1}. If the toluene concentration in the groundwater is 4.5 mg L^{-1}, calculate the concentration of toluene adsorbed onto the sedimentary particles in the aquifer.

59. Log K_{oc} = 2.36 for the carbamate pesticide Carbaryl (Karickhoff, 1981). Rainwater percolating down through the soil contains 5 ppb Carbaryl. Organic matter makes up 2% of the soil. Calculate the amount of Carbaryl adsorbed per gram of soil.

60. *m*-Xylene enters the groundwater system. The average concentration of *m*-Xylene in the groundwater is 100 ppm. If the groundwater at the top of the saturated zone is in equilibrium with air, calculate the concentration of *m*-Xylene in the air in mol L^{-1}.

61. In a particular system, the half-life of Lindane undergoing aerobic decomposition is 210 days. Calculate the length of time required for 90% of the Lindane to decompose.

62. Because of an oil spill a marine sediment becomes contaminated with napthalene. With reference to Case Study 5–8, calculate the length of time required for 99% of the napthalene to decompose.