Handbook of Environmental Data on Organic Chemicals

VOLUME 1

Handbook of Environmental Data on Organic Chemicals

Fourth Edition

VOLUME 1

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VOLUME 1

INTRODUCTION

Since the publication of the first edition of this handbook in 1977, much more information has become available about the presence and fate of new and existing organic chemicals in the environment. These data, when given a wide distribution, will no doubt reduce the misuse of dangerous chemicals and hence their impact on the environment. The *Handbook of Environmental Data on Organic Chemicals* has now been updated for the third time and covers individual substances as well as mixtures and preparations.

I. ARRANGEMENT OF CATEGORIES

The information in the categories listed below is given for each product in the sequence indicated; where entries are incomplete, it may be assumed that no reliable data were provided by the references utilized.

- *Name:* the commonly accepted name is the key entry.
- *Synonym:* alternative names, as well as trivial names and identifiers, are indicated. Obsolete and slang names have been eliminated as far as possible.
- *Formula:* the molecular and structural formulas are given.
- CAS: the Chemical Abstracts Service number
- *Manufacturing source*
- *Use, users, and formulations*
- *Natural sources and occurrence*
- *Man-caused sources*

A. PROPERTIES The chemical and physical properties typically given are physical appearance; molecular weight (mw); melting point (mp); boiling point (bp) at 760 mm Hg unless otherwise stated; vapor pressure (vp) at different temperatures; relative vapor density (vd), the relative vapor density of air = 1; saturation concentration in air at different temperatures (sat. conc.); the maximum solubility in water at various temperatures (solub.); the liquid or solid density at room temperature; the logarithm of the octanol/water partition coefficient (log P_{oct}); the logarithm of the dimensionless constant of Henry (log *H).*

B. AIR POLLUTION FACTORS The following data are given: conversion factors (between volume and mass units of concentration); odor threshold values and characteristics; atmospheric reactions; natural sources (and background concentrations); man-made sources (and ground level concentrations caused by such sources); emission control methods (and results); methods of sampling and analysis.

C. WATER AND SOIL POLLUTION FACTORS Analogous to the previous category, the following data are listed: biodegradation rate and mechanisms; oxidation parameters, such as BOD, COD, and ThOD; impact on treatment processes and on the BOD test; reduction of amenities through taste, odor, and color of the water or aquatic organisms; the quality of surface water and underground water and sediment; natural sources; man-made sources; waste water treatment methods and results; methods of sampling and analysis.

D. BIOLOGICAL EFFECTS Residual concentrations, bioaccumulation values, and toxicological effects of exposing the products to ecosystems, bacteria, plants, algae, protozoans, worms, molluscs, insects, crustaceans, fishes, amphibians and birds.

The "explanatory notes" give a more detailed description of the compiled data, explain the definitions and abbreviations used throughout the book, and indicate how the data can be used to prevent or reduce environmental pollution.

II. ARRANGEMENT OF CHEMICALS

The chemicals are listed in strict alphabetical order; those that comprise two or more words are

alphabetized as though they were a single word. The many prefixes used in organic chemistry are disregarded in alphabetizing because they are not considered an integral part of the name; these include *ortho-, meta-, para-, alpha-, beta-, gamma-, sec, tert, sym-, as-, uns-, cis-, trans-, d-, l-, dl-, n,* and N-, as well as all numerals denoting structure. However, there are certain prefixes that are an integral part of the names (iso-, di-, tri-, tetra-, cyclo-, bio-, neo-, pseudo-), and in these cases, the name is placed in its normal alphabetical position. For example, dimethylamine appears under D and isobutane under I.

III. ORDER OF ELEMENTS

Readers who are not acquainted with the definitions and abbreviations used throughout the book should consult the appropriate sections of this chapter. The data are given in the following sequence (each item will be discussed in detail).

A. PROPERTIES

1. formula
2. physical appearance
3. molecular weight (mw)
4. melting point (mp)
5. boiling point (bp)
6. vapor pressure (vp)
7. vapor density (vd)
8. saturation concentration (sat. conc.)
9. solubility (solub.)
10. density (d)
11. logarithm of the octanol/water distribution coefficient (log P_{oct})
12. logarithm of the dimensionless Henry's constant (log *H)*

B. AIR POLLUTION FACTORS

13. conversion factors
14. odor
15. atmospheric reactions
16. natural sources
17. man-made sources
18. control methods
19. air quality

C. WATER AND SOIL POLLUTION FACTORS

20. biodegradation
21. oxidation parameters
22. impact on biodegradation processes
23. odor and taste thresholds
24. water, soil, and sediment quality
25. natural sources
26. man-made sources
27. waste water treatment
28. degradation in soil
29. soil sorption

D. BIOLOGICAL EFFECTS

- residual concentrations
- bioaccumulation values
- toxicological effects

30. ecosystems
31. bacteria

32. algae
33. plants
34. worms
35. molluscs
36. insects
37. crustaceans
38. fishes
39. amphibians
40. birds

IV. EXPLANATORY ELEMENTS

A. PROPERTIES

Only the most relevant chemical and physical properties are given. Flash points, flammability limits, autoignition temperature, and the like have been omitted because they are not of direct concern to the environmentalist. These and other dangerous properties of chemicals can be found in *Dangerous Properties of Industrial Materials* by I. Sax. Chemicals are never 100% pure, but the nature and quantity of the impurities can have a significant impact on most environmental qualities. The following parameters are very sensitive to the presence of impurities: water solubility, odor characteristic and threshold values, BOD, and toxicity.

The following data (from Shell's *Chemical Guide*) illustrate this point:

- product: *diethylene glycol* $O(CH_2CH_2OH)_2$

	Normal grade	*Special grade*
distillation range:	240-255°C	242-250°C
acidity (as CH_3COOH):	max. 0.2 wt%	max. 0.002 wt%
ash content:	max. 0.05 wt%	max. 0.002 wt%
BOD_5:	0.12	0.05
COD:	1.49	1.51
goldfish 24h LD_{50}:	5,000 mg/l	5,000 mg/l

- product: *ethyleneglycol* $HOCH_2\text{-}CH_2OH$

	Normal grade	*Special grade*
distillation range:	194-205°C	max. 2°C, incl. 197.6°C
ash content:	max. 0.002 wt%	max. 0.001 wt%
BOD_5:	0.47	0.15
BOD_5 after adaptation:	0.81	0.67
COD:	1.24	1.29
goldfish 24h LD_{50}:	5,000 mg/l	5,000 mg/l

When no data are available, the distillation range can give a first indication on the presence of impurities. Therefore, in this work, whenever a distillation range (boiling range) is given, the environmental data should be interpreted carefully.

- product: *triethanolamine* $N(CH_2CH_2OH)_3$

	Normal grade	*85%*
triethanolamine content:	min. 80 wt%	min. 85 wt%
BOD_5:	0.02	0.03
BOD_5 after adaptation:	0.17	0.90
COD:	1.50	1.50

After adaptation of the culture, the "85%" grade is much more biodegradable than the less pure "commercial" grade.

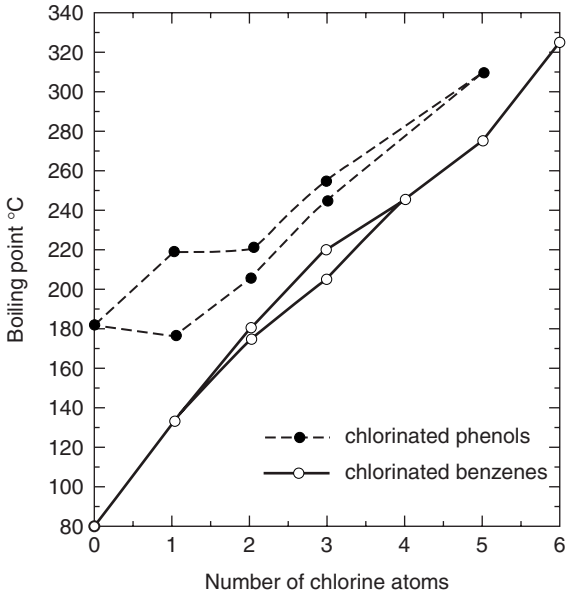


Figure 1. Relationship between boiling point and molecular weight for chlorinated benzenes and phenols.

1. Boiling Points

The boiling points of the members of a given homologous series increase with increasing molecular weight. The boiling points rise in a uniform manner as shown in Figure 1.
If a hydrogen atom of one of the paraffin hydrocarbons is replaced by another atom or a group, an elevation of the boiling point results. Thus alkyl halides, alcohols, aldehydes, ketones, acids, etc. boil at higher temperatures than the hydrocarbons with the same carbon skeleton.
If the group introduced is of such a nature that it promotes association, a very marked rise in boiling point occurs. This effect is especially pronounced in the alcohols and acids, because hydrogen bonding can occur.

2. Vapor Pressure

The vapor pressure of a liquid or solid is the pressure of the gas in equilibrium with the liquid or solid at a given temperature. Volatilization, the evaporative loss of a chemical, depends on the vapor pressure of the chemical and on environmental conditions that influence diffusion from the evaporative surface. Volatilization is an important source of material for airborne transport and may lead to the distribution of a chemical over wide areas and into bodies of water (e.g., in rainfall) far from the site of release. Vapor pressure values give indications of the tendency of pure substances to vaporize in an unperturbed situation and thus provide a method for ranking the relative volatilities of chemicals. Vapor pressure data combined with solubility data permit calculations of rates of evaporation of dissolved organics from water using Henry's Law constants, as discussed by MacKay and Leinonen (1943) and Dilling (1944).

Chemicals with relatively low vapor pressures, high adsorptivity onto solids, or high solubility in water are less likely to vaporize and become airborne than chemicals with high vapor pressures or less affinity for solution in water or adsorption to solids and sediments. In addition, chemicals that are likely to be gases at ambient temperatures and that have low water solubility and low adsorptive tendencies are less likely to transport and persist in soils and water. Such chemicals are less likely to biodegrade or hydrolyze but are prime candidates for photolysis and for involvement in adverse atmospheric effects (such as smog formation and stratospheric alterations). On the other hand, nonvolatile chemicals are less frequently involved in significant atmospheric transport, so concerns regarding them should focus on soils and water.

Vapor pressures are expressed in mm Hg (abbreviated mm), in atmospheres (atm), in mbars, or in hectoPascals (hPa).

If vapor pressure data for certain compounds are not available, they can be derived graphically from the compounds' boiling points and the boiling point/vapor pressure relationship for homologous series. An example is shown in Figure 2.

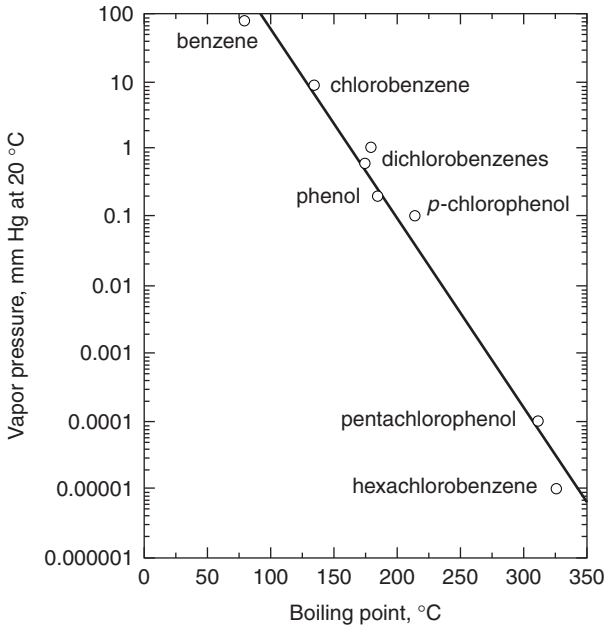


Figure 2. Relationship between boiling point and vapor pressure for homologous series of chlorinated benzenes and phenols.

3. Vapor Density

The density of a gas indicates whether it will be transported along the ground, possibly subjecting surrounding populations to high exposure, or will disperse rapidly.

The concentration term *vapor density* is often used in discussion of vapor phase systems. Vapor density is related to equilibrium vapor pressure through the equation of state for a gas:

$$PV = nRT$$

When the mass of the substance and the gram molecular weight are substituted for the number of moles n, the following equation is obtained:

$$\text{vapor density (vd)} = PM/RT$$

where

P = equilibrium vapor pressure in atmospheres
R = 0.082 liter atmospheres/mol/K
M = gram molecular weight
T = absolute temperature in kelvins (K)

In this book the relative vapor density (air = 1) is given because it indicates how the gas will behave upon release.

4. Water Solubility

4.1. Objectives. The water solubility of a chemical is an important characteristic for establishing that chemical's potential environmental movement and distribution. In general, highly soluble chemicals are more likely than poorly soluble chemicals to be distributed by the hydrological cycle.

Water solubility can also affect adsorption and desorption on soils and volatility from aquatic systems. Substances that are more soluble are more likely to desorb from soils and less likely to volatilize from water. Water solubility can also affect possible transformation by hydrolysis, photolysis, oxidation, reduction, and biodegradation in water. Finally, the design of most chemical tests and of many ecological and health tests requires precise knowledge of the water solubility of chemicals. Water solubility is an important parameter for assessment of all solid and liquid chemicals. Water solubility is generally not useful for gases, because their solubility in water is measured when the gas above the water is at a partial pressure of one atmosphere. Thus the solubility of gases does not usually apply to environmental assessment, because the actual partial pressure of a gas in the environment is extremely low.

4.2. Interpretation of Data. It is not unusual to find in the literature a wide range of solubilities for the same product. The oldest literature generally yields the highest solubility values. The reasons are twofold: First, in the years before and immediately after World War II, products were not as pure as they are today. Second, recent determinations are based on specific methods of analysis, such as gas chromatography. Nonspecific determinations do not distinguish between the dissolved product and the dissolved impurities; the latter, when they are much more soluble than the original product, move to the aqueous phase and are recorded as dissolved product. Nonspecific methods include turbidity measurement and TOD (Total Oxygen Demand).

The measurement of aqueous solubility does not usually impose excessive demands on chemical techniques, but measuring the solubility of very sparingly soluble compounds requires specialized procedures. This problem is well illustrated by the variability in the values quoted in the literature for products such as DDT and PCBs. This situation happens to be of some consequence; many of the compounds that are known to be significant environmental contaminants, such as DDT and PCBs, are those that have very low water solubilities.

4.3. Influence of the Composition of Natural Waters. The composition of natural waters can vary greatly. Environmental variables such as pH, water hardness, cations, anions, naturally occurring organic substances (e.g., humic and fulvic acids and hemicelluloses), and organic pollutants all affect the solubility of chemicals in water. Some bodies of water contain enough organic and inorganic impurities to significantly alter the solubility of poorly soluble chemicals.

The solubility of lower *n* -paraffins in salt water compared with fresh, distilled water is higher by about one order of magnitude, this difference decreasing with an increase in the molecular weight of the hydrocarbon. The increased solubility in seawater is due to simultaneous physical and chemical factors. The solubility of several higher *n* -paraffins (C_{10} and higher) has been determined in both distilled water and seawater. In all cases, the paraffins were less soluble in seawater than in distilled water. The magnitude of the salting out effect increases with increasing molar volume of the paraffins, in accordance with the McDevit-Long Theory. This theory of salt effects attributes salting in or salting out to the effect of electrolytes on the structure of water. Because the data in the literature indicate that the lower paraffins (below C_{10}) are more soluble, and the higher *n* -paraffins (C_{10} and higher) less soluble, in seawater than in distilled water, it is possible to speculate upon the geochemical fate of dissolved normal paraffins entering the ocean from rivers. If fresh water is saturated or near saturated with respect to normal paraffins (e.g., because of pollution), salting out of the higher paraffins will occur in the estuary. The salted out molecules may either adsorb on suspended minerals and on particulate organic matter or rise to the surface as slicks. In either case, they will follow a different biochemical pathway than if they had been dissolved. The salting out of dissolved organic molecules in estuaries applies not to *n* -paraffins alone, but to all natural or pollutant organic molecules whose solubilities are decreased by addition of electrolytes.
Thus it is possible that regardless of the levels of dissolved organic pollutants in river water, only given amounts will enter the ocean in dissolved form because of salting out effects of estuaries. Estuaries may act to limit the amount of dissolved organic carbon entering the ocean, but they may increase the amount of particulate organic carbon entering the marine environment.

4.4. Molecular Structure-Solubility Relationship. Because water is a polar compound, it is a poor solvent for hydrocarbons. Olefinic and acetylenic linkages and benzenoid structures do not greatly affect the polarity. Hence, unsaturated or aromatic hydrocarbons are not very different from paraffins in their water solubility. The introduction of halogen atoms does not alter the polarity appreciably. It does increase the molecular weight, and for this reason the water solubility always falls off. On the other hand, salts are extremely polar. Other compounds lie between these two extremes. Here are found the alcohols, esters, ethers, acids, amines, nitriles, amides, ketones, and aldehydes-to mention a few of the classes that occur frequently.

As might be expected, acids and amines generally are more soluble than neutral compounds. The amines probably owe their abnormally high solubility to their tendency to form hydrogen-bonded complexes with water molecules. This theory is in harmony with the fact that the solubility of amines diminishes as the basicity decreases. It also explains the observation that many tertiary amines are more soluble in cold than in hot water. Apparently, at lower temperatures the solubility of the hydrate is involved, whereas at higher temperatures the hydrate is unstable and the solubility measured is that of the free amine.

Monofunctional ethers, esters, ketones, aldehydes, alcohols, nitriles, amides, acids, and amines may be considered together with respect to water solubility. As a homologous series is ascended, the hydrocarbon (nonpolar) part of the molecule continually increases while the polar function remains essentially unchanged. There follows, then, a trend toward a decrease in the solubility in polar solvents such as water.

In general, an increase in molecular weight leads to an increase in intermolecular forces in a solid. Polymers and other compounds of high molecular weight generally exhibit low solubilities in water and ether. Thus formaldehyde is readily soluble in water, whereas paraformaldehyde is insoluble:

$$\underset{\text{water soluble}}{CH_2O} \rightarrow \underset{\text{water insoluble}}{HO(CH_2O)_xH}$$

Methyl acrylate is soluble in water, but its polymer is insoluble:

$$\underset{\text{water soluble}}{CH_2{=}CHCOOCH_3} \rightarrow \underset{\text{water insoluble}}{(-CH_2CH(COOCH_3)-)_x}$$

Glucose is soluble in water, but its polymers-starch, glycogen, and cellulose-are insoluble. Many amino acids are soluble in water, but their condensation polymers, the proteins, are insoluble.

Lindenberg (1803) proposed a relationship between the logarithm of the solubility of a hydrocarbon in water and the molar volume of the hydrocarbon. If the logarithm of the solubilities of the hydrocarbons in water is plotted against the molar volumes of the hydrocarbons, a straight line is obtained. This relationship has been worked out further by C. McAuliffe, and solubilities as a function of molar volumes for a number of homologous series of hydrocarbons have been presented graphically.

From the given correlation between molecular structure and solubility, the following conclusions may be drawn:

Branching increases water solubility for paraffin, olefin, and acetylene hydrocarbons, but not for cycloparaffins, cyclo-olefins, and aromatic hydrocarbons.

For a given carbon number, *ring formation* increases water solubility.

Addition of a *double bond* to the molecule, ring, or chain increases water solubility. The addition of a second and third double bond to a hydrocarbon of given carbon number proportionately increases water solubility (Table 1).

A *triple bond* in a chain molecule increases water solubility to a greater extent than two double bonds.

Cary T. Chiou *et al.* (382) found a good correlation between solubilities of organic compounds and their octanol/water partition coefficients. Furthermore, functional groups such as chlorine atoms,

Table 1. Influence of Double Bonds on Aqueous Solubility of Cyclic Hydrocarbons (at room temperature) (242).

Hydrocarbon	Solubility, mg/l
Cyclohexane	55
Cyclohexene	213
1,4-Cyclohexadiene	700
Benzene	1,780

methyl groups, hydroxyl groups, and benzene rings showed additive effects on the logarithm of the octanol/water partition coefficient (log P_{oct}) of the parent molecule.

This allowed the calculation of log P_{oct} values for many organic compounds based on the log P_{oct} value for the parent compound and the additive effects of the functional groups. Because of the correlation between solubilities of organic compounds and log P_{oct}, it is not surprising to find the same additive effects of functional groups on their water solubility. Table 2 shows this influence of functional groups on the solubility of benzene derivatives. Solubilities of homologous series of organic compounds are plotted in Figures 3, 4, and 5.

Effects that cannot be accounted for by this additive-constitutive character of the solubility are

- steric effects that cause shielding of an active function
- intra- and intermolecular hydrogen bonding (e.g., trihydroxyphenols)
- branching
- inductive effects of one substituent on another
- conformational effects, such as "balling up" of an aliphatic chain

Table 2. Influence of Functional Groups on Solubility of Benzene Derivatives.

	Functional Group	$S_{mg/l}$ Solubility mg/l (temp., °C)		log $S_{mg/l}$	$\Delta\log S_{mg/l}$ log $S_{C_6H_5X}$ –log $S_{C_6H_6}$
Aniline	—NH_2	34,000	(20°)	4.53	1.28
Phenol	—OH	82,000	(15°)	4.91	1.66
Benzaldehyde	—COH	3,300		3.52	0.27
Benzoic acid	—COOH	2,900		3.46	0.21
Nitrobenzene	—NO_2	1,900		3.28	0.03
Benzene	–	1,780		3.25	0.00
Fluorobenzene	—F	1,540	(30°)	3.19	–0.06
Thiophenol	—SH	470	(15°)	2.67	–0.58
Toluene	—CH_3	515		2.71	–0.54
Chlorobenzene	—Cl	448	(30°)	2.65	–0.60
Bromobenzene	—Br	446	(30°)	2.65	–0.60
Iodobenzene	—I	340	(30°)	2.53	–0.72
Diphenylether	O—⬡	21	(25°)	1.32	–1.93
Diphenyl	—⬡	7.5	(25°)	0.88	–2.37

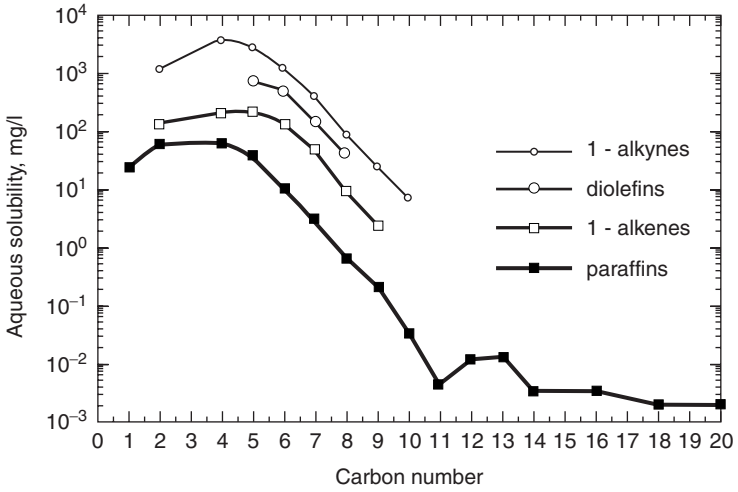


Figure 3. Relationship between aqueous solubility and molecular weight for saturated and unsaturated straight-chain hydrocarbons.

4.5. Solubility of Mixtures. Mixtures of compounds, whether they are natural such as oil or formulations such as many pesticides, behave differently from the single compounds when brought into contact with water. Indeed, each component of the mixture will partition between the aqueous phase and the mixture.

Components with a high aqueous solubility tend to move toward the aqueous phase while the "unsoluble" components remain in the other phase. From this, it follows that the fractional composition of the water soluble fraction (WSF) will differ from the original composition of the mixture and that concentrations of the components of the WSF are generally lower than the maximum solubilities for the individual components. Examples are shown in Tables 3 and 4.

5. Octanol/Water Partition Coefficient

The ability of some chemicals to move through the food chain, resulting in higher and higher concentrations at each trophic level, has been termed *biomagnification* or *bioconcentration.* The widespread distributions of DDT and the polychlorinated biphenyls (PCBs) have become classic examples of such movement.

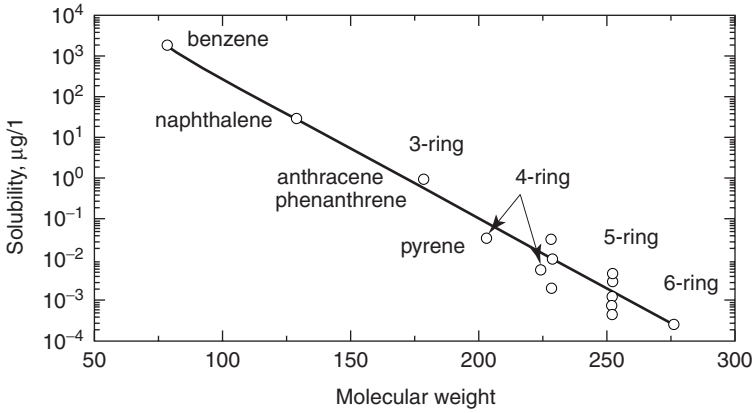


Figure 4. Relationship between aqueous solubility and molecular weight for benzene, naphthalene, and polynuclear aromatic hydrocarbons.

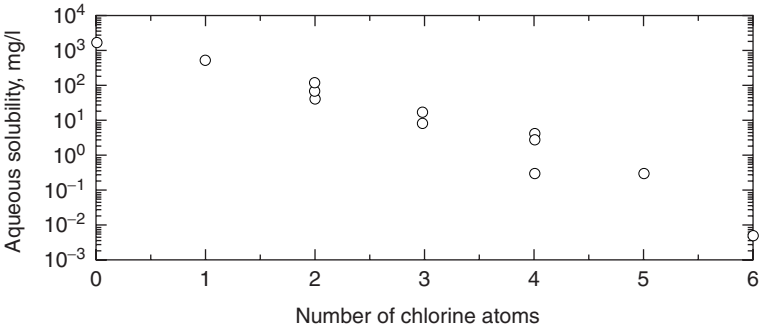


Figure 5. Relationship between aqueous solubility and molecular weight for homologous series of chlorinated benzenes.

From an environmental point of view, this phenomenon becomes important when the acute toxicity of the agent is low and the physiological effects go unnoticed until the chronic effects become evident. For this reason, prior knowledge of the bioconcentration potential of new or existing chemicals is desired. However, determining the bioconcentration factor of a chemical on a number of animals or in a food chain is expensive and time-consuming. If a simple relationship could be established between physico-chemical properties of a chemical and its ability to bioconcentrate, it would be of great benefit in planning the future direction of any development work on a new chemical and in directing research efforts to determine the distribution and ultimate fate of a limited number of selected chemicals.

5.1. Definition. The partition coefficient P_{oct} is defined as the ratio of the equilibrium concentrations C of a dissolved substance in a two-phase system consisting of two largely immiscible solvents, in this case *n* -octanol and water:

$$P_{oct} = \frac{C_{octanol}}{C_{water}}$$

In addition to the above, the partition coefficient is ideally dependent on only temperature and pressure. The partition coefficient P_{oct} is the quotient of two concentrations and is a constant without dimensions. It is usually given in the form of its logarithm to base ten (log P_{oct}).

The *n*-octanol/water partition coefficient has proved useful as a means of predicting soil adsorption (419), biological uptake (416), lipophilic storage (415), and biomagnification (417, 418, 339, 193).

The bioconcentration of several chemicals in trout muscle was found to follow a straight-line relationship with *n-octanol/water partition coefficient* (193). Bioconcentration in this work was

Table 3. Comparison of Aqueous Solubility of Some PCB Isomers in the Water Soluble Phase of Aroclor 1242 with Maximum Solubility of Individual Isomers (1909).

Isomer	Solubility, μg/l, in WSF of Aroclor 1242	Max. Solubility, μg/l, for Individual Compounds	
4-	15	2,000	(calculated)
2,2′-	21	900	
2,4′-	138	637	
2,5,2′-	61	248	
2,5,2′,5′-	22	26	

The same is true for many mineral oils and petroleum products, the WSF of which consists mainly of the more soluble aromatic compounds benzene, toluene, xylene and their alkyl homologs.

Table 4. Composition of Aroclor 1242 and Its Water Soluble Fraction (WSF) (1909).

	Aroclor wt %	WSF wt %	WSF/Aroclor ratio of wt %
monochlorobiphenyls	3	19.4	6.5
dichlorobiphenyls	13	31.8	2.4
trichlorobiphenyls	28	31.3	1.1
tetrachlorobiphenyls	30	16.5	0.55
pentachlorobiphenyls	22	—	0.04
hexachlorobiphenyls	4		>0.02
	—		—
	100	100	

defined as the ratio of concentration of the chemical between trout muscles and the exposure water measured at equilibrium. The relationship was established by measuring the bioconcentration, in trout, of a variety of chemicals over a wide range of partition coefficients. An equation of the straight line of best fit was determined and used to predict the bioconcentration of other chemicals from their *n*-octanol/water partition coefficients. The predicted values agreed with the experimental values in the literature. Values are expressed as their decimal logarithms.

The linear relationship between bioconcentration factor and partition coefficient is given by

$$\log B_f = 0.542 \log P_{oct} + 0.124 \quad (1)$$

where B_f = bioconcentration factor and P_{oct} = octanol/water partition coefficient.

The relationship is shown in Figure 6.

The largest compilation of *n*-octanol/water partition coefficients has been made by Albert Leo et al. (1457).

By far the most extensive and useful partition coefficient data were obtained by the classical way of shaking a solute with two immiscible solvents and then analyzing the solute concentration in one or both phases.

Examples of physico-chemical determinations that may be appropriate are

- Photometric methods
- Gas chromatography
- HPLC
- Back-extraction of the aqueous phase and subsequent gas chromatography

5.2. Calculation of Partition Coefficients. Since partition coefficients are equilibrium constants, it should not be surprising that one finds extrathermodynamic relationships between values in different solvent systems. This relationship can be expressed by the general equation:

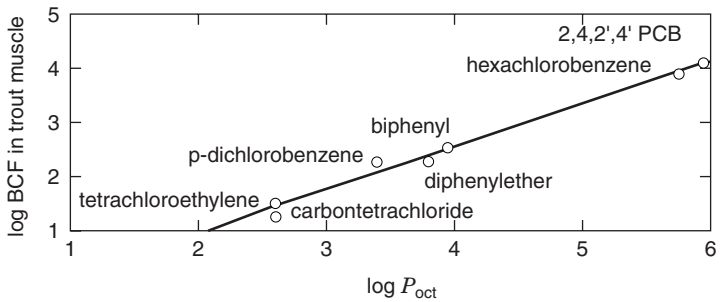


Figure 6. Relationship between octanol/water partition (P_{oct}) coefficient and bioaccumulation factor (BCF) in trout muscle (1448).

$$\log P_2 = a \log P_1 + b \tag{2}$$

for example:

$$\log P_{\text{toluene}} = 1.135 \log P_{\text{oct}} - 1.777$$
$$(n = 22;\ r = 0.980;\ s = 0.194) \tag{3}$$

$$\log P_{\text{cyclohexanone}} = 1.035 \log P_{\text{oct}} + 0.896$$
$$(n = 10;\ r = 0.972;\ s = 0.340) \tag{4}$$

Many log P_{oct} partition coefficients in this book were calculated by A. Leo *et al.* (1457) using the above and other equations. Furthermore, it was found that the log P_{oct} of a compound could be calculated from the log P_{oct} of another compound of the same homologous series by adding or subtracting a number of times a constant value (Table 5).

Additivity was first established for a wide variety of groups in a study of the substituent constant, π, defined by the following equation:

$$\pi_X = \log P_X - \log P_H \tag{5}$$

where P_X is the derivative of a parent molecule P_H and thus π is the logarithm of the partition coefficient of the function X. For example π_{Cl} could be obtained as follows:

$$\pi_{Cl} = \log P_{\text{chlorobenzene}} - \log P_{\text{benzene}} \tag{6}$$

It has been found that π values are relatively constant from one system to another as long as there are no special steric or electronic interactions of the substituents not contained in the reference system. π Values for aliphatic and aromatic positions are shown in Table 6. Other effects that must be taken into account in the additive-constitutive character of log P_{oct} are

- steric effects, which can cause shielding of an active function by inert groups
- inductive effects of one substituent on another
- intra- and intermolecular hydrogen bonding
- branching
- conformational effects, such as "balling up" of an aliphatic chain

Because of the difficulties of estimating the influence on log P_{oct} of steric, inductive, and conformational effects, calculated log P_{oct} values of complex molecules can only be approximate and can be wrong by 1 or 2 orders of magnitude. However, for most simple molecules, calculated values are correct within 1 order of magnitude.

5.3. Relationship between Aqueous Solubility and Octanol/Water Partition Coefficient. Unfortunately, the partition coefficients of many components of environmental significance are not always available, despite a recent extensive compilation (1457), or cannot be easily calculated from parent molecules. Assessment of partition coefficients from a more readily available physical parameter would therefore be useful. By definition, the partition coefficient expresses the equilibrium concentration ratio of an organic chemical partitioned between an organic liquid (such as *n*-octanol) and water. This partitioning is, in essence, equivalent to partitioning an organic chemical between itself and water. Consequently, one would suspect that a correlation might exist between the partition coefficient and the aqueous solubility. Based on experimental values of aqueous solubility and *n*-octanol/water partition coefficient for various types of chemicals, the following regression equati on was found (382):

$$\log P_{oct} = 5.00 - 0.670 \log S \tag{7}$$

where S is the aqueous solubility in μmol/l. If the solubility is expressed in mg/l, Eq. (7) becomes

$$\log P_{oct} = 4.5 - 0.75 \log S \text{ (mg/l)} \tag{8}$$

or

Table 5. Influence of Functional Groups on *n*-Octanol/Water Partition Coefficient of Benzene Derivatives.

Product	Functional Group	log P_{oct}	Δ log P_{oct} log $P_{C_6H_5X}$ –log $P_{C_6H_6}$
benzenesulfonic acid	—SO_3H	–2.25	–4.38
benzenesulfonamide	—SO_2NH	0.31	–2.44
aniline	—NH_2	0.90	–1.23
phenol	—OH	1.46	–0.67
benzaldehyde	—COH	1.48	–0.65
benzonitrile	—CN	1.56	–0.57
benzoic acid	—COOH	1.87	–0.28
nitrobenzene	—NO_2	1.85	1.88
benzene	–	2.13	–
fluorobenzene	—F	2.27	+0.14
thiophenol	—SH	2.52	+0.39
toluene	—CH_3	2.80	+0.67
chlorobenzene	—Cl	2.84	+0.71
bromobenzene	—Br	2.99	+0.86
iodobenzene	—I	3.25	+1.12
diphenyl	—C_6H_5	3.6	+1.47
diphenlether	—O—C_6H_5	4.21	+2.08

$$\log P_{oct} = 7.5 - 0.75 \log S \ (\mu g/l)$$

This equation has been obtained empirically. This correlation covers many classes of chemicals from

Table 6. Comparison of Aromatic and Aliphatic π Values.

Function	Aromatic π log $P_{C_6H_5X}$–log P_{C6H6}	Aliphatic π log P_{RX}– log P_{RH}
NH_2	–1.23	–1.19
I	1.12	1.00
S—CH_3	0.61	0.45
$COCH_3$	–0.55	–0.71
$CONH_2$	–1.49	–1.71
Br	0.86	0.60
CN	–0.57	–0.84
F	0.14	–0.17
Cl	0.71	0.39
COOH	–0.28	–0.67
OCH_3	–0.02	–0.47
OC_6H_5	2.08	1.61
$N(CH_3)_2$	0.18	–0.30
OH	–0.67	–1.16
NO_2	–0.28	–0.85
CH_2	0.50	0.50

hydrocarbons and organic halides to aromatic acids, pesticides, and PCBs. It also spans chemicals of different polarities (from nonpolar to polar) and of different molecular states (both liquid and solid).

Cary T. Chiou *et al.* (382) found for Eq. (7) a correlation coefficient of 0.970, which allows an estimation within 1 order of magnitude of the partition coefficient of a given compound from its aqueous solubility. However, when more data points are added, the scatter increases considerably for solubilities >100 mg/l. A few products even deviate considerably from the regression Eqs. (7) and (8), as shown in the following data.

pentachlorophenol		
aqueous solubility		14 mg/l at 20°C
log P_{oct}: experimental		*5.01*
calculated	Eq. (7)	3.8
	Eq. (8)	3.76
l-tyrosine		
aqueous solubility		480 mg/l at 25°C
log P_{oct}: experimental		*–2.26*
calculated	Eq. (7)	+2.7
	Eq. (8)	+2.5

The regression equation, however, remains the same, although P_{oct} values calculated from its aqueous solubility may be wrong by more than 1 order of magnitude. Obviously, Eqs. (7) and (8) would be unlikely to apply for salts, strong acids, and bases, because the activities of these solutes in this case cannot be approximated by their concentrations. Moreover, with materials such as aliphatic acids and bases, the partition coefficient can vary drastically with changes in pH.

As previously stated, the partition coefficient is related to physical adsorption on solids, biomagnification, and lipophilic storage. Equation (9) would extend these correlations to cover compounds using their aqueous solubilities without requiring the partition coefficient data. Based on reported biomagnification data of some selected organic chemicals in rainbow trout *(Salmo gairdneri)*, the following regression equation was calculated:

$$\log (\text{BCF}) = 3.41 - 0.508 \log S \tag{9}$$

where BCF is the bioconcentration factor in rainbow trout and S is aqueous solubility in μmol/l. If the aqueous solubility is expressed in mg/l, Eq. (9) becomes

$$\log (\text{BCF}) = 3.04 - 0.568 \log S_{mg/l} \tag{10}$$

where $S_{mg/l}$ is the aqueous solubility in mg/l.

5.4. Ecological Magnification (E.M.). The process of bioaccumulation involves a number of fundamental events:

1. partitioning of the foreign molecule under consideration between the environment and some surface of the organism
2. diffusional transport of these molecules across cell membranes
3. transport mediated by body fluids, such as exchange between blood vessels and serum lipoproteins
4. concentration of the foreign molecule in various tissues depending on its affinity for certain biomolecules, such as nerve lipids
5. biodegradation of the foreign material

The bioaccumulation process is thus seen to be a result of both kinetic (diffusional transport and biodegradation) and equilibrium (partitioning) processes. A molecule will not bioaccumulate in an organism if its degradation rate is greater than its accumulation rate. Experience with DDT may be considered a massive experiment from which it may be concluded that degradation occurred too slowly compared to the transport and partitioning of DDT into the higher levels of the food chain, thus permitting toxic levels to result. R.L. Metcalf and co-workers (1643) have correlated the ecological magnification values for a number of organic compounds (pentachlorobiphenyl,

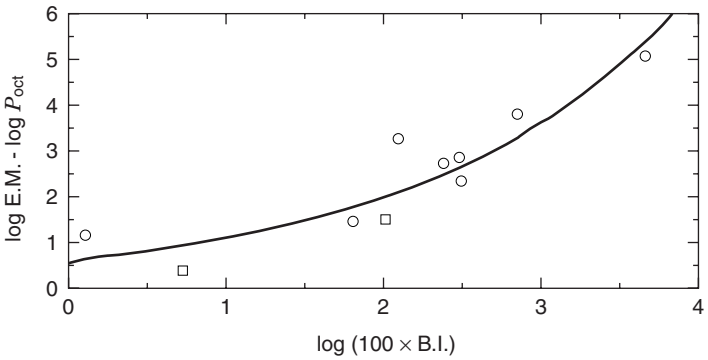


Figure 7. Influence of biodegradability of DDT analogs on experimental and predicted ecological magnification.

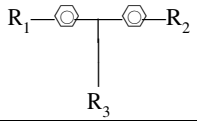
tetrachlorobiphenyl, trichlorobiphenyl, DDE, chlorobenzene, benzoic acid, anisole, nitrobenzene, and aniline) from the fishes of model ecosystems with both water solubility and the octanol/water partition value. For the limited number of compounds included, the correlation between physical properties and biomagnification is excell ent. The regression equations were

$$\log \text{ E.M.} = 4.48 \log - 0.47 \text{ S } (\mu g/l)$$
$$\log \text{ E.M.} = 0.75 + 1.16 \log P_{oct} \quad (11)$$

where S = aqueous solubility; P_{oct} = octanol/water partition coefficient

The correlations between ecological magnification and water solubility or octanol/water partition coefficient, as described above, are valid only for compounds that do not exhibit significant biodegradation.

Table 7. Biodegradability and Ecological Magnification in Fish of DDT Analog.



Number of DDT Analog	R_1	R_2	R_3	log P_{oct}[a]	log E.M.	log P_{oct} minus log E.M.	log (100 × B.I.)	log H_2O solub. ppb[b]
	Cl	Cl	CCl_3	6.1	4.93	1.17	0.18	0.9
	Cl	Cl	$HCCl_2$	5.4	4.92	0.48	0.73	1.8
1	CH_3O	CH_3O	CCl_3	4.7	3.19	1.51	1.97	2.7
2	CH_3	CH_3	CCl_3	6.0	2.15	3.85	2.85	1.0
3	CH_3S	CH_3S	CCl_3	5.9	0.74	5.16	3.67	1.1
4	Cl	CH_3	CCl_3	6.05	3.15	2.9	2.53	0.9
5	CH_3	C_2H_5O	CCl_3	5.9	2.60	3.3	2.08	1.1
6	CH_3O	CH_3S	CCl_3	5.3	2.49	2.81	2.44	1.9
7	CH_3O	CH_3O	$C(CH_3)_3$	4.7	3.21	1.49	1.81	2.7
8	Cl	Cl	$HC(CH_3)NO_2$	4.4	2.05	2.35	2.51	3.1

Calculated from data from Metcalf *et al.* (1940), Kapoor *et al.* (1937), and Hirwe *et al.* (1941).
B.I. = Biodegradability Index = ratio of polar compounds to nonpolar compounds.
[a] Calculated
[b] Derived from log P_{oct}.

Kapoor *et al* . (1937, 1938, 1939) studied in a model ecosystem the behavior of 8 DDT analogs covering a wide range of biodegradability. The basic methodology involved systematic study of the DDT molecule by replacing the environmentally stable C-Cl bonds with other groups of suitable size, shape, and polarity that could serve as degradophores by acting as substrates for the mixed-function oxidase enzymes widely distributed in living organisms. The action of the enzymes was shown to result in substantial changes in the polarity of the molecule, so that the degradation products were excreted rather than stored in lipids as was DDT and its chief degradation product DDE. A summary of model ecosystem data for a number of DDT analogs with degradaphores incorporated into aromatic and aliphatic moieties of the molecule is presented in Table 7 and Figure 7. Figure 7 shows that the difference between octanol/water partition coefficient and ecological magnification for the DDT analogs can be lar gely explained by the biodegradability index. The higher the biodegradability index, the larger the difference between octanol/water partition coefficient (as a predictive measure of ecological magnification) and ecological magnification itself.

Most of the correlation equations between water solubility (or octanol/water partition coefficients) and ecological magnification have indeed been established on biorefractive compounds or on homologous series of compounds with comparable biodegradability characteristics. Therefore, the equations are not universally applicable, as shown by Figure 8, which represents the relationship between water solubility of DDT, DDE, DDD, and the DDT analogs and ecological magnification in mosquito fish of a terrestrial aquatic model ecosystem. More than 30 pesticides were studied by Metcalf and Sanborn (1881), who found a highly significant correlation between log E.M. and log water insolubility. Similar correlations also exist for phenol and chlorinated derivatives and other chemical classes.

Because pesticides are now being "engineered" to be less "persistent," correlations between physico-chemical properties of compounds and ecological magnification will become less meaningful for such compounds unless degradation velocity is taken into account. For this reason, the following equation is proposed. It predicts the upper limit for ecological magnification based on aqueous solubility

$$\log \text{ E.M.} = 6 - 0.66 \log S \ (\mu g/l) \tag{12}$$

This correlation is only very approximate, so preference has been given to an easy-to-remember equation. The equation is therefore not based on a regression analysis.

The real E.M.s are 1 to 2 orders of magnitude smaller than the E.M.s predicted from Eq. (12). Indeed, of 43 compounds, 17 true E.M. values are smaller by less than 1 order of magnitude than the predicted values, 18 E.M. values differ by more than 1 but less than 2 orders of magnitude, and 6 E.M. values differ by more than 2 orders of magnitude.

5.5. Adsorption. The following factors influence the extent to which the adsorption of a compound from solution onto a solid occurs.

- The physical and chemical characteristics of the adsorbent (adsorbing surface)
- The actual surface area of the solid
- The nature of the binding sites on these surfaces and the actual distribution of these adsorption sites

An index of the tendency to adsorb onto a solid is the solubility of the compound. For homologous series of compounds, decreasing solubility can be interpreted as an increasing tendency to leave the water. Also, the *n*-octanol/water partition coefficient (log P_{oct}) has proved useful as a means of predicting soil adsorption, as shown in Figure 9.

5.6. Structure-Toxicity Correlations. Kopperman and co-workers (1832) noted that structure-toxicity correlations are possible only when the compounds examined have an identical mode of action. However, if toxic mechanisms of similar compounds are identical, then the internal concentration of toxicant required to elicit a specific biological response should be consistent. Because the internal concentration equals the external concentration multiplied by the partition coefficient, the external concentration is proportional to the reciprocal of the partition coefficient, and a plot of log external concentration vs. log partition coefficient should have a slope of –1.

T. Wayne Schultz and co-workers (1662) have observed excellent correlation between toxicity to

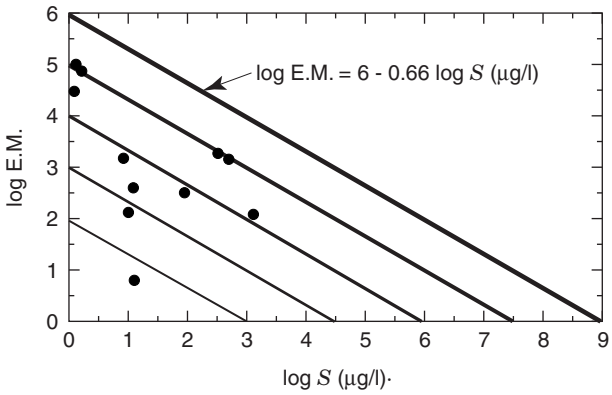


Figure 8. Relationship between water solubility of DDT, DDE, DDD, and DDT analogs and ecological magnification in mosquito fish of a terrestrial-aquatic model ecosystem.

the ciliate *Tetrahymena pyriformis* and partition coefficient within the following series of organic contaminants: pyridines, anilines, phenols, quinolines, and benzenes. However, no significant correlation between toxicity and partition coefficient was observed when data from all the tested contaminants were combined. Generally, an increase in alkyl substitution increases toxicity and decreases solubility. Furthermore, hetero-atom substitution into or onto the ring severely alters both the toxicity and the solubility of the compound (Figure 10). Kunio Kobayashi (1850) found that an increase of the Cl-atom number in the chlorophenols promoted an accumulation of the chlorophenols by fish and led their concentration in the fish to a lethal level, even when guppies were exposed to rather low concentrations, and consequently increased the fish-toxicity of chlorophenols. Kopperman *et al.* (1832) found approximately the same correlation for goldfish (Figure 11). The data are summarized in Table 8.

Because all the correlations obtained are valid only within homologous series and only for the test organism concerned, their predictive power is limited. Moreover, concentration values have been expressed largely in moles/liter. Although this is certainly more accurate from a scientific point of view than using mg/l, it is advisable to express concentration in µg/l or mg/l in order to make using the correlations more practicable.

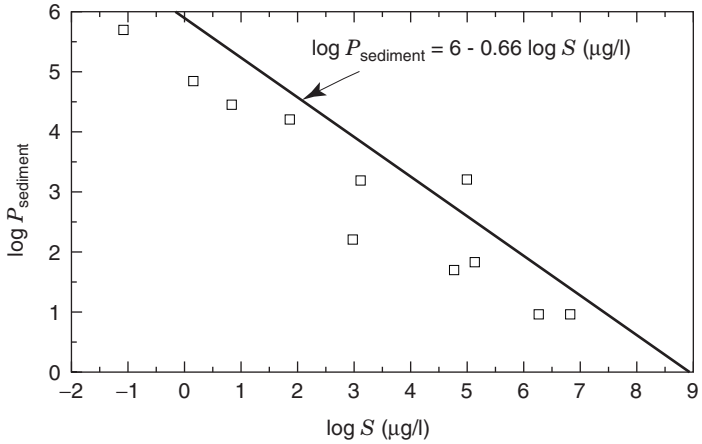


Figure 9. Plot of log water solubility and log partition coefficient (log $P_{sediment}$) for organic compounds adsorbed on natural sediment collected in Coyote Creek, California (from EPA-60017-78-074, May 1978).

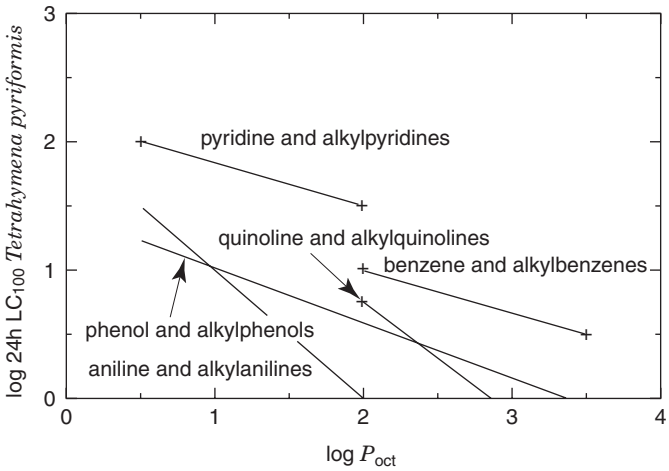


Figure 10. A least squares linear regression of log 24h LC_{100} (mMole/l) vs. log P_{oct} for the ciliate *Tetrahymena pyriformis.*

Table 8. Phenol and Chlorinated Phenols: Structure–Toxicity Data.

	24h LC_{50} (ppm)[a]					
	goldfish (1850)	guppies (1833)	solub.ppm	log P_{oct} exp.	log P_{oct} calculated	BFC goldfish[b]
phenol	60	30	67,000 (10°C)	1.47	1.55	1.9
o-chlorophenol	16	11	28,500 (20°C)	2.17	2.27	6.4
m-chlorophenol	–	6.5	–	2.48	2.27	–
p-chlorophenol	9.0	–	27,100 (20°C)	2.41	2.27	10.0
2,4-dichlorophenol	7.8	4.2	4,600 (20°C)	–	2.93	34
3,5-dichlorophenol	–	2.7	–	–	2.93	–
2,4,6-trichlorophenol	10.0	–	800 (24°C)	3.37	3.69	20
2,4,5-trichlorophenol	1.7	–	1,190 (25°C)	3.72	3.69	62
2,3,5-trichlorophenol	–	1.6	–	–	3.69	–
2,3,6-trichlorophenol	–	5.1	–	–	3.69	–
3,4,5-trichlorophenol	–	1.1	–	–	3.69	–
2,3,4,6-tetrachlorophenol	0.75	–		–	4.42	93
2,3,4,5-tetrachlorophenol	–	0.77	–	–	4.42	–
2,3,5,6-tetrachlorophenol	–	1.37	–	–	4.42	–
pentachlorophenol	0.27	0.38	14 (20°C)	5.01	5.19	475

[a]pH 7.3
[b]Values were obtained in goldfish that died in the concentration of each chlorophenol closest to 24h LC_{50}.

Figure 12 shows that the correlation between the aqueous solubility expressed in ppm (mg/l) and LD_{50} for goldfish are still good enough.

6. Henry's Constant (H)

Henry's constant *(H)* is a physical property of a chemical that is a measure of its partitioning nature between the two phases in an air-water binary system. By virtue of its definition, *H* often dictates where and how a chemical tends to concentrate or "accumulate" at equilibrium. Chemicals with low *H* tend to accumulate in the aqueous phase, whereas those with high *H* partition more into the gas phase.

Because air and water are the major "compartments" of the model ecosphere, and water is considered to act as the link between all its other compartments, knowledge of *H* is very important in assessing the environmental risks associated with a chemical. *H* is also a key parameter in determination of the "cleanup" process of choice for contaminated sites and in detailed design of decontamination processes.

Henry's constant is also called the "air-to-water ratio" or the "air-water partition coefficient" and can consequently be expressed as the ratio of concentrations of a chemical in air and in water at equilibrium.

$$H = \frac{C_L}{C_W}$$

where C_L = concentration of the chemical in the air in mg/m^3
C_W = concentration of the chemical in the water in µ*m*µg/l (= mg/m^3)

This equation represents the dimensionless *H* because the concentrations have been expressed in the

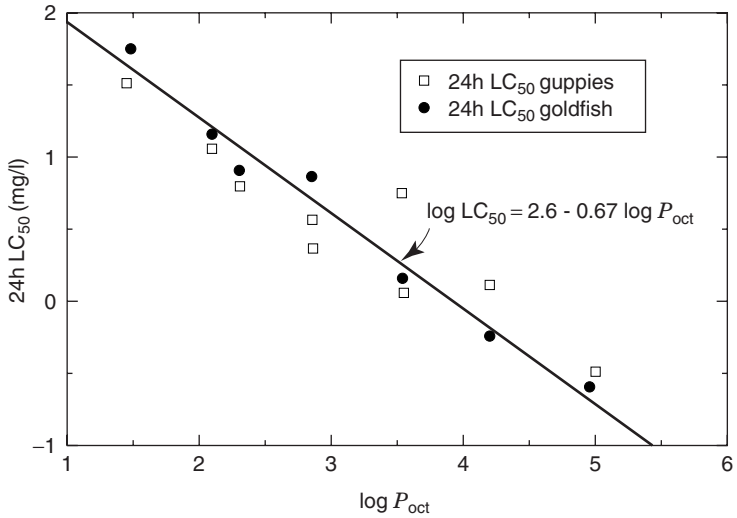


Figure 11. Toxicity versus octanol/water distribution coefficient for goldfish and guppies (after 1833 and 1850) exposed to phenol and chlorinated phenols.

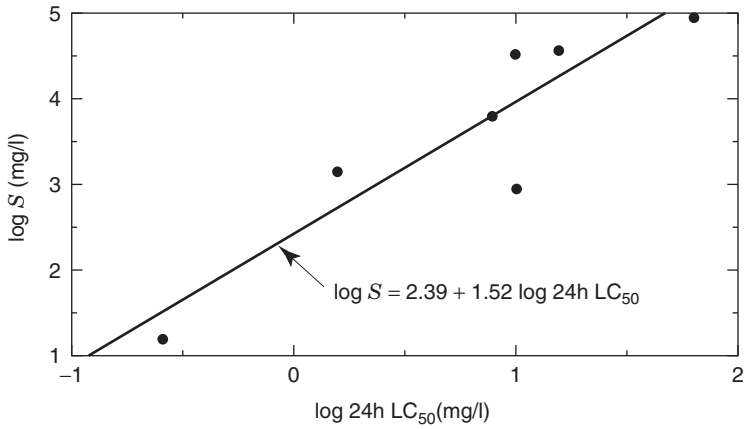


Figure 12. Toxicity and accumulation of phenols in goldfish compared to the aqueous solubility and octanol/water partition coefficients (after 1850).

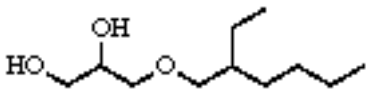


Figure 13. Relationship between Henry's constant *(H)* and the water solubility *(S)* of *n* - alkanes.

same unit. This is the most convenient way of expressing H because it yields right away the necessary information about the partitioning of a chemical between the two phases air and water.

If a chemical behaves as an ideal gas in the atmosphere, then H can be calculated from the saturation concentration in the air and in the water (solubility).

The vapor pressure and a chemical's water solubility are the key physical properties that are used in the calculation of H.

A number of simple equations have been proposed by different researchers to calculate H. Henry's constant can be written in the form

$$H = \frac{P_{vp}}{S}$$

where P_{vp} is the vapor pressure in atm, and S is the aqueous solubility in mol/m^3. The dimension of this form is atm × m^3/mol. I must confess that with this way of expressing Henry's constant, I lose the sense of the partitioning of a chemical between air and water. Most environmental advisors share this feeling. However, the equation can easily be transformed to yield a dimensionless H .

where

$$H = \frac{P_{vp} \times \text{mw}}{0.062 \times S \times T}$$

P_{vp} = vapor pressure in mm Hg
mw = molecular weight
S = water solubility in mg/l
T = temperature in K
0.062 = universal gas constant

or, if the vapor pressure is expressed in pascals, then

$$H = \frac{P_{vp} \times \text{mw}}{8.3 \times S \times T}$$

where P_{vp} = vapor pressure in Pa and 8.3 = universal gas constant. In both equations, H is dimensionless.

Mackay and Shiu have critically reviewed Henry's constant for 167 chemicals of environmental concern. They used vapor pressure and solubility data to calculate a "recommended" Henry's constant in the absence of experimental data and concluded that "considerable discrepancies exist in the literature even for common compounds." An important reason for these discrepancies is the lack of reliable solubility data for compounds that have a poor solubility and the interacting forces on the molecular level for polar compounds, which generally have a very high solubility. The outlier in Figure 15 (a too-low calculated *H in comparison with the curve) is probably caused by a too-low vapor pressure mentioned in the literature.*

I believe that bringing together vapor pressure, solubility, and H data for homologous series of chemicals will promote the establishment of more accurate values for all properties. Figures 12, 13, and 14 present, for a number of homologous series of chemicals, the relationship among these three parameters.

In Figures 12, 13, 14, and 15, a relationship is shown between H and water solubility in order to complement the relationships that exist in homologous series between water solubility and (for example) toxicity toward aquatic organisms, biodegradability in soil, and soil sorption (K_{oc}).

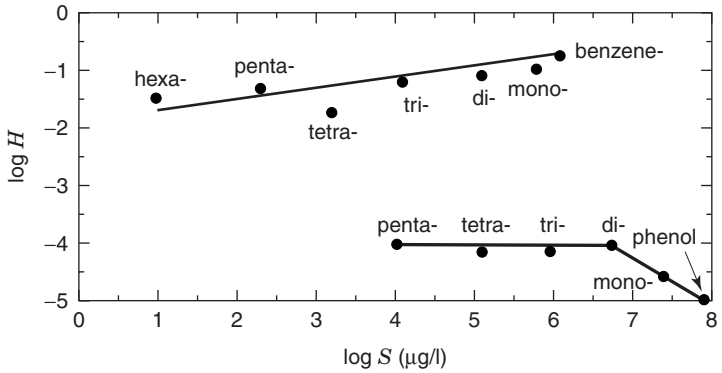


Figure 14. Relationship between the calculated Henry's constant *(H)* and water solubility (*S*) of benzene, phenol, and their chlorinated derivatives.

B. AIR POLLUTION FACTORS

1. Conversion between Volume and Mass Units of Concentration

The physical state of gaseous air pollutants at atmospheric concentrations may be described generally by the ideal gas law:

$$pv = nRT \tag{1}$$

where p = absolute pressure of gas
v = volume of gas
n = number of moles of gas
T = absolute temperature (K)
R = universal gas constant

The number of moles *(n)* may be calculated from the weight of pollutant *(W)* and its molecular weight *(m)* by

$$n = \frac{W}{m} \tag{2}$$

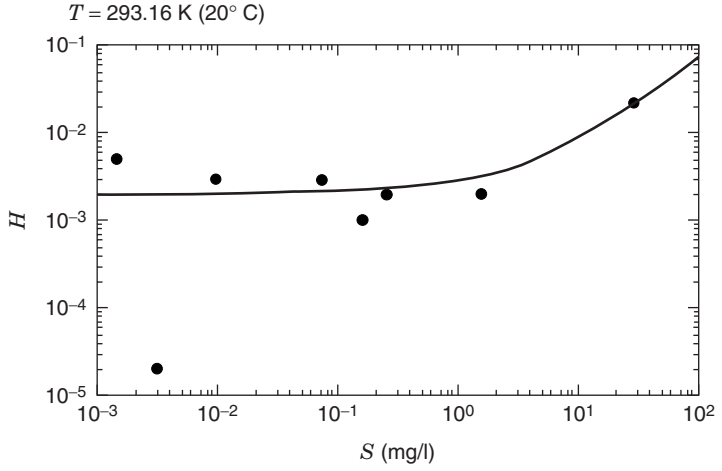


Figure 15. Relationship between the calculated Henry's constant *(H) and water solubility of polycyclic aromatics.*

Substituting Eq. (2) into Eq. (1) and rearranging yield

$$v = \frac{WRT}{pm} \tag{3}$$

Parts per million refers to the volume of pollutant *(v)* per million volumes of air *(V):*

$$ppm = \frac{v}{10^6 V} \tag{4}$$

Substituting Eq. (3) into Eq. 4 yields

$$ppm = \frac{W}{V}\,\frac{RT}{pm\ 10^6} \tag{5}$$

By using the appropriate values for variables in Eq. (5), a conversion from volume to mass units of concentration for methane may be derived as shown below:

$$\begin{aligned} T &= 293.16\ \text{K}\ (20°\text{C}) \\ p &= 1\ \text{atm} \\ m &= 16\ \text{g/mol} \\ R &= 0.08205\ \text{1-atm/mol K} \end{aligned}$$

$$\text{ppm} = \frac{W(\text{g}) \times 10^3\ (\text{mg/g})}{V(1) \times^{-3}\ (\text{m}^3/\text{l})} \times \frac{0.08205\ (\text{1-atm/mol K}) \times 293.16\ (\text{K})}{1(\text{atm}) \times 16\ (\text{g/mol}) \times 10^6}$$

$$1\ \text{ppm} = 0.665\ \text{mg/m}^3$$

$$1\ \text{mg/m}^3 = 1.504\ \text{ppm}$$

Whenever conversion factors are used, reference must be made to the pressure and temperature at which the conversion factors have been calculated. Unfortunately, the conditions of "Air at Normal Conditions" or "Standard Air" or "Air at STP" (STP = Standard Temperature and Pressure) often vary from country to country. ASTM D1356-60 defines "Air at Normal Conditions" as follows: "Air at 50 percent relative humidity, 70°F (21°C), and 29.92 inches of mercury (760 millimeters of mercury). These conditions are chosen in recognition of the data which have been accumulated on air-handling equipment. They are sufficiently near the 25°C and 760 millimeters of mercury commonly used for indoor air contamination work that no conversion or correction ordinarily need be applied."

For outdoor air (ambient air) pollution control, it is important to use the correct conversion factors. "Normal conditions" vary from 0°C and 760 mm Hg (dry) for Canada over 20°C and 760 mm Hg for Australia to 25°C and 760 mm Hg for Brazil.

Calculations of minimum chimney heights, in order to ensure sufficient dispersion of the waste gases before they reach ground level, are often based on the difference between Maximum Immission Concentration (M.I.C.) and the existing pollutant concentration at ground level. Significant differences in chimney heights can be obtained by not using the appropriate conversion factors.

Because of the lack of "standardization" of "standard" conditions worldwide, and because outdoor and indoor conditions are different, different conversion factors will continue to be used. The conversion factors on the data sheets should, therefore, be regarded only as approximate values. Knowing the molecular weight of the compound, one can find the correct values at 0°C and 20°C in Tables 9 and 10.

2. Odor

2.1. Threshold Odor Concentration (T.O.C.). A starting point in relation to quantification of odors seems to be the definition of a threshold odor concentration. At least three different odor thresholds have been determined: the absolute perception threshold, the recognition threshold, and the objectionability threshold.

At the perception threshold concentration, one is barely certain that an odor is detected, but it is

Table 9. Gaseous Air Pollutants: Conversion between Volume Units (ppm) and Mass Units (mg/m^3) of Concentration at 0°C and 760 mm Hg (m = molar weight).

m	1 ppm = mg/m^3	1 mg/m^3 = ppm	m	1 ppm = mg/m^3	1 mg/m^3 = ppm	m	1 ppm = mg/m^3	1 mg/m^3 = ppm	m	1 ppm = mg/m^3	1 mg/m^3 = ppm
16	0.714	1.401	51	2.277	0.439	86	3.839	0.260	121	5.401	0.185
17	0.759	1.318	52	2.321	0.431	87	3.884	0.257	122	5.446	0.184
18	0.804	1.244	53	2.366	0.423	88	3.929	0.255	123	5.491	0.182
19	0.848	1.179	54	2.411	0.415	89	3.973	0.252	124	5.536	0.181
20	0.892	1.121	55	2.455	0.407	90	4.018	0.249	125	5.580	0.179
21	0.937	1.067	56	2.500	0.400	91	4.062	0.246	126	5.625	0.178
22	0.982	1.018	57	2.545	0.393	92	4.107	0.243	127	5.670	0.176
23	1.027	0.974	58	2.598	0.386	93	4.152	0.241	128	5.714	0.175
24	1.071	0.934	59	2.634	0.380	94	4.196	0.238	129	5.759	0.174
25	1.116	0.896	60	2.679	0.373	95	4.241	0.236	130	5.804	0.172
26	1.161	0.861	61	2.723	0.367	96	4.286	0.233	131	5.848	0.171
27	1.205	0.830	62	2.768	0.361	97	4.330	0.231	132	5.893	0.170
28	1.250	0.800	63	2.812	0.356	98	4.375	0.229	133	5.937	0.168
29	1.295	0.772	64	2.857	0.350	99	4.420	0.226	134	5.982	0.167
30	1.339	0.747	65	2.902	0.344	100	4.464	0.244	135	6.027	0.166
31	1.384	0.722	66	2.946	0.339	101	4.509	0.222	136	6.071	0.165
32	1.429	0.700	67	2.991	0.334	102	4.554	0.217	137	6.116	0.164
33	1.473	0.679	68	3.036	0.329	103	4.598	0.217	138	6.161	0.163
34	1.518	0.659	69	3.080	0.325	104	4.643	0.215	139	6.205	0.161
35	1.562	0.640	70	3.125	0.320	105	4.687	0.213	140	6.250	0.160
36	1.607	0.622	71	3.170	0.315	106	4.732	0.211	141	6.295	0.159
37	1.652	0.605	72	3.214	0.311	107	4.777	0.209	142	6.339	0.158
38	1.696	0.590	73	3.259	0.307	108	4.821	0.207	143	6.384	0.157
39	1.741	0.574	74	3.304	0.303	109	4.866	0.206	144	6.429	0.156
40	1.786	0.560	75	3.348	0.299	110	4.911	0.204	145	6.473	0.154
41	1.830	0.546	76	3.393	0.295	111	4.955	0.202	146	6.518	0.153
42	1.875	0.533	77	3.437	0.291	112	5.000	0.200	147	6.562	0.152
43	1.920	0.521	78	3.482	0.287	113	5.045	0.198	148	6.607	0.151
44	1.964	0.509	79	3.527	0.284	114	5.089	0.197	149	6.652	0.150
45	2.009	0.498	80	3.571	0.280	115	5.134	0.195	150	6.696	0.149
46	2.054	0.487	81	3.616	0.277	116	5.179	0.173	151	6.741	0.148
47	2.098	0.477	82	3.661	0.273	117	5.223	0.192	152	6.786	0.147
48	2.143	0.467	83	3.705	0.270	118	5.268	0.190	153	6.830	0.146
49	2.187	0.457	84	3.750	0.267	119	5.312	0.188	154	6.875	0.145
50	2.232	0.448	85	3.795	0.264	120	5.357	0.187	155	6.920	0.145

too faint to identify further. Furthermore, the sense-of-smell results must be a statistical average because of biological variability. The thresholds normally used are those for 50% and for 100% of the odor panel. When the T.O.C. is given without any qualification, it is usually the 50% recognition threshold.

For the sake of clarity, a number of definitions are listed here:

- *Hedonic Tone:* the pleasure or displeasure that the odor judge associated with the odor quality being observed.
- *Absolute Odor* Threshold: the concentration at which 50% of the odor panel detected the odor.
- *50% Recognition Threshold:* the concentration at which 50% of the odor panel defined the odor as being representative of the odorant being studied.
- *100% Recognition Threshold:* the concentration at which 100% of the odor panel defined the odor as being representative of the odorant being studied.

Table 10. Gaseous Air Pollutants: Conversion between Volume Units (ppm) and Mass Units (mg/m^3) of Concentration at 20°C and 760 mm Hg (m = molar weight).

m	1 ppm = mg/m^3	1 mg/m^3 = ppm	m	1 ppm = mg/m^3	1 mg/m^3 = ppm	m	1 ppm = mg/m^3	1 mg/m^3 = ppm	m	1 ppm = mg/m^3	1 mg/m^3 = ppm
15	0.624	1.603	51	2.120	0.472	87	3.617	0.276	123	5.113	0.196
16	0.665	1.504	52	2.162	0.463	88	3.658	0.273	124	5.155	0.194
17	0.707	1.414	53	2.203	0.454	89	3.700	0.270	125	5.196	0.192
18	0.748	1.337	54	2.245	0.445	90	3.741	0.267	126	5.238	0.191
19	0.790	1.266	55	2.286	0.437	91	3.783	0.264	127	5.280	0.189
20	0.831	1.203	56	2.328	0.340	92	3.824	0.261	128	5.321	0.188
21	0.873	1.145	57	2.369	0.422	93	3.866	0.259	129	5.363	0.186
22	0.915	1.093	58	2.411	0.415	94	3.908	0.256	130	5.404	0.185
23	0.956	1.046	59	2.453	0.408	95	3.949	0.253	131	5.446	0.184
24	0.998	1.002	60	2.494	0.401	96	3.991	0.251	132	5.488	0.182
25	1.039	0.962	61	2.536	0.394	97	4.032	0.248	133	5.529	0.181
26	1.081	0.925	62	2.577	0.388	98	4.074	0.245	134	5.570	0.180
27	1.122	0.891	63	2.619	0.382	99	4.115	0.243	135	5.612	0.178
28	1.164	0.859	64	2.660	0.376	100	4.157	0.241	136	5.654	0.177
29	1.206	0.829	65	2.702	0.370	101	4.199	0.238	137	5.695	0.176
30	1.247	0.802	66	2.744	0.364	102	4.240	0.236	138	5.737	0.174
31	1.289	0.776	67	2.785	0.359	103	4.282	0.233	139	5.778	0.173
32	1.330	0.752	68	2.827	0.354	104	4.323	0.231	140	5.820	0.172
33	1.372	0.729	69	2.868	0.349	105	4.365	0.229	141	5.861	0.171
34	1.413	0.708	70	2.910	0.344	106	4.406	0.227	142	5.903	0.169
35	1.455	0.687	71	2.951	0.339	107	4.448	0.225	143	5.945	0.168
36	1.487	0.668	72	2.993	0.334	108	4.490	0.223	144	5.986	0.167
37	1.538	0.650	73	3.035	0.329	109	4.531	0.221	145	6.028	0.166
38	1.580	0.633	74	3.076	0.325	110	4.573	0.219	146	6.070	0.165
39	1.621	0.617	75	3.118	0.321	111	4.614	0.217	147	6.111	0.164
40	1.663	0.601	76	3.159	0.317	112	4.656	0.215	148	6.152	0.163
41	1.704	0.587	77	3.201	0.312	113	4.697	0.213	149	6.194	0.161
42	1.746	0.572	78	3.242	0.308	114	4.739	0.211	150	6.236	0.160
43	1.788	0.559	79	3.284	0.305	115	4.780	0.209	151	6.277	0.159
44	1.829	0.547	80	3.326	0.301	116	4.822	0.207	152	6.319	0.158
45	1.871	0.534	81	3.367	0.297	117	4.864	0.206	153	6.360	0.157
46	1.912	0.523	82	3.409	0.293	118	4.905	0.204	154	6.402	0.156
47	1.954	0.512	83	3.450	0.290	119	4.947	0.202	155	6.443	0.155
48	1.995	0.501	84	3.492	0.286	120	4.988	0.200	156	6.485	0.154
49	2.037	0.491	85	3.533	0.283	121	5.030	0.199	157	6.526	0.153
50	2.079	0.481	86	3.575	0.280	122	5.072	0.197	158	6.568	0.152

- P.P.T.$_{50}$ *(Population Perception Threshold):* the concentration at which 50% of the people who have a capable sense of smell are able to detect an odor.
- P.I.T.$_{50}$ *(Population Identification Threshold):* the concentration at which 50% of the population can identify and describe the odor, or at least compare its quality with another odor.
- I.P.T. *(Individual Perception Threshold):* the lowest concentration of a particular odor at which a subject gave both an initial positive response and a repeated response when the same stimulus was given a second time.
- T.O.N. *(Threshold Odor Number):* the number of times a given volume of the sample has to be diluted with clean, odorless air to bring it to the threshold level (detected by 50% of a panel of observers). The T.O.N. is thus the value of the intensity of an odor expressed in odor units.
- O.I. *(Odor Index):* a dimensionless term that is based on vapor pressure and odor recognition threshold (100%) as follows:

$$\text{O.L.} = \frac{\text{vapor pressure (ppm)}}{\text{odor recognition threshold (100\%) (ppm)}}$$

where 1 atm = 1,000,000 ppm.

The O.I. is, in essence, a ratio between the driving force to introduce an odorant into the air and the ability of an odorant to create a recognized response. It is a concept that provides information pertaining to the potential of a particular odorant to cause odor problems under evaporative conditions. The O.I. was first proposed by T.M. Hellman and F.H. Small in 1973 as a tool to predict whether complaints are likely to arise under certain evaporative conditions. Examples of evaporative conditions include spills, leaks, and solvent evaporation processes. The O.I. takes into account the vapor pressure of a compound, which is a qualitative measure of the potential of an odorant to get into the air, as well as the odor recognition threshold, which is a measure of the detectability of an odorant in the air. The values of O.I. listed in Table 11 range from a high of 1,052,000,000 for isopropylmercaptan to a low of 0.2 for maleic anhydride.

In its present form, the O.I. does not differentiate between "good" and "bad" odor qualities. It could incorporate a quality factor that would reflect consideration of the odor quality, e.g., a "bad" odor might have a higher quality factor than a "good" odor. Because the O.I. is proposed as a general indicator of odor pollution, it would be reasonable to utilize categories of odor index values for comparison, rather than comparing individual values. These values can be separated into three categories: Category I-O.I. higher than 1,000,000 (high odor potential); Category II-O.I. between 100,000 and 1,000,000 (medium odor potential); Category III-O.I. lower than 100,000 (low potential). The odor indexes calculated by the author are based on the highest 100% recognition levels mentioned in the literature, including those mentioned by Hellman and Small. The compounds have been arranged per chemical class in Table 12.

The threshold odor concentrations for 100% recognition and the associated odor indexes are shown graphically in Figures 16, 17, and 18. For each chemical class, we observe a smooth evolution of the O.I. and of the 100% recognition level as a function of the molecular weight of the compounds.

The odor index, which is a function of the vapor pressure of the product, must be calculated at the temperature of the evaporating product. The O.I. values mentioned in the foregoing tables have all been calculated at 20°C. It is clear that certain products, in practice, will have a higher odor index than mentioned in these lists because they are handled at higher temperatures.

The 100% recognition level has been taken as the basis for calculation of the O.I. The 100% recognition level is the concentration at which all members of an odor panel recognize the odor. It shows less variation than the absolute perception level, which is much lower. For this reason, the highest recognition level mentioned in the literature has been taken as the basis for these calculations.

In general, we can say that straight-chain aliphatic molecules have the highest recognition level and that the level decreases with increasing molecular weight. For nearly every class of straight-chain molecules, the threshold odor concentration decreases with increasing molecular weight. Tables 12 and 13 show the influence of functional groups on the 100% recognition levels and on the odor indexes. The functional groups of the small molecules have dominating influence on their threshold, as shown in Table 14 for molecules with one carbon atom. Branched chains often exhibit different results, probably because of steric effects. The functional groups can intensify each other's effects on the threshold odor concentration, but they can also reduce the effect, depending on their position in the molecule. In general, a double bond reduces the threshold odor concentration. This is the case in aliphatic compounds, mercaptans, and ketones, but not in aldehydes, as shown in Table 15. The merit of th e previous analysis is that the T.O.C. of products for which only the formula is known can be estimated by extrapolation.

2.2. Comparison of Techniques for Organoleptic Odor-Intensity Assessment

1. Odor room. Odor threshold can be determined by using an *odor room* . A known volume of odorous air is admitted to the room of volume V until the volume S of odorous air is found that just, and only just, allows the odor to be detected within the room. The ratio V/S at this point is the threshold dilution.

Table 11. 100% Odor Recognition Concentration and Odor Index of Chemicals, Arranged by Chemical Class.

Chemical	Formula	Molecular Weight	Odor Index	100% Odor Recognition Concentration
BTX aromatics				
benzene	C_6H_6	78	300	300 ppm
toluene	$C_6H_5CH_3$	92	720	40 ppm
xylenes	$C_6H_4(CH_3)_2$	106	360–18,200	0.4–20 ppm
1,2,3,5-tetramethyl-benzene	$C_6H_2(CH_3)_4$	134	136,000	2 ppb
isopropylbenzene	$C_6H_5CH(CH_3)_2$	120	89,600	40 ppb
ethylesters				
ethylacetate	$CH_3COOC_2H_5$	88	1,900	50 ppm
ethylbutyrate	$C_3H_7COOC_2H_5$	116	1,982,000	7 ppb
ethyl n-valerate	$C_4H_9COOC_2H_5$	132	178,000	60 ppb
ethylhexanoate	$C_5H_{11}COOC_2H_5$	144	760,000	4 ppb
ethylpelargonate	$C_8H_{17}COOC_2H_5$	186	109,000	1 ppb
ethyldecanate	$C_9H_{19}COOC_2H_5$	200		0.17 ppb
ethylundecylate	$C_{10}H_{21}COOC_2H_5$	214		0.56 ppb
methylesters				
methylformate	$HCOOCH_3$	60	300	2,000 ppm
methylacetate	CH_3COOH_3	74	1,100	200 ppm
methylbutyrate	$C_3H_7COOH_3$	102	19,000,000	2 ppb
ketones				
acetone	CH_3COCH_3	58	720	300 ppm
methylethylketone	$CH_3COC_2H_5$	72	3,800	30 ppm
diethylketone	$C_2H_5COC_2H_5$	86	1,900	9 ppm
methylisobutylketone	$CH_3COCH_2CH(CH_3)_2$	100	1,000	8 ppm
methylisoamylketone	$CH_3COCH_2CH_2CH(CH_3)_2$	114	75,100	70 ppb
ethylisoamylketone	$C_2H_5COCH_2CH_2CH(CH_3)_2$	128	660	4 ppm
2 pentanone	$CH_3—CO—CH_2—CH_2—CH_3$ $CH_3—CO—CH_2CH_2—$	86	2,000	8 ppm
2-heptanone	$CH_2CH_2CH_3$	114	171,000	20 ppb
2-octanone	$CH_3CO(CH_2)_5CH_3$	128	4	250 ppm
diisobutylketone	$[(CH_3)_2CHCH_2]_2CO$	142	45	50 ppm
mercaptans				
isoamylmercaptan	$(CH_3)_2CHCH_2CH_2SH$	104.2		0.2 ppb
methylmercaptan	CH_3SH	48	53,300,000	35 ppb
ethylmercaptan	CH_3CH_2SH	62	289,500,000	2 ppb
propylmercaptan	$CH_3CH_2CH_2SH$	76	263,000,000	0.7 ppb
isopropylmercaptan	$(CH_3)_2CHSH$	76	1,052,000,000	0.2 ppb
butylmercaptan	$CH_3CH_2CH_2CH_2SH$	90	49,000,000	0.8 ppb
isobutylmercaptan	$(CH_3)_2CHCHSH$	90.2		0.83 ppb
t butylmercaptan	$(CH_3)_3CSH$	90.2		0.81 ppb
phenylmercaptan	C_6H_5SH	110	940,000	0.2 ppb
o-tolylmercaptan	$C_6H_5(CH_3)SH$	125	39,000	2 ppb

Table 11. (*Continued*)

Chemical	Formula	Molecular Weight	Odor Index	100% Odor Recognition Concentration
sulfides				
hydrogen sulfide	H_2S	34	17,000,000	1 ppm
methylsulfide	$(CH_3)_2S$	62	2,760,000	0.1 ppm
ethylsulfide	$(CH_3—CH_2)_2S$	90	14,400,000	4 ppb
propylsulfide	$(C_3H_7)_2S$	118		19 ppb
butylsulfide	$(CH_3CH_2CH_2CH_2)_2S$	146	658,000	2 ppb
isoamylsulfide	$(CH_3)_2CHCH_2CH_2]_2S$	174	1,640,000	0.4 ppb
phenylsulfide	$(C_6H_5)_2S$	186	14,000	4 ppb
pentysulfide	$(C_5H_{11})_2S$	174		0.028 ppb
di-isopropylsulfide	$(CH_3)_2CH]_2S$	118		3.2 ppb
acrylates				
ethylacrylate	$CH_2═CH—COOC_2H_5$	100	138,160,000	1 ppb
isobutylacrylate	$CH_2═CH—COOCH_2—CH(CH_3)_2$	128	525,000	20 ppb
ethylhexylacrylate	$CH_2═CH—COOC_8H_{17}$	184	7,300	150 ppb
butylrates				
methylbutyrate	$CH_3—CH_2—CH_2—COOCH_3$	102	11,000,000	3 ppb
ethylbutyrate	$CH_3—CH_2—CH_2COOC_2H_5$	116	1,982,000	7 ppb
amines				
ammonia	NH_3	17	167,300	55 ppm
methylamine	CH_3NH_2	31	940,000	3 ppm
ethylamine	$CH_3CH_2NH_2$	45	1,445,000	0.8 ppm
isopropylamine	$(CH_3)_2CHNH_2$	59	637,000	1 ppm
butylamine	$CH_3(CH_2)_3NH_2$	73	395,000	0.3 ppm
dimethylamine	$(CH_3)_2NH$	45	280,000	6 ppm
diethylamine	$(C_2H_5)_2NH$	73	880,000	0.3 ppm
dipropylamine	$(C_3H_7)_2NH$	101	395,000	0.1 ppm
di-isopopylamine	$[(CH_3)_2CH]_2NH$	101	108,000	0.8 ppm
dibutylamine	$(C_4H_9)_2NH$	129	5,500	0.5 ppm
trimethylamine	$(CH_3)_3N$	59	493,500	4 ppm
tri-ethylamine	$(C_2H_5)_3N$	101	235,000	0.3 ppm
ethanolamine	$HOCH_2CH_2NH_2$	61	130	5 ppm
methylethanolamine	$HOCH_2CH_2NHCH_3$	75	400	3 ppm
dimethylethanolamine	$HOCH_2CH_2N(CH_3)_2$	89	292,000	40 ppb
alkanes				
ethane	CH_3CH_3	30	25,300	1,500 ppm
propane	C_3H_8	44	425	11,000 ppm
butane	C_4H_{10}	58	480	5,000 ppm
isobutane	C_4H_{10}	58	3,000,000	2 ppm
pentane	C_5H_{12}	72	570	900 ppm
heptane	C_7H_{16}	100	200	200 ppm
octane	C_8H_{18}	114	100	200 ppm
nonane	C_9H_{20}	128	9,800	0.4 ppm
undecane	$C_{11}H_{24}$	156	8,400	0.2 ppm

Table 11. (*Continued*)

Chemical	Formula	Molecular Weight	Odor Index	100% Odor Recognition Concentration
alkenes				
ethene	$CH_2=CH_2$	28	57,100	800 ppm
propene	$CH_3CH=CH_2$	42	14,700	80 ppm
1-butene	$CH_3CH_2CH=CH_2$	56	43,480,000	0.07 ppm
2-butene	$CH_3CH=CHCH_3$	56	3,330,000	0.6 ppm
isobutene	$(CH_3)_2C=CH_2$	56	4,640	0.6 ppm
1-pentene	$CH_3CH_2CH_2CH=CH_2$	70	376,000,000	2 ppb
1-decene	$CH_3(CH_2)_7CH=CH_2$	140	3,900,000	20 ppb
ethers				
ethylether	$CH_3CH_2OCH_2CH_3$	74	1,939,000	0.3 ppm
isopropylether	$(CH_3)_2CHOCH(CH_3)_2$	100	3,227,000	0.06 ppm
butylether	$C_4H_9OC_4H_9$	130	13,400	0.5 ppm
phenylether	$C_6H_5OC_6H_5$	170	130	0.1 ppm
aldehydes				
formaldehyde	HCHO	30	5,000,000	1 ppm
acetaldehyde	CH_3CHO	44	4,300,000	0.3 ppm
propionaldehyde	CH_3CH_2CHO	58	3,865,000	0.08 ppm
acrylaldehyde (acroleine)	$CH_2=CHCHO$	56	19,300	20 ppm
butyraldehyde	$CH_3CH_2CH_2CHO$	72	2,395,000	40 ppb
isobutyraldehyde	$(CH_3)_2CHCHO$	72	948,000	300 ppb
crotonaldehyde	$CH_3CH=CHCHO$	70	125,000	0.2 ppm
methylpentaldehyde	$C_5H_{12}CHO$	101	131,500	0.15 ppm
furfuraldehyde	C_4H_3OCHO	96	5,260	0.2 ppm
benzaldehyde	C_6H_5CHO	106	22,000	5 ppb
cinnamaldehyde	$C_6H_5CH=CHCHO$	132	131,500	2 ppb
acids				
formic acid	HCOOH	46	2,200	20 ppm
acetic acid	CH_3COOH	60	15,000	2 ppm
propionic acid	CH_3CH_2COOH	74	112,300	40 ppb
butyric acid	$CH_3(CH_2)_2COOH$	88	50,000	20 ppb
valeric acid	$CH_3(CH_2)_3COOH$	102	256,300	0.8 ppb
caproic acid	$CH_3(CH_2)_4COOH$	116	43,900	6 ppb
enanthic acid	$CH_3(CH_2)_5COOH$	130	7,900	20 ppb
caprylic acid	$CH_3(CH_2)_6COOH$	144	104,500	8 ppb
pelargonic acid	$CH_3(CH_2)_7COOH$	158	164,000	0.7 ppb
capric acid	$CH_3(CH_2)_8COOH$	172		1.96 ppb
lauric acid	$CH_3(CH_2)_{10}COOH$	200.3		3.4 ppb
alcohols				
methanol	CH_3OH	32	22	6,000 ppm
ethanol	CH_3CH_2OH	46	11	6,000 ppm
propanol	$CH_3CH_2CH_2OH$	60	480	45 ppm
butanol	$CH_3(CH_2)_2CH_2OH$	74	120	5,000 ppm
pentanol	$CH_3(CH_2)_3CH_2OH$	88	368	10 ppm
hexanol	$CH_3(CH_2)_4CH_2OH$	102	14,300	0.09 ppm
heptanol	$CH_3(CH_2)_5CH_2OH$	116	23,100	0.06 ppm
octanol	$CH_3(CH_2)_6CH_2OH$	130	33,000	2 ppb
decanol	$CH_3(CH_2)_8CH_2OH$	158	31,000	6 ppb
dodecanol	$CH_3(CH_2)_{10}CH_2OH$	186	1,800	7 ppb

Table 11. (*Continued*)

Chemical	Formula	Molecular Weight	Odor Index	100% Odor Recognition Concentration
phenolics				
phenol	C_6H_5OH	94	16	20 ppm
cresols	$(CH_3)C_6H_4OH$	108	60–260	0.2–0.7 ppm
acetates				
methylacetate	CH_3COOH_3	74	1,100	200 ppm
ethylacetate	$CH_3COOC_2H_5$	88	1,900	50 ppm
propylacetate	$CH_3COOC_3H_7$	102	1,600	20 ppm
isopropylacetate	$CH_3COO(iC_3H_7)$	102	2,100	30 ppm
butylacetate	$CH_3COOC_4H_9$	116	1,200	15 ppm
isobutylacetate	$CH_3COO(iC_4H_9)$	116	3,300	4 ppm
amylacetate	$CH_3COOC_5H_{11}$	130	2,500	20 ppm
isoamylacetate	$CH_3COO(iC_5H_{11})$	130	526,000	20 ppm
sec. hexylacetate	$CH_3COO(sec.C_6H_{13})$	144	12,500	0.4 ppm
octylacetate	$CH_3COOC_8H_{17}$	172	2,800	300 ppb

2. The syringe method. In the *ASTM syringe method* (ASTM D1391-57), variable volumes of odorous sample air are made up to 100 m^3 with clean air in a series of syringes. Variable volume samples may then be taken from these syringes and similarly made up to achieve yet higher dilutions and so on until odor threshold is reached. Assessment for odor is by injection into the nostril of panel members, one syringe being supplied to each person for each dilution tested. Hypodermic needles were sealed to produce end caps or joined together to produce transfer tubes in order to retain the sample within the syringes until required and to effect the dilution operations, respectively.
3. The dynamic dilution method. The general concept of *dynamic dilution* involves the mixing of sample air supplied at a known flowrate with dilution air at known flowrates. After each change in dilution flowrate, panel members to whom the issuing mixture is presented register the presence or absence of odor, and in this manner threshold dilutions are determined. In

Table 12. Classification of Chemical Classes According to Their 100% Recognition Threshold.

	Highest Odor Threshold
	alkanes
	BTX-aromatics
	alcohols
	chlorinated alkanes
	amines: tri-alkylamines
	di-alkylamines
	mono-alkylamines
	carboxylic acids
to	alkenes
	aldehydes
	sulfides
	disulfides
	trisulfides
	mercaptans
	unsaturated mercaptans
	Lowest Odor Threshold

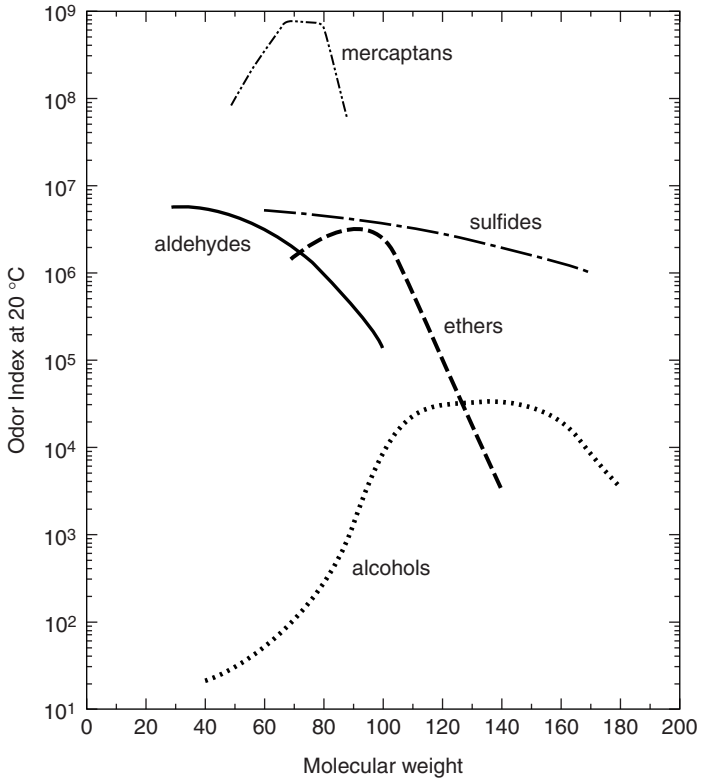


Figure 16. Odor index (at 20°C) of mercaptans, sulfides, ethers, aldehydes, and alcohols.

order to achieve a sufficiently wide range of dilutions, it is customary to use a two-stage system in which a sample of diluted odorous air from the first dilution operation is introduced to a second mixing chamber and is there diluted with flowing clean air in the second stage.

3. Hazard Potentials of Atmospheric Pollutants

Hazard potentials of atmospheric pollutants are defined by their effects on the main components of the physical environment. These effects and related hazard potentials are as follows:

Effects	*Hazard potentials*
• Global warming	Global Warming Potential (GWP)
• Ozone depletion	Ozone Depletion Potential (ODP)
• Photochemical smog formation	Photochemical Ozone Creation Potential
• Acidification	Acidification Potential (AP)
• Eutrophication	Eutrophication Potential (EP)

The atmospheric media provide an excellent matrix for photochemical or oxidative alterations of chemical contaminants. The energy provided by sunlight is able to break carbon-carbon and carbon-hydrogen bonds, cause the photodissociation of nitrogen dioxide to nitric oxide and atomic oxygen, and photolytically produce significant amounts of hydroxyl radicals. The relatively high concentration of oxygen (21 Vol %) makes it one of the most important participants in various reactions with air pollutants because the rates are concentration dependent. Similar reasoning can be used for reactions with water vapor (0.1-5 Vol %) and carbon dioxide (0.03-0.1 Vol %).

Although hydrocarbons are essential to the formation of photochemical smog, not every hydrocarbon produces the manifestations (such as eye irritation, plant damage, and visibility

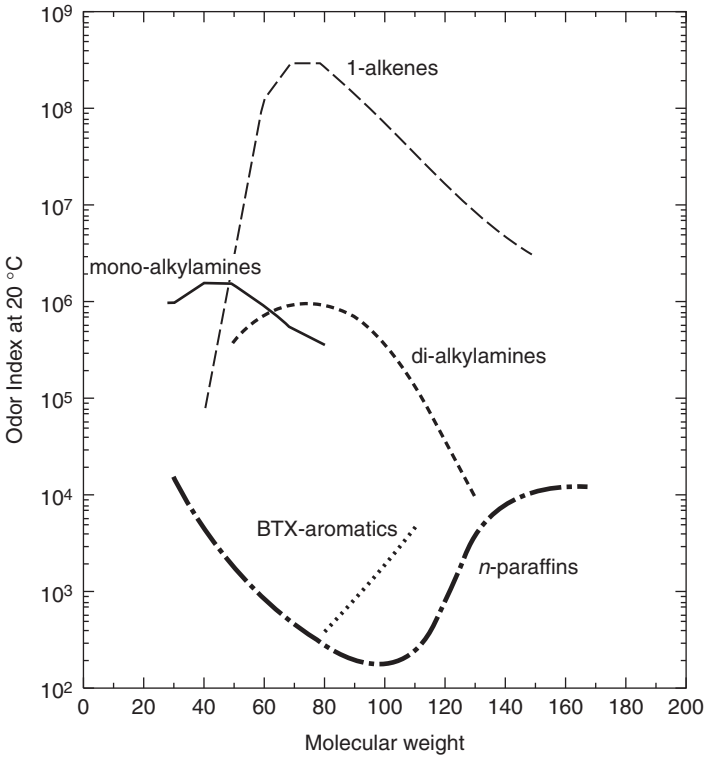


Figure 17. Odor index (at 20°C) of alkenes, mono-, di-, and tri-alkylamines, BTX-aromatics, and *n-paraffins.*

reduction) that are usually associated with smog. The reason for this is the differences in reactivity and chemical structure of hydrocarbons. We will define "reactivity" as the tendency of an atmospheric system containing organic products and nitrogen oxides to undergo a series of reactions in the presence of sunlight. However, because of the variety of ways in which smog is manifested, a number of reactivity scales have been developed. These scales cover

1. rates of hydrocarbon consumption (hydroc. cons.)
2. rates of photooxidation of NO to NO_2 (NO ox.)
3. eye irritation (EI)
4. chemical reactivity
5. OH rate constants

Relative reactivity scales were developed for the sake of comparison, using as a standard a fast hydrocarbon, set at a value of 1-100. In the Glasson-Tuesday Scale, sometimes referred to as the Jackson Scale, 2,3-dimethyl-2-butene is the reference hydrocarbon; it has a relative reactivity for NO oxidation (NO_2 formation) of 100. Table 16 presents an abbreviation of this scale.

The natural atmospheric environment is a complex, highly reactive system involving photochemical and secondary dark reactions to both organic and inorganic substances. To reproduce such a complex system in the laboratory, the following parameters must be controlled.

- spectral distribution and intensity of the light
- concentrations of the reactants in the test chamber
- temperature
- surface reactions (major difference between results in test reactors and in the atmosphere)

Four general laboratory procedures have been used to study atmospheric degradation: long-path

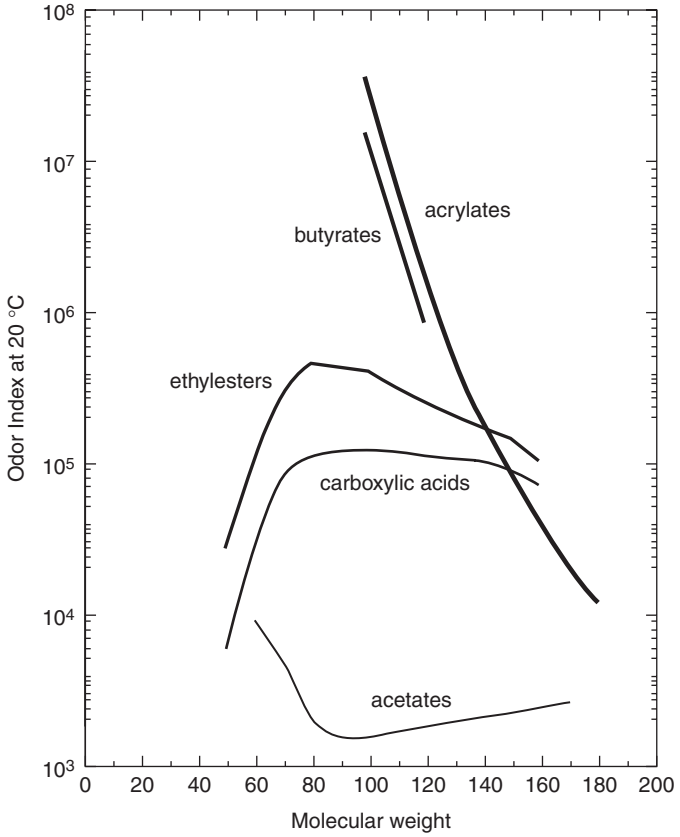


Figure 18. Odor index of butyrates, acrylates, ethylesters, carboxylic acids, and acetates.

Table 13. Classification of Chemical Classes According to Their Odor Index (at 20°C).

O.I. > 10^6:	mercaptans	
	alkenes	
	sulfides	
	butyrates	of low molecular weight
	acrylates	
	aldehydes	
	ethers	
	alkylamines	
O.I. between 10^4 and 10^6:	di-alkylamines	
	tri-alkylamines	
	higher ethylesters	
	carboxylic acids	
	aldehydes	of high molecular weight
	ethers	
	alcohols	
O.I. < 10^4:	alkanes	
	acetates	
	BTX-aromatics	
	lower alcohols	
	phenolics	

infrared (LPIR) cells, plastic containers, glass flask reactors, and smog chambers. With LPIR cells, the test chemical is placed into the cell and irradiated.

The rate of reaction is determined by following the disappearance of the test chemical and the formation of some products by *infrared analysis.* Fluorescent lights are usually used for irradiation,

Table 14. Influence of Functional Groups on T.O.C. (100% Recognition).

C_1	T.O.C. (100% recognition)
CH_4	±10,000 ppm
CH_3OH	6,000 ppm
$CHCl_3$	300 ppm
CH_2Cl_2	214 ppm
CCl_3F	209 ppm
CCl_4	200 ppm
$CH_2(OH)_2$	60 ppm
CH_3Cl	30 ppm
HCOOH	20 ppm
HC≡N	5 ppm
CH_3NH_2	3 ppm
CCl_3NO_2	1 ppm
HCOH	1 ppm
CIC≡N	1 ppm
CH_3SH	0.035 ppm
CHI_3	0.00037 ppm

and various configurations and chamber materials (stainless steel, Teflon-coated interior, and Pyrex glass) have been used. Known amounts of nitric oxide and nitrogen dioxide can be added to simulate air pollution situations.

A popular method for studying the atmospheric chemistry of both artificial and natural atmospheric samples is the use of plastic containers made of either FEP (fluorinated ethylene-propylene), Teflon, Tedlar, or Mylar. The sample is placed in the bag, irradiated with either natural or artificial sunlight, and analyzed periodically, usually by gas chromatography. Glass flask reactors are used in a similar way, but they are usually smaller in volume than the plastic bags and are more commonly irradiated with artificial lights.

Table 15. Influence of Double Bonds on the Odor Recognition Threshold.

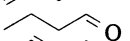
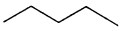
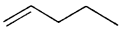
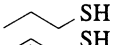
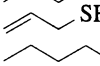
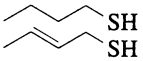
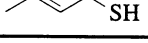
Product	Formula	100% Recognition Threshold
propionaldehyde		0.08 ppm
acroleine		20 ppm
butyraldehyde		0.04 ppm
crotonaldehyde		0.2 ppm
butane		5,000 ppm
1-butene		0.07 ppm
pentane		900 ppm
1-pentene		0.002 ppm
propylmercaptan		0.7 ppb
allylmercaptan		0.05 ppb
butylmercaptan		0.8 ppb
crotylmercaptan		0.055 ppb

Table 16. Abbreviated Glasson-Tuesday (Jackson) Reactivity Scale (Basis NO_2 Formation).

Product	Relative Reactivity
methane	0
acetylene	0
ethylene	2.9
propylene	5.9
butane	1.3
1-butene	6.0
2-butene	15
pentane	1.6
1-pentene	4.6
2-pentene	11
hexane	1.6
hexene	3.4
benzene	0.56
toluene	2.2

In order to study air pollution reactions, many researchers have resorted to large *photochemical smog chambers.* These chambers are extremely complicated and expensive to build and operate. Most chambers can be run in a dynamic or a static mode, although for simplicity and precision, the static procedure is more often used.

3.1. Atmospheric Lifetime. The temporal and spatial scales at which a component will be dispersed in the atmosphere, and therewith the potential environmental risk of a substance, are largely determined by its atmospheric residence time as illustrated by Table 17.

The removal processes from the atmosphere can be summarized as follows:

- dry deposition: uptake of material at the earth's surface by soil, water, or vegetation.
- wet deposition: uptake of material in cloud or rain droplets followed by droplet removal by precipitation.
- chemical reactions: strictly speaking, not a "real" removal mechanism (the species is transformed into another that may remain in the atmosphere), but chemical transformation may have a large impact on the removal rates by deposition.

The atmospheric lifetime may be defined as

$$\pi = \frac{1}{k_{\mathrm{d}} \times k_{\mathrm{w}} \times k_{\mathrm{c}}}$$

where k_{d} and k_w are representative removal rates for dry and wet deposition, respectively, and k_c is the pseudo-first-order chemical transformation rate.

The dry deposition rate depends strongly on the vapor/particulate partition of the compound. In the solid phase (aerosols), the particle size determines the deposition rates. Organic compounds with a vapor pressure exceeding about 10^{-4} Pa occur in the atmosphere in general in the gaseous phase. Organic compounds having lower vapor pressures are bound to aerosols, or, depending on temperature and the available aerosol surface, an equilibrium between the gaseous and aerosol forms will be established. For most of the gaseous organic compounds, the deposition velocity will be very low.

The wet removal is very efficient for particulate pollution. Again, the particle size determines the efficiency of the wet deposition process for aerosols. For gaseous compounds the solubility (Henry's constant, H) is the rate-determining factor.

In the atmospheric degradation of a compound, the following processes may contribute:

- direct photolysis

Table 17. Correspondence between Spatial and Temporal Scales (2853).

Horizontal Transport		Time	Transport Vertical
local	0–10 km	minutes	
	0–30 km	hours	boundary layer
mesoscale	>1,000 km	day	
continental	>3,000 km	several days	troposphere
hemisphere		month	
global		year	stratosphere

- reaction with hydroxyl radicals (OH radicals, OH^o)
- reaction with ozone (O_3)
- reaction with nitrate radicals (NO_3^o) and other photochemically generated species

3.1.1. DIRECT PHOTOLYSIS. For material in the troposphere (the lowest 10-12 km of the atmosphere), the UV-B and UV-A regions (wavelengths 290-450 nm) are important. Solar radiation with wavelength shorter than 290 nm hardly reaches the troposphere because it is absorbed by ozone and oxygen in the stratosphere, and radiation with longer wavelengths is in general too "soft" to break a chemical bond.

Energetically, 290-400 nm is the most important portion of the spectrum, because the associated energies are comparable to chemical bond energies (Table 18). The energy (*E)* of each quantum, in kcal, is related to the wavelength (λ) by

$$E = Lhc/\lambda$$

where

L = Avogadro's number (6.0×10^{23} molecules/mole)
h = Planck's constant (6.6×10^{-27} erg sec)
c = the speed of light (3×10^{10} cm/sec)

The energy available to bring about direct photochemical transformations amounts to about 96 kcal/mole at 300 nm, 82 kcal/mole at 350 nm, and 72 kcal/mole at 400 nm. For comparison, the energy required to break the carbon-carbon bond in ethane is about 88 kcal/mole, and a carbon-hydrogen bond in the same molecule requires about 98 kcal/mole. Energy absorption is, of course, the prime requisite for a chemical reaction. Because many pesticides absorb sunlight in the range of 290-400 nm, many different chemical transformations have been observed.

Long-living species, with atmospheric lifetimes of more than one year, will be transported to the atmosphere. Here radiation with shorter wavelengths (200-290 nm) may be of importance. Examples

Table 18. Typical Bond Dissociation Energies Related to Wavelength of Absorbed Light.

Bond	*E*, kcal/mole	λ, nm	
$CH_3CO—NH_2$	99	288	
$C_2H_5—H$	98	291	
$CH_3CO—OCH_3$	97	294	
$C_6H_5—Cl$	97	294	
$(CH_3)_2N—H$	95	300	
$H—CH_2OH$	94	303	
$CH_3—OH$	91	313	
$C_6H_5—Br$	82	347	
$C_6H_5CH_2—COOH$	68	419	(2919)

Table 19. Atmospheric Lifetimes (in hours) for Several Organic Compounds.

Compound	τ_{OH}^{o}	τ_{O3}	τ_{NO3}^{O}
methane	28,000	2.0×10^8	$>2.9 \times 10^6$
ethane	840	3.0×10^7	1.4×10^5
n-pentane	57	2.8×10^7	1.4×10^4
benzene	180	3.8×10^6	$>3.6 \times 10^4$
toluene	37	2.8×10^5	1.7×10^4
p-xylene	15	7.1×10^5	2,600
ethene	27	160	5,800
1-butene	7.4	26	93
isoprene	2.3	20	1.4
ethyne	300	2.8×10^4	2.3×10^4

include the fully halogenated chlorofluorocarbons (CFCs) and nitrous oxide (N_2O), which are nearly inert in the troposphere but are efficiently photolyzed in the stratosphere.

At present there are no structure-activity relations (SARs) or related procedures available from the literature to estimate the photolysis rate (2853).

3.1.2. REACTION WITH HYDROXYL RADICALS (OH RADICALS, OH^O). Reaction with OH radicals is the main oxidation pathway for the majority of organic pollutants. Various procedures are available to estimate the OH^o reaction rate constant. For a first estimate of k_{OH}, the SAR approach as proposed by Atkinson (2850, 2851) is recommended. It is simple to use and applicable to many classes of substituents. In general the method is accurate to within a factor of 2 for most aliphatics, olefins, and simple aromatics.

3.1.3. REACTION WITH OZONE (O_3). Ozonolysis, the reaction with ozone, is important only for unsaturated compounds containing double or triple bonds. Structure-activity relations have been developed by Atkinson and Carter (2852).

3.1.4. REACTION WITH NITRATE RADICALS (NO_3^o) AND OTHER PHOTOCHEMICALLY GENERATED SPECIES. In the atmosphere numerous other reactions will occur that may initiate the atmospheric degradation of organic compounds. Although most of these reactions are still poorly elucidated, it is expected that these degradation pathways will play only a minor role with respect to the OH and O_3 reactions. One exception may be the reaction between the NO_3^o radical and unsaturated hydrocarbons. NO_3^o is efficiently photolyzed, so this type of reaction is important only in night-time chemistry. Estimation procedures for k_{NO3} are not yet available.

The total pseudo-first-order phototransformation rate k_c, and therefore the phototransformation lifetime $\tau = 1/k_c$, is estimated by

$$k_c = J + k_{OH}[OH^o] + k_{O3}[O_3] + k_{NO3}[NO_3^O]$$

where J is the direct photolysis rate and [OH], [O_3], and [NO_3^o] are the atmospheric concentrations of the OH radical, of ozone, and of the nitrate radical, respectively.

As an illustration, Table 19 gives the decay times τ_X for various organic compounds.

$$\tau_X = 1/k_X[X]$$

where k_X is the rate constant and [X] is a representative concentration of OH^o, O_3, or NO_3^O (2853).

The decay times were calculated assuming the following representative boundary layer concentrations (2854): [O_3] = 40 ppb = 9.8 10^{11} mol/cm^3, a typical Northern hemisphere value [OH^o] = 1.2×10^6 mol/cm^3, an average daytime value [NO_3^O] = 10 ppt = 2.4×10^8 mol/cm^3, a typical night-time value for a clean atmosphere (2853)

3.2. Phototransformation. Phototransformations have to be taken into account for gases and compounds that occur in the gas phase in environmentally significant quantities. The probability that

a compound occurs in the gas phase depends not only on its vapor pressure but also on its water solubility and adsorption/desorption behavior. Therefore, even substances that have a relatively low vapor pressure (down to 10^{-3} Pa) can be found in the atmosphere in measurable quantities.

The main transformations leading to the removal of chemicals from the atmosphere involve reactions with photochemically generated species such as the hydroxyl radical (OH^o), ozone (O_3), the hydroxyperoxyl radical (HO_2^o), singlet oxygen, and the nitrate radical (NO_3^o). Direct phototransformation-that is, all transformations resulting from direct photoexcitation of the molecule-may also be important.

It is broadly agreed that reaction with OH^o is the dominant photo-induced reaction of hydrocarbons in the atmosphere. The only class of compounds known not to react rapidly with OH^o are the fully halogenated alkanes, as can be seen from Table 20, in which half-life times are given for reactions of a variety of compounds with OH^o, O_3, and HO_2. Reactions with OH^o are generally the fastest. Only for some alkenes, alkadienes, and terpenes does the rate of removal by O_3 exceed that by OH^o, and in these cases the lifetime derived from K_{OHo} is, in any case, very short (a fraction of a day). The similarity between the reactions of OH^o and O_3 molecules with these unsaturated hydrocarbons explains these observations in that both add to the double bond, forming an additional complex that afterwards disintegrates to the reaction products. In those cases where abstraction of an H atom by OH^o is the dominant pathway, the competitive reaction with O_3 is expected to be very much slower. It follows that the reaction with O_3 is usually of secondary importance in considering the fate of organic chemicals in the atmosphere. Reaction with O_3 is of interest, however, when atmospheric processes related to smog formation (where higher levels of O_3 occur) are involved.

Some evidence has been obtained that alkenes, phenols, and cresols react with NO_3^o radicals formed in photochemical smog systems. It is therefore concluded that these NO_3^o reactions are of limited importance and apply only to special environmental situations-e.g., at night in a moderately polluted atmosphere. The rate constants for reactions with singlet oxygen are very low, and this reaction can be neglected as an elimination pathway for organic molecules.

Direct phototransformation is a possible removal pathway only for those chemicals that absorb in the region of solar radiation.

Chemicals may be sorbed onto aerosol particles from the vapor phase and thence removed from the atmosphere with the aerosol. The mechanism of phototransformation of a chemical in an aerosol is not the same as that of the chemical in air because its adsorbed state, and the physiochemical properties of the aerosol substrate, influence the reactions (2716).

3.3. Global Warming. The impact of a substance on global warming depends on its IR absorption characteristics and on its atmospheric lifetime. When the substance shows absorption bands in the so-called atmospheric window (8.5-11 mm), it must be marked as a potential greenhouse gas. In this case, it is necessary to estimate the global warming potential (GWP).

The GWP is defined as the ratio of the calculated warming for each unit of mass of a gas emitted into the atmosphere to the calculated warming for a mass unit of the reference gas CFC-11 (trichlorofluoromethane). The GWP provides a measure of the cumulative effect on the radiative balance over the chemical lifetime of a mole mass emitted in the atmosphere compared to the cumulative effect of a mole mass of CFC-11.

Next to the IR absorption strength, the atmospheric lifetime is the dominant factor for the GWP. For species with lifetimes less than 1-2 years, GWP values less than 0.03 are in general expected.

A first approximation of the GWP value of a substance X is obtained by

$$GWP_x = \frac{\text{atm. lifetime}_x}{\text{atm. lifetime}_{CFC\text{-}11}} \bullet \frac{mw_{CFC\text{-}11}}{mw_x} \bullet \frac{IR_{abs_x}}{IR_{abs_{cfc\text{-}11}}}$$

where IR_{abs} is the IR absorption strength in the interval 800-1200 cm^{-1} and mw is the molecular weight.

More detailed estimates of GWP can be made by means of global atmospheric models. In these models, the fate of a pollutant is estimated by taking into account atmospheric transport and dispersion and chemical and physical transformation and removal processes on a global scale (2853, 2855, 2856).

Table 21 gives a comparison between GWP values estimated using the aforementioned equation and those calculated by means of global atmospheric models for a number of CFCs and their

Table 20. Environmental Half-lives for Reactions with OH^o, O_3, and HO_2^o and for Direct Photolysis. (*t*/2 is in days.)

Compound	*t*/2 OH^o	*t*/2 O_3	*t*/2 HO_2^o	t/2 Direct Photolysis
Alkanes				
methane	1,000	6,000,000		
ethane	30	7,000,000		
propane	7.3	1,000,000		
iso-butane	3.6	4,000,000		
n-butane	3.0	800,000	>13,000	
Haloalkane				
bromomethane		210		150,000
Aldehydes				
formaldehyde	0.8		0.6	0.23
acetaldehyde	0.5	235		1.1
Alkenes				
ethene	1.0	4.2	>13,000	
propene	0.3	0.6	>13,000	
1-butene	0.2	0.7	>13,000	
2-*cis-butene*	0.2	0.5		
2-*trans-butene*	0.1	0.03		
2-methyl-2butene	0.1	0.02		
2,3-dimethyl-2-butene	0.05	0.005	>10,000	
1-pentene	0.3	0.75		
cis-2-pentene	0.1	0.02		
1-hexene	0.25	0.7		
1-heptene	0.2	1.0		
cyclohexene	0.1	0.05		
Haloalkenes				
chloroethene	1.2	4.0		
trichloroethene	3.6	1,300		
tetrachloroethene	47	4,700		
Alkadiene				
1,3-butadiene	0.1	0.95		
Terpene				
pinene	0.3	0.05		
Alkyne				
ethyne	11	100		
Alkylbenzenes				
benzene	5.7	170,000		
toluene	1.3	29,000		
1,2-dimethylbenzene	0.6	5,000		
1,3-dimethylbenzene	0.4	6,200		
1,4-dimethylbenzene	0.8	5,000		
1,3,5-trimethylbenzene	0.2	1,100		
ethylbenzene	1.1	14,000		
2-propylbenzene	1.0	14,000		

Table 21. Comparison of GWP Values Calculated by Different Methods.

Component	Chemical Formula	IR_{abs}, cm^{-2} atm^{-1}	Atmospheric Lifetime, years	GWP by Equation	GWP by Global Model
CFC-11*	CCl_3F	2389	60	1.0	1.0
CFC-12	CCl_2F_2	3240	120	3.1	2.8–3.4
CFC-113	CCl_2FCClF_2	3401	90	1.6	1.3–1.4
CFC-114	$CClF_2CClF_2$	4141	200	4.6	3.7–4.1
CFC-115	$CClF_2CF_3$	4678	400	11.6	7.5–7.6
HCFC-22	$CHClF_2$	2554	15	0.36	0.34–0.37
HCFC-123	CF_3CHCl_2	2859	1.	0.029	0.017–0.02
HCFC-124	CF_3CHClF	4043	6.	0.19	0.092–0.10
HCFC-125	CF_3CHF_2	3908	28	0.88	0.51–0.65
HCFC-134a	CF_3CH_2F	3272	15	0.48	0.25–0.29
HCFC-141b	CCl_2FCH_3	1912	7.	0.12	0.087–0.097
HCFC-142b	$CClF_2CH_3$	2577	19	0.47	0.34–0.39
HCFC-143a	CF_3CH_3	3401	41	1.6	0.72–0.76
HCFC-152a	CHF_2CH_3	1648	1.	0.041	0.026–0.033
tetrachloromethane	CCl_4	1195	50	0.37	0.34–0.35
methylchloroform	CCl_3CH_3	1209	6.	0.055	0.022–0.026

(2853)

*Reference compound

alternatives. Provided that the atmospheric lifetimes and the IR absorption strengths are known, the former simple equation gives an approximation of GWP values within a factor of 2 compared to the GWP values calculated by means of complex atmospheric models.

3.4. Atmospheric Ozone. Concerning atmospheric ozone, it is necessary to distinguish between the possible impact of pollutants on stratospheric ozone (the ozone layer at an altitude of about 15-50 km) and the potential ozone formation in the troposphere (the lower part of the atmosphere up to about 12 km).

3.5. Stratospheric Ozone. A pollutant may have an effect on stratospheric ozone when

- it contains a Cl or Br substituent
- the atmospheric lifetime is long enough to allow for transport to the stratosphere

The potential risk of a chemical can be estimated from its ozone depletion potential (ODP). The ODP is defined as the ozone depletion in the stratosphere caused by the emission of a mass unit of a chemical relative to the ozone depletion caused by the release of a mass unit of CFC-11.

In order for a compound to have a low ODP, it must also have a very short tropospheric lifetime, so that a large fraction is destroyed before reaching the ozone layer in the stratosphere. The algorithm that has been developed for ODP has the form

$$\mathrm{ODP} = A \bullet F_r \bullet F_s$$

where A is the normalizing constant, F_r is a reactivity factor depending on the number of chlorine atoms in the molecule, and F_s is a survival factor (the fraction of molecules surviving transport to the stratosphere). ODP values range from 0.000 for trifluoromethane to 0.23 for 1,1,1-trichloro-2,2-difluoroethane (2446).

In general, ODP values approach zero for species with atmospheric lifetimes less than one year. A first approximation of the ODP value of a chemical can be based on atmospheric lifetime and the number of Cl and Br atoms per molecule and can be obtained by

Table 22. Comparison of ODP Values Calculated by Different Methods.

Component	Chemical Formula	Atmospheric Lifetime, years	ODP by Equation	ODP by Global Model
CFC-11*	CCl_3F	60	1.0	1.0
CFC-12	CCl_2F_2	120	1.5	0.87–1.0
CFC-113	CCl_2FCClF_2	90	1.1	0.76–0.83
CFC-114	$CClF_2CClF_2$	200	1.8	0.56–0.82
CFC-115	$CClF_2CF_3$	400	2.0	0.27–0.45
HCFC-22	$CHClF_2$	15	0.14	0.032–0.072
HCFC-123	CF_3CHCl_2	1.6	0.016	0.013–0.027
HCFC-124	CF_3CHClF	6.6	0.037	0.013–0.030
HCFC-125	CF_3CHF_2	28	0	0
HCFC-134a	CF_3CH_2F	15	0	0
HCFC-141b	CCl_2FCH_3	7.8	0.10	0.065–0.14
HCFC-142b	$CClF_2CH_3$	19	0.15	0.035–0.077
HCFC-143a	CF_3CH_3	41	0	0
HCFC-152a	CHF_2CH_3	1.7	0	0
tetrachloromethane	CCl_4	50	0.99	0.95–1.2
methylchloroform	CCl_3CH_3	6.3	0.11	0.092–0.20
halon-1301	$CBrF_3$	107	16	13
halon-1211	$CBrClF_2$	15	2.1	2.2
halon-1202	CBr_2F_2	1.5	0.3	0.3
halon-2402	CF_2BrCF_2Br	28	4.9	6.2
hexachlorobenzene	C_6Cl_6	1	0.02	—
pentachlorophenol	C_5Cl_5OH	>0.1	0.001	—

*Reference compound

$$\mathrm{ODP_x} = \frac{\text{atm. lifetime}_x}{\text{atm. lifetime}_{\text{CFC-11}}} \bullet \frac{\mathrm{mw_{CFC\text{-}11}}}{\mathrm{mw_x}} \bullet \frac{n_{\mathrm{Cl}} + 30 n_{\mathrm{Br}}}{3}$$

where mw is the molecular weight and n_{Cl} and n_{Br} are the numbers of Cl and Br atoms respectively, per molecule.

More detailed estimates of ODP can be made by means of global atmospheric models. Table 22 gives, for various species, a comparison between approximated ODP (see the foregoing equation) and the ODP calculated by means of global models.

3.6. Tropospheric Ozone. At present there is no procedure available to estimate the effect on tropospheric ozone when only the basic characteristics of a substance are known. However, a first indication of episodic ozone formation can be obtained from a reactivity scale based on the rate constant for the (OH + hydrocarbon) reaction and the molecular weight. OH-scale values can easily be estimated using structure-reactivity relations. There is a reasonable correlation between the POCP (Photochemical Ozone Creation Potential) scale and the OH-reactivity scales, and therefore the OH-scale value may, for the time being, be used as an indication for episodic ozone formation (Table 23).

The tropospheric lifetime *(T)* is the inverse of the rate constant for reaction with OH^o:

$$T = 1/k'$$

$$R\text{—H} + {}^{o}\mathrm{OH} \rightarrow \mathrm{R}^{o} + \mathrm{H_2O}$$

$$\text{Rate} = -d(\mathrm{RH})/dt = k({}^{o}\mathrm{OH})(\mathrm{RH}) = k'(RH)$$

Table 23. Comparison of Photochemical Ozone Creation Potential (POCP) Values Obtained by Derwent and Jenkin (2857) with an OH^o-Reactivity Scale, Relative to Ethylene = 100.

Compound	POCP	OH^o-scale	K_{OH}
methane	0.7	0.2	8.4×10^{-15}
ethane	8	3	2.7×10^{-13}
propane	42	9	1.2×10^{-12}
n-pentane	41	19	4.1×10^{-12}
benzene	19	5	1.3×10^{-12}
toluene	56	22	6.2×10^{-12}
p-xylene	89	47	1.5×10^{-11}
m-xylene	99	76	2.5×10^{-11}
o-xylene	67	46	1.5×10^{-11}
ethylene	100	100	8.5×10^{-12}
formaldehyde	42	99	9.0×10^{-12}
acetaldehyde	53	121	1.6×10^{-11}

As a molecule travels upward from the surface of the earth, it can be decomposed either in the troposphere (primarily by reaction with OH^o or, in some cases, photolysis) or in the stratosphere (by photolysis from the shorter-wavelength light). The lifetime is defined as the time it takes for the quantity of a chemical released to drop to $1/e$ or approximately 37% of its initial value. This lifetime corresponds to 1.41 half-lives.

OH-scale value is calculated as follows:

$$\text{OH-scale value} = \frac{k_x}{\text{mw}_x} \bullet \frac{\text{mw}_{\text{ethylene}}}{k_{\text{ethylene}}} \bullet 100$$

where k_X is the rate constant at $t = 298$ K for the reaction of X with the OH radical, mw_X is the molecular weight of compound X, and K_{OH} is in $\text{mol}^{-1}\ \text{cm}^3\ \text{sec}^{-1}$ (2853).

4. Natural Sources

Although the amount of manmade organic chemicals (excluding lubricants) that enter the environment may be as much as 20 million tons a year, this total is very small in comparison with the enormous tonnages of organic compounds naturally produced. Over the ages, degradation and emanation cycles have become established through which an equilibrium seems to be maintained. Although we know a great deal about the detailed mechanisms involved, the way in which many cycles operate is still obscure. Some of them are on a massive scale; for instance, it has been estimated that swamps and other natural sources emit as much as 1600 million tons of methane into the atmosphere each year. Even cattle, which emit methane equivalent to 7% of their energy intake, must contribute a world total of several million tons. It is estimated that the world's atmosphere contains 4800 million tons of methane, and it is evident that a balance exists.

Terpene-type hydrocarbons emitted into the air by forests and other vegetation amount to an estimated 170 million tons a year. It is believed that these polymerize in the air and are eventually eliminated from the air by rainfall or deposition in aerosols.

5. Manmade Sources

Emission rates for various sources, such as diesel and gasoline engines, municipal waste incinerators, and central heating furnaces, as well as ground level concentrations in residential, urban, and industrial areas, have been considered.

6. Control Methods

6.1. Incinerability Index. Controlled, high-temperature incineration, in spite of the associated high costs, is a viable organic waste reduction technology. The current performance requirement in the U.S. states that the principal organic hazardous constituents designated in each waste must be

destroyed and/or removed to an efficiency of 99.99%. Organic hazardous compounds have been ranked by their heat of combustion by the U.S. Environmental Protection Agency in Appendix VIII of 40 CFR Part 261.3. This scale is based on the premise that the lower the heat of combustion, the more difficult the compound is to incinerate. Results of laboratory- and full-scale studies have indicated that this ranking is not consistent with the gas-phase thermal stability of numerous organic compounds.

It has been proposed that the temperature for 99% destruction at 2.0 sec. residence time is a viable method to determine the relative stability of organic compounds. Although destruction efficiencies are dependent upon residence time and temperature, relative destruction efficiencies are insensitive to these parameters. Consequently, it is believed that gas-phase thermal stability under oxygen-starved reaction conditions may be an effective predictor of relative destruction efficiency for organic compounds.

The thermal stability ranking of hazardous organic compounds is based on the temperature for 99% destruction at 2.0 sec. residence time under oxygen-starved reaction conditions. The ranking extends from 1 (highest thermal stability) for hydrogen cyanide to 320 (lowest thermal stability) for endosulfan (2390).

C. WATER POLLUTION FACTORS

1. Biodegradation

1.1. Objectives. The major use of data on biodegradation is for assessing the persistence of a chemical substance in a natural environment. The natural environment, for the purpose of such tests, is natural waters and various soils (including hydrosoils). If the compound does not persist, information is needed on whether the compound degrades to innocuous molecules or to relatively persistent and toxic intermediates. Secondary concerns for environmental persistence are the possibilities that (1) toxic substances may interfere with the normal operation of biological waste treatment units and that (2) toxic substances not substantially degraded within a treatment plant may be released to the natural environment.

The test procedures for biodegradation give an estimate of the relative importance of biodegradability as a persistence factor. The data are used to evaluate biodegradation rates in comparison with standard reference compounds. Most tests provide opportunities for biodegradation with relatively dense microbial populations that have been allowed to adapt to the test compound. Those compounds that degrade rapidly (in comparison with reference compounds) or extensively (as judged by such evidence as CO_2 evolution and loss of dissolved organic carbon) are likely to biodegrade rapidly in a variety of environmental situations. Even so, such compounds may persist in specialized environments and under circumstances that are poorly represented by these preliminary tests. Compounds that produce little indication of biodegradation in these tests may be relatively persistent in a wide variety of environments.

Reliable conclusions about biodegradation are not generally possible on the basis of structure alone. Biodegradation is the most important degradative mechanism for organic compounds in nature, in terms of mass of material transformed and extent of degradation. Therefore, information on biodegradability is very important in any evaluation of persistence and is generally needed on organic compounds that can be solubilized or dispersed in or on water. Highly insoluble compounds are not testable at present without the use of radioisotopes or complex analytical measurements, nor are there methods to study biodegradation with very low substrate concentrations.

These types of tests do not differentiate all chemical compounds as relatively nonbiodegradable or rapidly and extensively biodegradable. Results for many materials lead to intermediate conclusions. A more thorough understanding of the biodegradability of such compounds would result from advanced tests, such as those employing radiolabeled substrates.

Anaerobic microbial degradation of organic compounds is an important mechanism for degrading waste materials both in the natural environment and in waste treatment plants. However, there are few relatively simple state-of-the-art methods at present for evaluating the potential for anaerobic biodegradation. The types of methods most frequently cited employ microcosms such as flooded soils in flasks and require the use of radiolabeled substrate. Methane from fermentation of organic substrates is the end of a food chain that involves a wide variety of anaerobic bacteria.

The anaerobic digestion test compares the production of methane and CO_2 by anaerobic bacteria in sludge samples with and without added test material.

A desirable goal of degradation testing is to obtain some estimate of the rate at which a compound will degrade in the environment. It is relatively easy to estimate reaction rates for such degradation processes as hydrolysis, photolysis, and free-radical oxidations. Environmentally realistic reaction rates for biodegradation are much more difficult to obtain. Among the more important environmental variables that can affect the rate and the extent of biodegradation are (1) temperature, (2) pH, (3) salinity, (4) dissolved oxygen, (5) concentration of test substance, (6) concentration of viable microorganisms, (7) quantity and quality of nutrients (other than test substances), trace metals, and vitamins, (8) time, and (9) microbial species.

1.2. The Determination of Biodegradability. Biodegradability tests may be divided into two groups of tests: die-away tests in static systems and tests in flow-through systems (continuous cultures). In die-away tests, the concentration of the substance under investigation (the substrate) is determined analytically as a function of time. During the experiment, the substrate is contained in a fixed amount of test medium. In flow-through systems, a constant flow of the medium is fed into a completely mixed "reactor" in which the medium volume is also kept constant. The degradation is calculated from the difference between the substrate concentrations in the inlet and effluent streams.

1.2.1. BIODEGRADABILITY TESTS ACCORDING TO OECD GUIDELINES. The OECD published in 1981 a test system that was meant to evaluate the biodegradability of industrial chemicals. This test system is in principle suitable for a wide variety of chemicals. This system goes by the name *OECD hierarchy* because three different levels are distinguished: non-, ready, and inherent biodegradable.

"Ready Biodegradability" Tests (RBTs) are simple tests for quickly selecting "soft" chemicals; relying on them avoids time- and money-consuming further research. In all these tests, biodegradation is monitored as the degree of mineralization, by means of summary parameters such as oxygen uptake, carbon dioxide production, or elimination of dissolved organic carbon (DOC). Without the use of ^{14}C techniques, this is possible only if the test compound is the sole carbon and energy source for microorganisms. The test duration of 28 days allows some adaptation of the microorganisms to the compound, but mineralization as a test criterion adds some stringency because it prevents, from passing the test, chemicals that are only converted into persistent products. Table 24 presents a survey of the most important RBTs.

"Inherent Biodegradability" Tests (IBTs) are designed to demonstrate the potential degradability of a compound. These methods also have a screening function: to select "hard" chemicals. A negative result indicates that a chemical is too persistent so that, tentatively, no further research on biodegradation has to be done.

1.2.2. EEC MANOMETRIC RESPIROMETRIC METHOD. The purpose of this test method is to evaluate the biodegradability of organic substances in an aqueous medium in a closed respirometer that gives readings of the biochemical oxygen demand.

The method is applicable only to those organic test substances that, at the concentration used in the test, are not inhibitory to bacteria at the chosen concentration, do not reach and react with the CO_2 absorbent, and do not significantly absorb within the test system.

If the test material is not soluble at the test concentration (100 mg/l), special measures, such as the use of ultrasound dispersion or suitable emulsifiers, may have to be employed to achieve a good dispersion of the test substance.

Information on the toxicity of the chemical to microorganisms may be useful in the interpretation of low results and in the selection of appropriate test concentrations.

1.2.3. PRINCIPLE OF THE TEST METHOD. A measured volume of inoculated medium containing a known amount of test compound as the sole source of carbon is stirred in a closed flask at a constant temperature (±0.5°C) in the range 20-25°C in the dark or in diffuse light. The microorganisms used for inoculation are not preacclimated. Activated sludge is collected from a biological waste water treatment plant or a laboratory unit receiving solely or predominantly domestic sewage.

The consumption of oxygen is determined either by measuring the quantity of oxygen required to maintain constant gas volume in the respirometer flask or from the change in volume or pressure (or

Table 24. Ready Biodegradability Tests, Revised in 1990. (The concentration of microorganisms in the third column corresponds to the maximum amount of effluent or activated sludge that is allowed to be used as inoculum in the test. These values are derived from the literature.)

RBT	Summary Parameter	Population Density, CFU/ml
Modified OECD Screening Test	DOC	$(0.5–2.5) \bullet 10^2$
CO_2 Evolution	CO_2	$(2–10) \bullet 10^5$
[EEC]manometric respirometry	O_2	$(2–10) \bullet 10^5$
DOC Die-Away	DOC	$(2–10) \bullet 10^5$
Closed Bottle	O_2	$(0.5–2.5) \bullet 10^3$
MITI (I)	O_2	$(2–10) \bullet 10^5$

(2909)

a combination of the two) in the apparatus. Evolved CO_2 is absorbed in a solution of potassium hydroxide or another suitable absorbent. The degradation is followed over a 28-day period.

The amount of oxygen taken up by the test compound (corrected for the blank) is expressed as a percentage of the COD or the theoretical oxygen demand calculated from the formula of the compound.

The degree of biodegradability may also be calculated from supplemental chemical analyses such as dissolved organic carbon (DOC), or from specific analysis, made at the beginning and end of incubation (2790).

It may be concluded that 50% or more ThOD for a soluble substance indicates that it is readily biodegradable, provided that the % DOC removed is over 70%. The OECD recommendation of 60% or more ThOD is valid for insoluble substances.

1.2.4. MEASUREMENT OF DEGRADATION RATE. In general, the abiotic and biotic degradation of chemicals in water seems to follow a logarithmic correlation. Therefore, the degradation rate constant *(K)* is determined from the assumed first-order process in which

$$C_t = C_0\ e^{-}kt$$

Accordingly,

$$\ln\ C_t = \ln\ C_0 - kt$$

where C_t is the concentration of the pesticide in culture medium after time t (days) and C_0 is the initial concentration of pesticide. The half-lives were determined from the expression

$$\frac{C_0}{C_r} = 2 = e^{kt}$$

or

$$\ln\ 2 = kt$$

$$t_{0.5}\ \text{(days)} = 0.693/k$$

The real biodegradation rate constant (K_b) is calculated by the following equation:

$$K_b = K\ \text{(metabolism or cometabolism)} - K\ \text{(control)}$$

1.2.5. MINERALIZATION OF ACETATE IN METHANOGENIC RIVER SEDIMENT. In industrialized regions, sediments receive a high input of organic matter. High numbers of bacteria are present, and oxygen supplied by the overlying water will be rapidly consumed in the top layer of the sediment. The underlying part of the sediment is anoxic, and there biodegradation of natural as well as anthropogenic organic substrates is dependent on anaerobic processes. Anaerobic

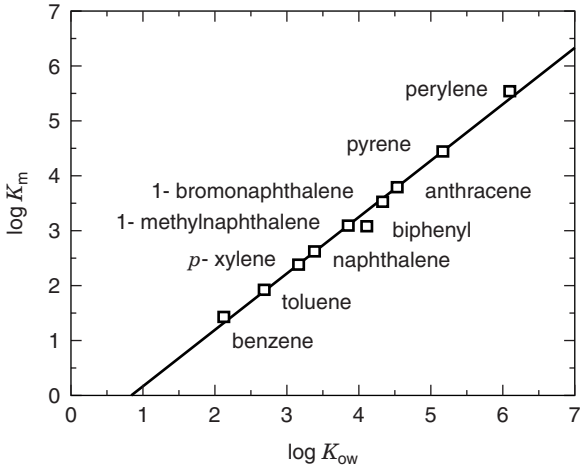


Figure 19. Relationship between micelle-water partition coefficient (K_m) and octanol-water partition coefficient (K_{ow}).

mineralization of organic matter by microorganisms is an essential component of the carbon cycle. Acetate is a key intermediate in the anaerobic degradation of organic matter and a major component of anaerobic waste waters.

Organic polymers like proteins, carbohydrates, and lipids are hydrolyzed to amino acids, sugars, and fatty acids. These are converted by acidogenic bacteria to produce hydrogen, acetate, propionate, butyrate, lactate, and alcohols. Acetogenic bacteria convert these products to acetate. About 70% of the methane formation in anaerobic freshwater sediments is derived from acetate. The following reaction is performed:

$$CH_3COOH \rightarrow CH_4 + CO_2$$

The mineralization of acetate under methanogenic conditions is performed by a few specialized methanogenic bacteria, such as *Methanosarcina* sp., because most methanogens are not able to split acetate into methane and carbon dioxide. This is in contrast with the aerobic mineralization of acetate that a multitude of species can perform.

The functioning of anaerobic bacteria in river sediments is vital for the stability of freshwater ecosystems. The sensitivity of these organisms to pollutants is therefore important for the establishment of valid sediment quality criteria. Acetate is a key intermediate in the carbon cycle and was chosen as a model substrate for the activity of anaerobic bacteria. The effect of pollutants on the anaerobic mineralization of acetate is studied in sediment microcosms. A small amount of ^{14}C-labeled acetate is added to bottles with fresh anaerobic river sediment. The acetate is converted to methane and $^{14}CO_2$, with a half-life of 0.2-0.5 h. Adding a toxicant decreases the mineralization rate of acetate. The IC_{10} is defined as the toxicant concentration that decreases the mineralization rate of acetate with 10% (2693).

1.2.6. EFFECTS OF SURFACTANTS ON WATER SOLUBILITY. Aqueous surfactant solutions have the ability to solubilize compounds that are otherwise relatively water insoluble. This phenomenon is the basis for the use of surfactants as solubilizing agents for enhancing biological remediation technologies, pump-and-treat operations, and soil-washing operations. In an experimental study (2361), the linear relationship shown in Figure 19 was found between the octanol-water partition coefficient (K_{ow}) and the micelle-water partition coefficient (Km) for a number of aromatic hydrocarbons, using the anionic surfactant dodecylsulfate.

2. Oxidation Parameters

The conventional oxidation parameters, such as biological oxygen demand (BOD), chemical oxygen demand (COD) using potassium dichromate, permanganate value ($KMnO_4$), total organic carbon (TOC), total oxygen demand (TOD), and theoretical oxygen demand (ThOD) are mentioned

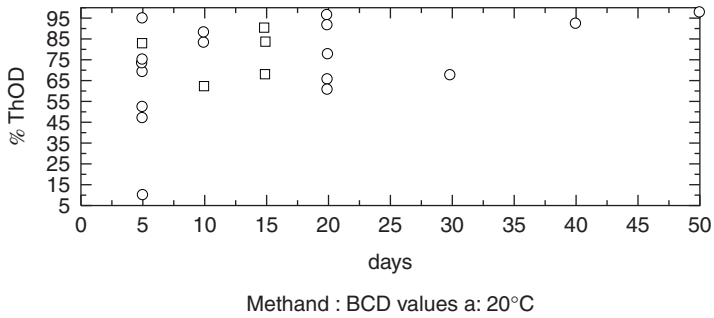


Figure 20. The variation in BOD values.

here. The oxidation parameters are dimensionless (grams oxygen consumption per gram of product), unless stated otherwise. BOD values are assumed to be measured at 20°C, unless indicated otherwise.

2.1. Biochemical Oxygen Demand (BOD). When water containing organic matter is discharged into a river, lake, or sea, natural purification by biological action takes place. Thus biochemical oxidation is brought about by naturally occurring microorganisms that use the organic matter as a source of carbon. Dissolved oxygen in the water sustains respiration. Naturally, this is a simplified picture of a very complex set of reactions, the rates of which depend on the temperature, the type of organic matter present, the type of microorganisms, the aeration, and the amount of light available. A number of years ago an attempt was made to produce a test that would match the rate of biochemical oxidation that would occur in a river into which organic-containing water was discharged. The 5-day test has been generally adopted with the knowledge that this does not necessarily represent the time required for total oxidation of the organic matter present. In some cases, a test period of longer tha n 5 days is specified. It follows, therefore, that the BOD_5 test should always be considered in conjunction with other data and with a knowledge of the system being studied. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria in the design of waste water treatment plants.

The BOD test is an empirical bioassay procedure that measures the dissolved oxygen that microbial life consumes while assimilating and oxidizing the organic matter present. The sample of waste, or an appropriate dilution, is incubated for 5 days at 20°C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand. The standard dilution method prescribes the use of several dilutions, because faulty results can be obtained because of the toxicity of the sample (yielding a low BOD) or by depletion of the oxygen by too high a concentration of biodegradable organics. The bottles that after 5 days still contain approximately 50% of the original oxygen content are selected for the BOD calculation. In 53 laboratories, 77 analysts analyzed natural water samples plus an exact increment of biodegradable organic compounds. At a mean value of 194 mg/l BOD, the standard deviation was ±40 mg/l. There is no acceptable proced ure for determining the accuracy of the BOD test.

BOD values sometimes show a wide range of variation. The main reason is that microorganisms have a tremendous capacity for adaptation. Whenever the samples are inoculated with microorganisms from a very polluted river, we may suppose that these microorganisms are already partly adapted to the specific organics. When an inoculum is taken from a polluted river or from an industrial waste water treatment plant, this should be mentioned. The foregoing is illustrated by Figure 20.

2.2. Chemical Oxygen Demand (COD). Because the BOD method takes 5 days to carry out, other methods have been sought for measuring oxygen requirements of a sample. The methods should be simple, quick, and reliable. One popular method is the chemical oxygen demand test based on the oxygen consumed from boiling acid potassium dichromate solution. This is a severe test, and a high degree of oxidation takes place. Interference from chloride ions can be a problem. Several procedures available to overcome this problem are based mainly on the complexion of the chloride

ion with mercuric sulfate. This procedure is recommended in many standard methods. It has been demonstrated that high COD results are achieved when chloride ions are present and that true compensation is not made. Finally, it should be noted that the COD test is not a measure of organic carbon, although the same reactions are involved.

In this procedure, organic substances are oxidized by potassium dichromate in 50% sulfuric acid solution at reflux temperature. Silver sulfate is used as a catalyst, and, as mentioned, mercuric sulfate is added to remove chloride interference. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as an indicator. In 58 laboratories, 89 analysts analyzed a distilled water solution containing oxidizable organic material equivalent to 270 mg/l COD. The standard deviation was ±27.5 mg/l COD, and the mean recovery was 96% of the true value.

Ideally, to measure the ultimate oxygen demand, the complete combustion of all the oxidizable elements in the sample is desired. Thus it is desired that the following reactions take place, because the end products listed represent the highest stable oxidation states of these elements (or ions) in nature.

$$C_nH_{2m} + \left(n + \frac{m}{2}\right) O_2 \rightarrow {}_nCO_2 + {}_mH_2O$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$2N^{3-} + 3O_2 \rightarrow 2NO_3^-$$

$$S^{2-} + 2O_2 \rightarrow SO_4^{2-}$$

$$SO^{2-}_3 + \frac{1}{2}O_2 \rightarrow SO^{2-}_4$$

$$N_2 + O_2 \rightarrow \text{no reaction}$$

When interpreting TOD values, keep in mind that not only hydrocarbons are oxidized but all oxidizable matter, as demonstrated by the foregoing reactions.

2.3. Total Organic Carbon (TOC). The instrument that measures the TOC of polluted water is very similar to the TOD analyzer, except for the last step. A microsample of the waste water to be analyzed is injected into a catalytic combustion tube that is enclosed by an electric furnace thermostated at 950°C. The water is vaporized, and the carbonaceous material is oxidized to carbon dioxide and steam. The carrier gas CO_2, O_2, and water vapor enter an infrared analyzer sensitized to provide a measure of CO_2. The amount of CO_2 present is directly proportional to the concentration of carbonaceous material in the injected sample.

2.4. Theoretical Oxygen Demand (ThOD). The theoretical oxygen demand is the amount of oxygen needed to oxidize hydrocarbons to carbon dioxide and water.

$$C_nH_{2m} + \left(n + \frac{m}{2}\right) O_2 \rightarrow {}_nCO_2 + {}_mH_2O$$

The ThOD of C_nH_2m equals

$$\frac{32\left(n + \frac{m}{2}\right) \text{g}}{(12n + 2m)\ \text{g}} = \frac{8(2n + m)}{6n + m}$$

When the organic molecule contains other elements, such as N, S, P, etc., the ThOD depends on the final oxidation state of these elements. Most authors do not bother to define the ThOD they mention in their publications; however, ThOD can easily be calculated.

Example: Ammonium acetate: CH_3COONH_4, mw = 77

(a) If N remains as NH_4^+, then

$$CH_3COONH_4 + 2O_2 \rightarrow 2CO_2 + H_2O + NH^{4+} + OH^-$$

or

$$\text{ThOD} = \frac{64\ \text{g}}{77\text{g}} = 0.83$$

(b) If N is oxidized to N_2, then

$$2CH_3COONH_4 + 5.5O_2 \rightarrow 4CO_2 + 7H_2O + N_2$$

or

$$\text{ThOD} = \frac{5.5 \times 32}{2 \times 77} = 1.14$$

(c) If N is oxidized to NO_3^-, then

$$2CH_3COONH_4 + 7.5O_2 \rightarrow 4CO_2 + 5H_2O + 2NO_3^- + 2H^+$$

or

$$\text{ThOD} = \frac{7.5 \times 32}{2 \times 77} = 1.56$$

The ThOD of the substance $C_cH_h\ Cl_{cl}\ N_n\ Na_{na}\ O_o\ P_p\ S_s$ of molecular weight mw can be calculated according to

$$\text{ThOD}_{NH3} = \frac{16[2c + 1/2(h - cl - 3n) + 3s + 5/2p + 1/2na - o]}{\text{mw}}$$

This calculation implies that *C* is mineralized to CO_2, H to H_2O, P to P_2O_5, and Na to Na_2O. Halogen is eliminated as hydrogen halide and nitrogen as ammonia.

Example: Glucose $C_6H_{12}O_6$, mw = 180

$$\text{ThOD} = \frac{16[2 \times 6 + 1/2 \times 12 - 6]}{180} = 1.07\ \text{mg}\ O_2/\text{mg glucose}$$

Molecular weights of salts other than those of the alkali metals are calculated on the assumption that the salts have been hydrolyzed.

Sulfur is assumed to be oxidized to the state of 6^+.

Example: Sodium *n*-alkylbenzenesulfonate, $C_{18}H_{29}SO_3Na$, mw = 348

$$\text{ThOD} = \frac{16[36 \times 29/2 \times 3 \times 1/2 - 3]}{348} = 2.34\ \text{mg}\ O_2/\text{mg glucose}$$

In case of a nitrogen-containing substance, the nitrogen may be eliminated as ammonia, nitrite, or nitrate corresponding to different theoretical biochemical oxygen demands.

$$\text{ThOD}_{NO}^{-2}\ \frac{16[2c \times 1/2(h - cl) \times 3s \times 3/2n + 5/2p + 1/2na - o]}{\text{mw}}$$

$$\text{ThOD}_{NO}^{-3}\ \frac{16[2c \times 1/2(h - cl) \times 3s \times 5/2n + 5/2p + 1/2na - o]}{\text{mw}}$$

Suppose full nitrate formation was observed by analysis in the case of a secondary amine: $(C_{12}H_{25})_2NH$; mw = 353

$$\text{ThOD}_{NO}^{-3} = \frac{16[48 + 51/2 + 5/2]}{353} = 3.44\ \text{mg}\ O_2/\text{mg substance}$$

Expressing other parameters, such as BOD and COD, as a percentage of ThOD can be highly misleading. In the standard BOD_5 test, nitrification does not occur yet, and consequently the BOD_5 values of compounds containing nitrogen can be expressed as a percentage of the ThOD, under the assumption that the nitrogen remains unchanged. In determining BOD with acclimated seed tested over a longer period, nitrification may occur. This alters the oxygen demand and also the ThOD,

because N is oxidized to NO_3^{-2}. When using ThOD values, one should mention the final oxidation state of the elements other than C, H, and O.

3. Impact on Biodegradation Processes

Certain compounds are very toxic to microorganisms used in waste water treatment processes and in the BOD test, and even at low concentrations, they inhibit the biodegradation processes.

Microbial activities are associated with three major biogeochemical cycles (carbon, nitrogen, and sulfur cycling) and with the decomposition of organic matter. Data obtained will provide preliminary indications of possible effects of the test chemical on the cycling of elements and nutrients in ecosystems. In addition, the test will aid in the formation of hypotheses about the ecological effects of chemicals, hypotheses that can be used in the selection of higher-level tests when appropriate.

Data on the effects of chemicals on microbial populations and functions can be obtained from laboratory studies employing nonradioisotopic analytical techniques. Studies of effects on microbial functions constitute a more direct approach and are preferred to studies of effects on populations. The activities to be observed are

- organic matter (cellulose) decomposition, by following CO_2 evolved from organically bound carbon
- nitrogen transformations, by following the release of organically bound nitrogen (in urea) and the formation of ammonia
- sulfur transformation, by following the reduction of sulfate to sulfide by *Desulfovibrio*

3.1. Nitrogen Transformation. Almost all microorganisms, higher plants, and animals require combined nitrogen. In addition, the nitrogen cycle is a major biogeochemical cycle. The main aspects of this cycle are fixation of gaseous nitrogen, ammonification of organically bound nitrogen, nitrification, and denitrification.

Ammonification is a key initial step in the reintroduction of nitrogen from protein wastes into the soil and is one of the more readily measured reactions of the nitrogen cycle. As soon as an organism dies and its organic waste returns to the soil, biological decomposition begins and fixed nitrogen is released. The breakdown of proteins and other nitrogen-containing organics in soil and the production of ammonia are the work of widespread and varied microflora. The amino groups are split off to form ammonia in a series of reactions collectively called ammonification. Urea, a waste product found in urine, is also decomposed by numerous microorganisms with the formation of ammonia. This reaction can serve as a convenient assay method for ammonification activity. There is a strong correlation between an organism's ability to degrade urea and its capacity to degrade protein. Information from such testing would be used to assess the likelihood that the test chemical interferes with the normal co nversion of organically bound nitrogen into ammonia.

Consideration of at least some aspects of the nitrogen cycle is essential for assessing the effects of substances on microorganisms. An easily measured feature of the nitrogen cycle is the oxidation of nitrite to nitrate by *Nitrobacter bacteria.* This focuses on a part of the nitrogen cycle that is less important than the critical step involving the conversion of organic nitrogen into ammonia. The method uses urea as a readily obtainable, reproducible nitrogenous organic compound. Some investigators have used pieces of liver or kidney tissue, vegetable meal, dried blood, and casein hydrolysate as nitrogen sources, but these substances are not standardizable. Percolation techniques may also be used for the same purposes in the study of soluble proteins, peptones, polypeptides, and amino acids in solution. Methodology using fertile soil and urea and following the evolution of ammonia nitrogen is relatively simple to conduct and will provide meaningful results. Urea is a suitable nitroge n source not only because it is readily available and relatively easy to handle, but also because the ability to degrade urea has been associated with general proteolytic capabilities.

Nitrification is one of the most sensitive conversions in the soil. Nitrification may be inhibited by concentrations of chemicals that do not inhibit other important biochemical reactions, so there are reasons for choosing nitrification as the process that may give the most useful results. One of the arguments against its use is that ammonification is a more vital part of the nitrogen cycle than nitrification. In addition, the temporary inhibition of nitrate formation is often beneficial in that it slows down the loss of nitrogen from the root areas of plants by leaching and denitrification. Finally, nitrification by *Nitrobacter* may be too sensitive to inhibition by chemicals in laboratory studies and may give results that are not representative of natural circumstances and environments. Although the

inhibition of nitrifying activity could lead to ammonium ion accumulation and serious problems such as root damage, ammonification is considered the more appropriate process to examine a s a first step in looking for effects of the nitrogen cycle.

4. Waste Water Treatment

4.1. Biological Oxidation. In order to describe the basic investigation procedures and results for a wide variety of biological test methods in a compact way, the information is presented in columns, using the following column headings: methods, feed mg/l, test duration, and % product removed or % theoretical oxidation demand (ThOD). The methods column describes experimental procedures and their sequence. For example, acclimation may have been achieved in activated sludge with assimilation or oxidation measured by respirometer, BOD, or other methods.

Biological treatment performance is difficult to evaluate without information on both percent oxidation and percent removed. A characteristic balance of time, oxidation, and biosorption is necessary for effective continuous treatment. Percent oxidation shows the degradation within the test period. It rarely exceeds 60% of the influent oxygen demand within the detention period of an activated sludge or other biological treatment unit. Percent *removal* may be 90% or more because biosorption retains a significant fraction of the remaining load. The retained material is subject to further oxidation in process, so it is not likely to degrade the effluent.

4.2. Stabilization Ponds. The principal design parameter is the first-order BOD removal coefficient, K . The evaluation of K is the key to the whole design process. The method described below has been proposed by Dhandapani Thirumurthi and is based on the following definitions:

1. Standard BOD removal coefficient K_s-a constant and standard value of K_s has been chosen that corresponds to an arbitrarily selected standard environment. Under these standard environmental conditions, a stabilization pond will perform with the BOD removal coefficient K_s.

   The standard environment consists of

- a pond temperature of 20°C
- an organic load of 60 lb/day/acre (672 kg/day/ha)
- absence of industrial toxic chemicals
- minimum (visible) solar energy at the rate of 100 langleys/day
- absence of benthal load

2. Design BOD removal coefficient, K -design coefficient K corresponds to the actual environment surrounding the pond. Hence the value of K will be used when a pond is being designed. When the critical environmental conditions deviate from one or more of the defined standard environmental conditions, suitable correction factors must be incorporated:

$$K = K_s C_{Te} C_o C_{Tox}$$

where

C = correction factor
Te = correction for temperature
o = correction for organic load
Tox = correction for industrial toxic chemicals

In the absence of industrial wastes, the factor C_{Tox} will equal unity. Laboratory investigations indicated that in the presence of certain industrial organic compounds, green algae could not synthesize chlorophyll pigment. Without chlorophyll production, photosynthesis cannot be sustained by algae, so oxygen production stops. The resultant decrease in dissolved oxygen (DO) concentration in the pond will result in a drastic reduction in BOD removal efficiency. Based on this observation, C_{Tox} values have been calculated for various concentrations of selected organic chemicals. Ponds designed to treat toxic industrial wastes will perform at lower efficiencies, so C_{Tox} values must be determined by laboratory investigations or by previous field experience.

4.3. The Activity of Mutant Microorganisms. In the normal biological cycle, adaptation and mutation are constantly taking place, permitting the survival of the participating microorganisms. Many of the

present-day organic toxicants with which we are contaminating our environment contain a large number of carbon-chlorine bonds in addition to other substitution groups that, because of their molecular configuration and complexity, do not permit the process of adaptation to proceed at a normal rate. In an effort to overcome this obvious biochemical disability, it was decided to obtain soil and marine samples from various parts of the world to isolate and study the naturally occurring microorganisms. The numerous isolates were tested to determine their ability to degrade low levels of various synthetic organic substrates such as aryl halides, aryl and alkyl amines, halogenated phenols, inorganic and organic cyanides, halogenated insecticides, halogenated herbicides, and various syntheti c surfactants. These various organic chemicals were selected for biodegradation studies because they are high on the list of toxic recalcitrant molecules with which we are defiling our environment.

After the capability of the various microorganisms to degrade selected organic molecules had been determined, tests were run to determine the maximum toxicant concentration to which they would adapt. Increasing concentrations of the challenging organic molecules were added to the growing cultures over a period of 21 days to determine the maximum level that the biomass would tolerate. Upon completion of the adaptation process, the microorganisms were exposed to programmed radiation to develop mutants with advanced biochemical capabilities. From the several thousand mutants obtained, 397 were isolated that were outstanding in their ability to degrade various types of inorganic and organic compounds. These included 180 pseudomonas, 45 nocardia, 102 streptomyces, 15 flavobacterium, 12 mycobacterium, 14 aerobacters, 14 achromobacters, 10 vibrio, and 10 micrococcus. Activated sludges were prepared from the various mutant microorganisms, and the maximum tolerated dose of toxicant, as determined by previous tests, was added to determine the maximum velocity and degree of molecular dismutation. It has been fairly well established that none of the highly halogenated organic compounds are used by microorganisms as a source of metabolic carbon. Degradation or molecular change has been found to occur most readily at levels of maximum metabolic activity. It is quite apparent that the observed changes are enzymatic and relate more to detoxification than to the use of highly halogenated organic compounds in metabolic processes. It is possible that the biodegradation observed in microbial sludges is caused essentially by extracellular enzymes that would cause desorption of the more soluble degradation intermediates.

4.4. Solvent Extraction: Distribution Coefficient. Water soluble organic compounds can be extracted from water by solvents that are much less soluble in water. The ratio of the concentration of the compound in the solvent to the concentration of the compound in the water, after a sufficient contact time, is called the *distribution coefficient.*

4.5. Stripping. Air stripping has been demonstrated to be a feasible technique for removing a portion of the organics from waste water. These operations are typically carried out in a cooling tower-type device (induced or forced draft) or in an air-sparged (bubble) vessel. Air stripping occurs to varying degrees in conventional waste water treatment techniques such as dissolved or dispersed air flotation and of course aerobic biodegradation. An analytical simulation model of desorption in aerated stabilization basins (1811) indicates that significant removals of selected industrial chemicals are occurring.

A study of ten common industrial chemicals in eleven full-scale aerated basins showed that 20%-60% removal efficiencies were possible without biochemical oxidation. Detention times ranged from 1.7 to 14 days. Laboratory observations of surface agitator desorbers support these data.

Equations have been derived to predict the evaporation rates of hydrocarbons and chlorinated hydrocarbons. These compounds have high rates of evaporation even though the vapor pressure is low. Evaporation "half-lives" of minutes and hours are due to the relatively high constant of Henry *(H)* of these components in aqueous solution.

Thus it appears that significant amounts of volatile components are being stripped and/or desorbed in conventional secondary treatment operations involving the use of air or the presence of large air-water interfaces.

4.5.1. FUNDAMENTAL DESORPTION CONCEPTS. The volatile character of dissolved constituents in waste water can be adequately quantified by the experimental determination of two parameters:

1. *Volatile fraction (Fv)* . This measure denotes the maximum amount (in %) of the original organic pollutants in a water sample that can be removed by air contact. This is also the maximum efficiency of treatment that can be achieved by stripping the waste water with air.

The organic pollutants in the waste water can be expressed as BOD, COD, TOC, and other gross pollutant measures and/or as concentration of individual constituents.

2. *Relative volatilization rate (K/a).* This measure denotes the ratio of the rate of volatile removal by air contact to the rate at which water is evaporated in the same apparatus. If the experimental value of *K/a* is greater than unity, stripping with air may be a feasible treatment operation for this waste water.

If *K/a* is unity, stripping will have no effect on removing volatile constituents from this waste water, and if *K/a* is less than unity or zero, stripping will result in an increase of this constituent in the waste water. This parameter, like F_v, is dimensionless, and both are determined from a single desorption experiment.

L.J. Thibodeaux (1812) used a desorption apparatus consisting of a packed column (Figure 21) and developed a mathematical model that, if the concentration of water is much greater than the concentration of the pollutant, yields the following solution:

$$\log X_1 = \log X_o - (k/a\ -) \log \frac{M_o}{M_t}$$

where

X_t = concentration of pollutant in the desorption apparatus at sample time t (mg/l)
X_o = concentration of pollutant in the desorption apparatus at start of experiment (mg/l)
M_t = quantity of water in the desorption apparatus at sample time t (g)
M_o = quantity of water in the desorption apparatus at start of experiment (g)
K = the specific desorption rate of the organic component in the packed column
a = the specific desorption rate of the water component in the packed column

The relative volatilization rate *K/a* can be obtained graphically be preparing a log-log plot of X_t and M_o/M_t. The slope of a straight line through these raw data points yields $(K/a - 1)$.

The relative volatilization rates shown in Table 25 were obtained for pure compounds at room temperature and initial concentrations of approximately 100-1000 mg/l.

From these experiments it appears that formic acid, acetic acid, propionic acid, and phenol have *K/a* values that are not significantly different from 1 and that therefore these compounds will not be removed significantly by air stripping. Acetaldehyde, acetone, and benzene show high relative volatilization rates and can thus be removed by stripping. Sucrose, on the contrary, concentrates in the solution upon stripping, as can be deduced from its *K/a* value of 0.26.

Experimental *K/a* values show a fair correlation with constants of Henry *(H)*, as illustrated by Figure 22.

4.6. Adsorption. The affinity of a chemical substance for particulate surfaces is an important factor affecting its environmental movement and ultimate fate. Chemicals that adsorb tightly may be less subject to environmental transport in the gaseous phase or in solution. However, chemicals that adsorb tightly to soil particles may accumulate in that compartment. Substances that are not tightly adsorbed can transport through soils, aquatic systems, and the atmosphere.

The experimental information is usually expressed as an *adsorption isotherm.* The adsorption isotherm is the relationship, at a given temperature, between the amount of the substance adsorbed and its concentration in the surrounding solution.

In very dilute solutions, such as are encountered in the environment or in waste waters, a logarithmic isotherm plotting usually gives a straight line. In this connection, a useful formula is the Freundlich equation, which relates the amount of impurity in the solution to that adsorbed:

$$\frac{x}{m} = KC^{1/n}$$

where

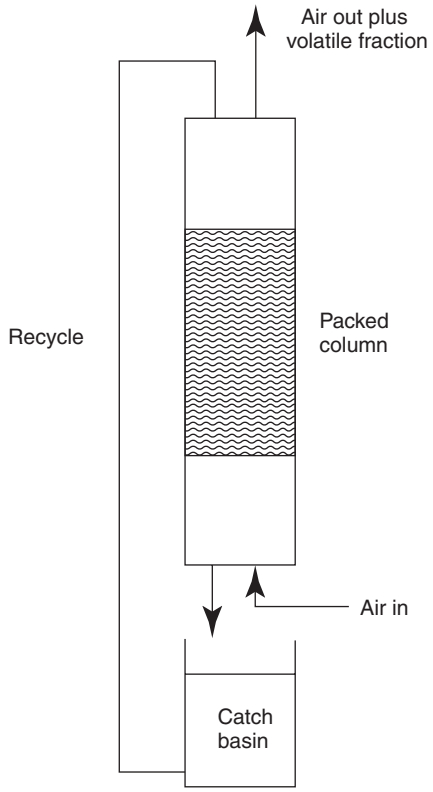


Figure 21. Volatile desorption apparatus.

Table 25. Experimental *K/a* Values Compared with Constants of Henry *(H)*.

	Experimental K/a	log *H*
methanol	7–13	–3.72
i-propanol	3–15	
n-propanol	12 –23	–3.56
n-butanol	10–18	–3.46
formic acid	4–7	
acetic acid	1–5	–4.91
propionic acid	0–1.5	–4.74
acetaldehyde	171–207	
aceton	36–100	–3.0
benzene	107	–0.65
phenol	0.5–1.9	–4.79
furfural	10	
sucrose	0.26	

x = amount of substance adsorbed
m = weight of the substrate
x/m = amount of substance adsorbed per unit weight of substrate
K, n = constants
C = unadsorbed concentration of substance left in solution or, in logarithmic form,

$$\log x/m = \log K + 1/n \log C$$

in which $1/n$ represents the slope of the straight-line isotherm (Figure 23). Isotherm tests also afford a convenient means of studying the effects of different adsorbents and the effects of pH and temperature.

Isotherm tests are also important in water purification by activated carbon. From an isotherm test it can be determined whether a particular purification can be effected. It will also show the approximate capacity of the carbon for the application and provide a rough estimate of the carbon dosage required.

The inherent adsorbability of a chemical in a pure-component test does not necessarily predict its degree of removal from a dynamic, multicomponent mixture. However, pure-component data do serve as a useful background for understanding why multicomponent interactions occur.

5. Alteration and Degradation Processes. The alteration and degradation processes can be divided into three categories:

1. *biodegradation*, effected by living organisms
2. *photochemical degradation*, i.e., nonmetabolic degradation requiring light energy
3. *abiotic degradation (chemical degradation)*, i.e., nonmetabolic degradation that does not require sunlight or living organisms.

Hydrolysis of environmental compounds has been extensively studied, and correlation between laboratory and field results is facilitated by the ease of measuring one of the more important rate-determining factors, pH, in both the laboratory and the field.

Chemical processes in soil can be studied after sterilization of the soil by autoclaving, chemical treatment, or γ-irradiation. The sterilization processes often alter the soil to such an extent that any process observed could be artificial. Nevertheless, any biodegradation technique where the test chemical is incubated with a natural medium (such as soil or water) would allow transformations effected by chemical agents to take place; therefore, these processes would be considered during biodegradation testing.

5.1. Photochemical Degradation. Chemicals introduced into aqueous media in the environment can undergo transformation by direct photolysis in sunlight into new chemicals with different properties from those of their precursors. Data on direct photolysis rate constants and half-lives establish the importance of direct photolysis in sunlight as a dominant transformation of chemicals in aqueous media.

Although numerous papers have been published on the photolysis of chemicals in solution, rate constants for direct photolysis of chemicals in water under environmental conditions (i.e., in sunlight) have emerged only in the last few years. Zepp and Cline (1948) published a paper on photolysis in aquatic environments with equations for direct photolysis rates in sunlight. These equations translate readily obtained laboratory data into rate constants and half-lives for photolysis in sunlight. Rate constants and half-lives can be calculated as functions of season, latitude, time of day, depth in water bodies, and the ozone layer. Several published papers concerning the photolysis of chemicals in the presence of sunlight verify this method.

The soil and water media do not provide as good a matrix as the atmosphere for photochemical alterations because of the attenuation of the incident light. Nevertheless, photochemical processes on soil or vegetable surfaces and in water have been shown to be important with some compounds, so experimental procedures have been developed to study these processes. A number of different procedures can be used to study photochemical reactions. The selections that have to be made include

- light source and apparatus of irradiation
- media of reaction: solution (choice of solvent), solid, adsorbed on another solid, thin film
- effect of environmental parameters: add sensitizer, effect of oxygen, pH

The use of sunlight as the irradiation source has been a common experimental technique. However, the inherent variation of sunlight in wavelength distribution and in intensity results in poor reproducibility, inconvenience, and lack of experimental control, and therefore many researchers

have resorted to artificial sources (such as medium- to low-pressure mercury lamps and fluorescent lamps).

Photochemical energy reaches the earth from the sun in the form of photons with wavelengths covering the spectrum from infrared to the far ultraviolet, including the visible. The principal energy sources of photons for environmental degradation reactions are those in the ultraviolet (UV) region. The UV radiation that reaches the earth's surface represents a wavelength range between 2,900 and 4,500 Å. Shorter-wavelength UV, with high energy, is prevented from reaching the earth's surface by absorption in the upper atmosphere.

Polynuclear aromatics are prime candidates for photochemical degradation, because they have high absorptivities in the environmental UV range. Some typical data for molar absorptivities at principal bands are the following:

	Maxima, Å	*Molar Absorptivity*	*Maxima, Å*	*Molar Absorptivity*
anthracene	3,560	8.5×10^3	3,750	8.6×10^3
1,2-dibenzanthracene	2,875	9.0×10^4	3,410	7.1×10^3
chrysene	3,200	1.2×10^4	3,610	6.9×10^2

Monoaromatics have much lower molar absorptivities in this range, generally in the region of 10^2–10^3 liters per mole-cm. Consequently, polynuclear aromatics should more readily absorb energetic radiation to put the molecule into a higher energy state for oxidative and other environmental reactions.

Studies made on benzo(a)pyrene show it to be particularly sensitive to light. Under white fluorescent light, the photooxidation of benzo(a)pyrene absorbed onto calcite suspended in water followed a first-order rate. One would anticipate that in a natural aquatic system, photooxidation

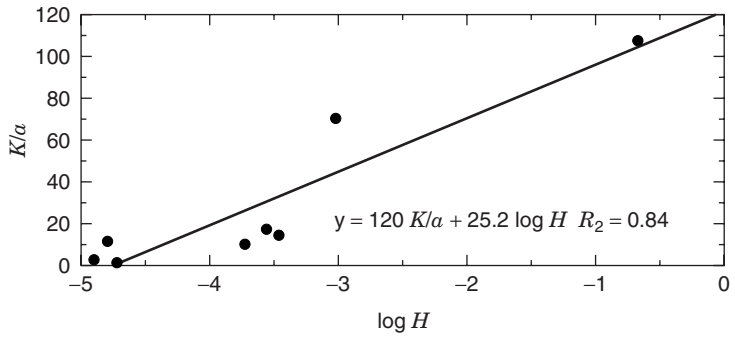


Figure 22. Relationship between experimental *K/a* values and constants of Henry *(H)* for the compounds mentioned in Table 25.

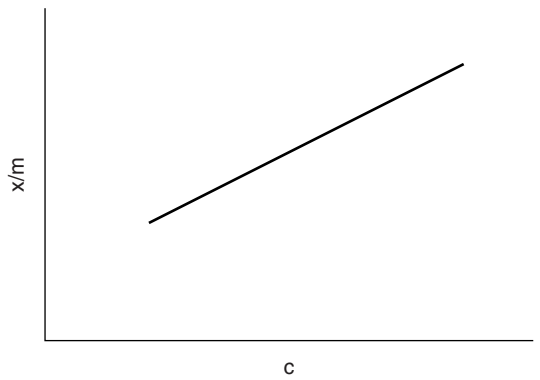


Figure 23. Freundlich isotherm.

rates would be greatest in shallow systems or in the upper layers of deeper waters. A report of the Stanford Research Institute gives a photooxidation half-life for benzo(a)pyrene in a lake environment of 7.5 hours. One would expect photooxidation to be low in sediments, however, because of a lack of penetrating radiation.

5.2. Photodissociation of Nitrate Ions. The excitation of nitrate ions in aqueous solution induces the oxidation of organic substrates. The photodissociation of nitrate ions leads to formation of the hydroxyl radical and atomic oxygen according to the following processes:

$$NO_3^- + h\nu \rightarrow \bullet\ NO_2 + O\bullet^-$$
$$O\bullet^- + H^+ + \rightarrow \bullet OH \text{ at pH} < 12$$
$$NO_3^- + h\nu \rightarrow NO_2^- + O$$

These reactions can occur under daylight irradiation because the first maximum of the absorption band of NO_3^- is located at 302 nm. Hydroxyl radicals are more reactive than atomic oxygen both in gas phase and in aqueous solution, and the observed oxidations are generally attributed to hydroxyl radicals. Nitrate ions are often considered one of the main sources of hydroxyl radicals in natural waters.

Nitrate ions have some useful influence in the photodegradation of organic pollutants. However, nitrate ions can also induce the formation of nitroderivatives and of nitrosophenol and lead to the formation of mutagenic compounds (2675).

5.3. Hydrolysis. Chemicals introduced into aqueous media in the environment can undergo hydrolysis and be transformed into new chemicals with properties different from those of their precursors. In addition, processes other than nucleophilic displacement by water may occur (e.g., elimination and isomerization). The importance of these transformations of chemicals as dominant pathways in aqueous media can be determined quantitatively from data on hydrolysis rate constants and half-lives.

Hydrolysis data will generally be important in assessing risks from organic chemicals that have hydrolyzable functional groups (such as esters, amides, alkyl halides, epoxides, and phosphoric esters). Hydrolysis refers to the reaction of an organic chemical (RX) with water with the resultant net exchange of the group X for the OH group from the water at the reaction center. Therefore,

$$RX + HOH \rightarrow ROH + HX$$

In the environment, hydrolysis of organic chemicals occurs in dilute solution. Under these conditions, water is present in a large excess, and the concentration of water is essentially constant during hydrolysis. Hence the kinetics of hydrolysis are pseudo-first-order at a fixed pH.

Processes other than nucleophilic displacement by water can take place. For example, X can be lost from RX via an elimination reaction. These elimination reactions exhibit kinetics behavior (i.e., pH independent or first-order acid or base dependent) similar to those reactions where OH substitution occurs.

The hydrolysis reaction can be catalyzed by acidic or basic species, including OH^- and H_3O^+ (H^+). The promotion of hydrolysis by H^+ or OH^- is known as *specific acid or specific base catalysis,* as contrasted to the general acid or base catalysis encountered with other cationic or anionic species. So far, the published laboratory data (1945, 1446, 1953, 1952) indicate that hydrolysis rates are the same in sterile natural freshwaters and in buffered distilled water at the same temperature and pH. Thus only specific acid or base catalysis, together with neutral water reaction, need be considered. Although other chemical species may catalyze hydrolysis reactions, the available concentrations of these species in the environment are usually too low to have an effect and are not expected to contribute significantly to the rate of hydrolysis (1954).

An extensive amount of information has been published on the hydrolysis of a wide variety of organic chemicals. However, most of the literature relating to environmental hydrolysis of chemicals pertains to pesticides. Much of this information is incomplete for the ranges of pH and temperature that are of environmental concern. Effects of buffer salts are often unrecognized.

D. BIOLOGICAL EFFECTS

1. Arrangement of Data.
The following classification has been followed in arranging the data on residues, bioaccumulation, and toxicity:

bacteria
algae
plants
protozoans (Phylum Protozoa)
worms (Phyla Platyhelminthes and Aschelminthes)
molluscs (Phylum Mollusca)
segmented worms (Phylum Annelida)
arthropods (Phylum Arthropoda)
    insects (Class Insecta)
    crustaceans (Class Crustacea)
    spiders and allies (Class Arachnidae)
chordates (Phylum Chordata)
vertebrates (Subphylum Vertebrata)
    fishes (Class Pisces)
    amphibians (Class Amphibia)
    reptiles (Class Reptilia)
    birds (Class Aves)
    mammals (Class Mammalia)

A more detailed classification list is given on the following pages, as well as a list of major organisms used throughout the book with their scientific and common names.

2. Classification List

protozoans	*(Phylum Protoza)*
	the flagellates (Class Mastigophora)
	rhizopods (Class Rhizopoda)
	amoebas (Order Amoebina)
	the spore-formers (Class Spirozoa)
	the ciliates (Class Ciliata)
mesozoans	*(Phylum Mesozoa)*
sponges	*(Phylum Parazoa)*
hydroids	*jellyfishes and corals (Phylum Cnidaria or Coelenterata)*
	sea firs (hydroids), hydras and siphonopheres (Class Hydrozoa)
	jellyfishes (Class Scyphozoa)
	sea anemones and corals (Class Anthozoa)
flatworms	flukes and tapeworms (Phylum Platyhelminthes)
roundworms	*rotifers and allies (Phylum Aschelminthes)*
	roundworms (Class Nematoda)
	rotifers (Class Rotifera)
molluscs	*(Phylum Mollusca)*
	gastropods (Class Gastropoda)
	Subclass Pulmonata
	bivalves (Class Bivalvia = Pelecypoda)
	Subclass Lamellibranchia
	squids, cuttlefishes, octopuses (Class Cephalopoda)
segmented worms	(Phylum Annelida)
	polychaetes (Class Polychaeta)
	nereids (Family Nereidae)
	Nereis diversicolor
	oligochaetes (Class Oligochaeta), including earthworms
	Family Tubificidae

Tubifex tubifex
leeches (Class Hirundinea)

arthropods *(Phylum Arthropoda)*
millipedes (Class Diplopoda)
centipedes (Class Chilopoda)
insects (Class Insecta)
exopterygote insects
mayflies (Order Ephemeroptera)
dragonflies (Order Odonata)
stoneflies (Order Plecoptera)
grasshoppers, crickets, and allies (Order Orthoptera)
cockroaches and praying mantids (Order Dictyoptera)
termites (Order Isoptera)
endopterygote insects
butterflies and moths (Order Lepidoptera)
flies (Order Diptera)
fleas (Order Siphonaptera)
ants, wasps, and bees (Order Hymenoptera)
beetles (Order Coleoptera)
crustaceans (Class Crustacea)
Subclass Branchiopoda
Order Anostraca
Artemia salina (brine shrimp)
Order Notostraca
Order Conchostraca
waterfleas (Order Cladocera)
Daphnia
copepods (Subclass Copepoda)
Order Calanoida
Calanus
Order Cyclopoida
Cyclops
malacostracans or higher crustaceans (Subclass Malacostraca)
isopods, sowbugs, and woodlice (Order Isopoda)
amphipods, scuds, and sideswimmers (Order Amphipoda)
Suborder Gammaridea
Gammarus
decapods (Order Decapoda)
Suborder Natantia
Section Caridea
Crangon vulgaris
Crangon crangon
Suborder Reptantia
Section Astacura
Homarus americanus
Homarus vulgaris
Nephrops norvegicus
Section Brachyura
Carcinus maenas (green crab)
Callinectus sapidus (blue crab)
spiders and allies (Class Arachnida)
scorpions (Order Scorpiones)
harvestmen (Order Opiliones or Phalangida)
ticks and mites (Order Acari)
spiders (Order Araneae)
starfishes, sea urchins, and allies (Phylum Echinodermata)

starfishes (Class Asteroidea)
sea urchins, sand dollars, and allies (Class Echinoidea)

chordates *(Phylum Chordata)*
vertebrates (Subphylum Vertebrata)
fishes (Class Marsipobranchii, Selachii, Bradyodonti, and Pisces)
amphibians (Class Amphibia)
newts and salamanders (Order Caudata)
frogs and toads (Order Salientia)
reptiles (Class Reptilia)
tortoises, terrapins, and turtles (Order Chelonia = Testudines)
crocodilians (Order Loricata = Crocodylia)
lizards and snakes (Order Squamata)
snakes (Suborder Ophidia = Serptentes)
birds (Class Aves)
mammals (Class Mammalia)
insect-eating mammals (Order Insectivora)
bats (Order Chiroptera)
the primates (Order Primates)
ant-eaters, sloths, armadillos (Order Edentator)
hares, rabbits, and pikas (Order Lagomorpha)
rodents (Order Rodentia)
whales (Order Cetacea)
flesh-eating animals (Order Carnivora)
dogs, cats, weasels, and bears (Suborder Fissipeda)
seals, sea lions, and walruses (Suborder Pinnipedia)
elephants (Order Proboscidea)

3. Organisms Used in Experimental Work with Polluting Substances or in Environmental Surveys

I

English name	**Latin name**
abalone	*Haliotis spp.*
American char	*Salvelinus fontinalis (Mitchell)*
American toad	*Bufo americanus*
anchovy	*Stolephorus purpureus*
anole	*Anolis carolinensis*
armadillo	*Daysypus novemcinctus*
Atlantic kelp	*Laminaria digitata,* L. *agadhii*
Atlantic menhaden	*Brevoortia tyrannus*
Atlantic ribbed mussel	*Volsella demissa*
Atlantic salmon	*Salmo salar*
barnade	*Balanus spp.*
barn owl	*Tyto alba*
bay anchovy	*Anchoa (Anchoiella) mitchilly*
bay mussel	*Mytilus edulis*
bay scallop	*Aequipecten (Pecten) irradians*
big brown bat	*Eptesicus fuscus*
bigmouth buffalo	*Ictiobus cyprinellus*
black bullhead	*Ameiurus melas* or*Ictalurus melas*
bleak	*Alburnus alburnus (L.)*
bloodworm	*Glycera dibranchiata*
blue crab	*Callinectes sapidus*
bluegill sunfish	*Lepomis macrochirus*
bobwhite quail	*Colinus virginianus*

English name	Latin name
box turtle	*Terrapene sp.*
brook trout	*Salvelinus fontinalis*
brown bullhead	*Ameiurus nebulosus* or *Ictalurus nebulosus*
brown shrimp	*Penaeus aztecus*
brown shrimp	*Crangon crangon*
brown trout	*Salmo trutta*
bullfrog	*Rana catesbiana*
bullheads	*Ameiurus* or*Ictalurus* (see also catfish)
bumble bee	*Bombus*
calico crab	*Ovalipes ocellatus*
calico scallop	*Aequipecten gibbus*
California ground squirrel	*Spermophilus beecheyi*
California sea mussel	*Mytilus californicus*
Canada goose	*Branta canadensis*
carp	*Cyprinus carpio*
cat	*Felis domestica*
catfish	*Ictalurus*
catfish (American)	*Ameiurus nebulosus (Le Sueur)*
channel catfish	*Ictalurus punctatus*
chicken	*Gallus domesticus*
chinook salmon	*Oncorhynchus tschawytscha*
chub	*Squalius cephalus (L.)*
coalfish	*Pollachius birens*
cod	*Gadus morhua*
coho salmon	*Oncorhynchus kisutch (Walbaum)*
common cockroach	*Periplaneta americana*
common earthworm	*Lumbricus terrestris*
common frog	*Rana temporaria*
common toad	*Bufo bufo*
cone shells	*Conus spp.*
copepod	*Pseudocalanus minutus*
cotton rat	*Sigmodon hispidus*
cottontail	*Sylvilagus sp.*
crab	*Ranina serrata*
	Pertunus sanquinolentes
	Podophtalmus vigil
creek chub	*Semolitus atromaculatus*
cricket	*Gryllus sp.*
croaker	*Mycorpogon undulatus*
crucian carp (goldfish)	*Carassius carassius*
cutthroat trout	*Salmo clarki*
dace	*Leuciscus leuciscus (L.)*
deer mouse	*Peromyscus maniculatus*
dog	*Canis familiaris*
domestic chicken	*Gallus gallus*
domestic New Zealand white rabbit	*Oryctolagus cuniculus*
Dungeness crab	*Cancer magister*
earthworm	*Lumbricus terrestris*
eastern oyster	*Crassostrea virginica*
eastern chipmunk	*Tamias striatus*
edible frog	*Rana esculenta*
eel	*Anguilla anguilla (L.)*
	Anguilla vulgaris
egret	*Ardeola sp.*

English name	Latin name
English sole	*Parophrys vetulus*
European badger	*Meles meles*
European hares	*Lepus europaeus*
fathead minnow	*Pimephales promelas*
field cricket	*Gryllus pennsylvanicus*
flatworms	*Platyhelminthes*
Fowler's toad	*Bufo fowleri*
fruit fly	*Drosophila sp.*
garter snake	*Thamnophis sirtalis*
goatfish	*Mulloidichthys spp.*
goldfish	*Carassius auratus*
green crab	*Carcinides maenas*
green frog	*Rana clamitans*
green sunfish	*Lepomis cyanellus*
gulf menhaden	*Brevoortia partonus*
guinea pig	*Cavia*
guppy	*Lebistes reticulatus*
hard clam	*Mercenaria (Venus) mercenaria*
hares	*Leporidea*
herring	*Lupea harengus*
honey bee	*Apis melliferra*
horned lizard	*Phrynosoma cornutum*
housefly	*Musca domestica*
house sparrow	*Passer domesticus*
Japanese quail	*Coturnix coturnix*
kangaroo rat	*Dipodomys sp.*
kelp	*Macrocystis pyrifera*
killifish	*Fundulus*
king crab	*Parlithoides camtschatica*
lake trout	*Salvelinus namaycush*
land snail	*Helix sp.*
largemouth bass	*Micopterus salmoides*
leopard frog	*Rana pipiens*
little neck clam	*Protothaca staminea*
lobster	*Panulirus japonicus: P. pencillatus*
longear sunfish	*Lepomis megalotis*
mallard	*Anas platyrhynchos*
marine pin perch	*Lagodon rhomboides*
meadow vole	*Microtus pennsylvanicus*
mealworm	*Tenebrio sp.*
Mexican axolotl	*Ambystoma mexicanum*
midge	*Chironomus plumosus*
milkfish	*Chanos chanos*
mink	*Mustela chanos*
minnow	*Phoxinus phoxinus*
mosquito fish	*Gambusia affinis*
mosquito fly	*Culex* *Aedes* *Anopheles*
mountain bass	*Kuhlia sandvicensis*
mullet	*Mugil cephalus*
mummichog	*Fundulus heteroclitus*
northern lobster	*Homarus americanus*
northern pike	*Esox lucius*

English name	Latin name
nutria	*Myocaster coypus*
old world mouse	*Mus musculus*
old world rat	*Rattus norvegicus*
opossum	*Didelphis virginianus*
Pacific herring	*Clupea pallasii*
Pacific oyster	*Crassostrea gigas*
Pacific sardine	*Sardinops caerula*
pack rat	*Neotoma lepida*
perch	*Perca fluviatilis*
pheasant	*Phasianus sp.*
pickerel frog	*Rana palustris*
pigeon	*Columba livia*
	Columba sp.
pinfish	*Lagodon rhomboides*
pink salmon	*Oncorhynchus gorbuscha*
pink shrimp	*Penaeus duorarum*
pismo clam	*Tivela stultorum*
plaice	*Pleuronectes platessa*
pollack	*Gadus pollachius*
pompano	*Trachinotus carolinus*
pompano, jack cravally	*Caranx spp.*
pumpkinseed	*Lepomis gibbosus*
purple sea urchin	*Stronglo centrotus purpuratus*
rabbits	*Sylvilagus*
rainbow trout	*Salmo gairdneri*
rainwater killifish	*Lucania parva*
razor clam	*Siliqua patula*
rat snake	*Elaphe sp.*
red algae	*Porphyra spp.*
red seaweed	*Gracileria virrucosa, G. foliifera*
red snapper	*Lutianus campechanus*
rhesus monkey	*Macaca mulatta*
ribbed limpet	*Siphonaria normalis*
ringnecked pheasant	*Phasianus colchicus*
roach	*Rutilus rutilus (L.)*
roundworms	*Aschelminthes*
sailfin molly	*Poecilia (Mollienisia) latipinna*
salmons	*Salmo* or *Oncorhynchus*
salmon (Atlantic)	*Salmo salar (L.)*
saltwater limpet	*Hecioniscus exaratus H. argentatus*
sand shrimp	*Crangon septemspinosa*
sandworm	*Nereis virens, Nereis vixillosa*
sea anemone	*Anthropleura elegantissima*
sea lamprey	*Petromyzon marinus*
sea lettuce	*Ulva spp.*
sea urchin	*Arbacid puntulata; Lytechnius spp.*
	Echinometra spp.
segmented worms	*Annelida*
scup	*Stenotomus chrysops*
shore crabs	*Hemigrapsus spp.*
sheep	*Ovis sp.*
sheepshead minnow	*Cyprinodon variegatus*
shiner perch	*Cymatogaster aggregata*
shrimp	*Crangon spp.*

English name	Latin name
	Pandalus spp.
sprat	*Clupea sprattus*
smallmouth bass	*Micropterus dolomieui*
snapping shrimp	*Crangon spp.*
snapping turtle	*Chelydra serpentina*
soft shell clam	*Mya arenaria*
southern flounder	*Paralichthys lethostigma*
spiny lobster	*Panuliris argus*
spring peeper	*Hyla crucifer*
stable fly	*Stomoxys calcitrans*
staghorn sculpin	*Leptocottus armatus*
starling	*Sturnis vulgaris*
starry flounder	*Platichthys stellatus*
stickleback (12-spined)	*Pygosteus pingitius (L.)*
striped bass	*Roccus saxatilis* *Morone saxatilis*
striped mullet	*Mugil cephalus*
suckers	*Catostomus* or *Ictiobus*
summer flounder	*Paralichthys dentatus*
sunfish (common)	*Lepomis humilis*
surf clam	*Spirula solidissima*
surgeon fish	*Acanthurus spp.*
swallows	*Hirundinidae*
swine (miniature)	*Sus scrofa*
squirrel monkey	*Saimiri sciureus*
tench	*Tinca tinca (L.)*
sea moss	*Chondrus crispus*
threespine stickleback	*Gasterosteus aculaetus*
treefrog	*Hyla versicolor*
trout	*Salmo* or *Salvelinus*
turkey	*Meleagris*
walleye	*Stizostedion vitreum*
water flea	*Daphnia*
water shrimp	*Gammarus pulex*
western chipmunk	*Eutamias sp.*
white shrimp	*Penaeus setiferus*
white sucker	*Catostomus commersoni*
whiting	*Gadus merlangus*
winter flounder	*Pseudopleuronectes americanus*
woodfrog	*Rana sylvatica*
yellow bullhead	*Ictalurus netalis*

II

Latin name	English name
Acanthurus spp.	surgeon fish
Aedes	mosquito fly
Aequipecen gibbus	calico scallop
Aequipectern (Pecten) irradians	bay scallop
Alburnus alburnus	bleak
Ambystoma mexicanum	Mexican axolotl
Ameiurus melas	black bullhead
Ameiurus nebulosus	brown bullhead or American catfish

Latin name	English name
Anas platyrhynchos	mallard
Anchoa (Anchoiella) mitchilly	bay anchovy
Anguilla anguilla	eel
Anguilla vulgaris	eel
Annelida	segmented worms
Anolis carolinensis	anole
Anthopleura elegantissima	mosquito fly
Apis	sea anemone
Apis melliferra	honey bee
Arbacid puntulata	sea urchin
Ardeola spp.	egret
Aschelminthes	roundworms
Balanus spp.	barnacle
Bombus	bumble bee
Branta canadensis	Canada goose
Brevoortia patronus	gulf menhaden
Brevoortia tyrannus	Atlantic menhaden
Bufo americanus	American toad
Bufo bufo	common toad
Bufo fowleri	Fowler's toad
Callinectes sapidus	blue crab
Cancer magister	Dungeness crab
Canis familiaris	dog
Caranx spp.	pompano, jack cravally
Carassius auratus	goldfish
Carassius carassius	crucian carp
Carcinedes maenas	green crab
Catostomus	suckers
Catostomus commersoni	white sucker
Chandrus crispus	sea moss
Chanos chanos	milkfish
Chelydra serpentina	snapping turtle
Chironomus plumosus	midge
Clupea harengus	herring
Clupea pallasii	Pacific herring
Clupea sprattus	sprat
Colinus virginianus	bobwhite quail
Columba livia	pigeon
Conus spp.	cone shells
Coturnix coturnix	Japanese quail
Crangon crangon	brown shrimp
Crangon septemspinosa	sand shrimp
Crangon spp.	snapping shrimp
Crassostrea gigas	Pacific oyster
Crassostrea virginica	eastern oyster
Culex	mosquito fly
Cymatogaster aggregata	shiner perch
Cyprinodon variegatus	sheepshead minnow
Cyprinus carpio	carp
Daphnia	water flea
Daysypus novemcinctus	armadillo
Didelphis virginianus	opossum
Dipodomys sp.	kangaroo rat
Drosophila sp.	fruit fly

Latin name	English name
Echinometra spp.	sea urchin
Elaphe sp.	rat snake
Eptesicus fuscus	big brown bat
Esox lucius	northern pike
Eutamias sp.	western chipmunk
Felis domestica	cat
Fundulus	killifish
Fundulus heteroclitus	mummichog
Gadus merlangus	whiting
Gadus morhua	cod
Gadus pollachius	pollack
Gallus gallus	domestic chicken
Gambusia affinis	mosquito fish
Gammarus pulex	water shrimp
Gasterosteus aculeatus	threespine stickleback
Glycera dibranchiata	bloodworm
Gracilaria verrucosa, G. foliifera	red seaweed
Gryllus pennsylvanicus	field cricket
Haliotis spp.	abalone
Helcioniscus exaratus, H. argentatus	saltwater limpet
Helix sp.	land snail
Hemigrapsus spp.	shore crabs
Hirudinidae	swallows
Homarus americanus	northern lobster
Hyla crucifer	spring peeper
Hyla versicolor	treefrog
Ictalurus	catfish
Ictalurus melas	black bullhead
Ictalurus natalis	yellow bullhead
Ictalurus nebulosus	brown bullhead
Ictalurus punctatus	channel catfish
Ictiobus	suckers
Ictiobus cyprinellus	bigmouth buffalo
Kuhlia sandvicensis	mountain bass
Lagodon rhomboides	marine pin perch
Laminaria digibacta, L. agardhii	Atlantic kelp
Lesbistes reticulatus	guppy
Lepomis cyanellus	green sunfish
Lepomis gibbosus	pumpkinseed
Lepomis humilis	common sunfish
Lepomis macrochirus	bluegill sunfish
Lepomis megalotis	longear sunfish
Leporidae	hares
Leptocottus armatus	staghorn sculpin
Lepus europaeus	European hares
Leuciscus leuciscus	dace
Lucania parva	rainwater killifish
Lumbricus terrestris	common earthworm
Lutianus campechanus	red snapper
Lytechnius spp.	sea urchin
Macaca mulatta	rhesus monkey
Macrocystis pyrifera	kelp
Meleagris	turkey
Meles meles	European badger

Latin name	English name
Mercenaria (Venus) mercenaria	hard clam
Micropogon undulatus	croaker
Micropterus dolomieui	smallmouth bass
Micropterus salmoides	largemouth bass
Microtus pennsylvanicus	meadow vole
Morone saxatilis	striped bass
Mugil cephalus	striped mullet
Mulloidichthys spp.	goatfish
Musca domestica	housefly
Mus musculus	old world mouse
Mustela vison	mink
Mya arenaria	soft shell clam
Myocaster coypus	nutria
Mytilus californicus	California sea mussel
Mytilus edulis	bay mussel
Neotoma lepida	pack rat
Nereis virens, Nereis vexillosa	sandworm
Oncorhynchus gorbuscha	pink salmon
Oncorhynchus kisuth	coho salmon
Oncorhynchus tschawytscha	chinook
Oryctolagus cuniculus	domestic New Zealand white rabbit
Ovalipes ocellatus	calico crab
Ovis sp.	sheep
Pandalus spp.	shrimp
Panulirus argus	spiny lobster
Panulirus japonicus, P. Pencillatus	lobster
Paralichthys dentatus	summer flounder
Paralichthys lethostigma	southern flounder
Paralithoides camtschatica	king crab
Parophrys vetulus	English sole
Passer domesticus	house sparrow
Penaeus aztecus	brown shrimp
Penaeus duorarum	pink shrimp
Penaeus setiferus	white shrimp
Perca fluviatilis	perch
Periplaneta americana	common cockroach
Peromyscus maniculatus	deer mouse
Petromyzon marinus	sea lamprey
Phasianus colchicus	ringnecked pheasant
Phoxinus phoxinus	minnow
Phrynosoma cornutum	horned lizard
Pimephales promelas	flathead minnow
Platichthys stellatus	starry flounder
Platyhelminthes	flatworms
Pleuronectes platessa	plaice
Podophthalmus vigil	crab
Poecilia (mollienesia) latipinna	sailfin molley
Pollachins birens	coal fish
Porphyra spp.	red algae
Portunus sanquinolentus	crab
Protothaca staminea	little neck clam
Pseudocalanus minutus	copepod
Pseudopleuronectes americanus	winter flounder
Pygosteus pungitius	stickleback (12-spined)

Latin name	English name
Rana catesbiana	bullfrog
Rana clamitans	green frog
Rana esculenta	edible frog
Rana palustris	pickerel frog
Rana pipiens	leopard frog
Rana sylvatica	woodfrog
Rana temporaria	common frog
Rana serrata	crab
Rattus norvegicus	old world rat
Roccus saxatilis	striped bass
Rutilus rutilus	roach
Saimiri sciureus	squirrel monkey
Salmo	trout
Salmo clarki	cutthroat trout
Salmo gairdneri	rainbow trout
Salmo salar	Atlantic salmon
Salmo trutta	brown trout
Salvelinus	trout
Salvelinus fontinalis	brown trout
Salvelinus namaycush	lake trout
Sardinops caerula	Pacific sardine
Semolitus atromaculatus	creek chub
Sigmodon hispidus	cotton rat
Siliqua patula	razor clam
Siphonaria normalis	ribbed limpet
Spermophilus beecheyi	California ground squirrel
Spirula solidissima	surf clam
Squalius cephalus	chub
Stenotomus chrysops	scup
Stizostedion vitreum	walleye
Stolephorus purpureus	anchovy
Stomoxys calcitrans	stable fly
Stronglo centrotus purpuratus	purple sea urchin
Sturnis vulgaris	starling
Sus scrofa	swine, miniature
Sylvilagus	rabbits
Sylvilagus sp.	cottontail
Tamias striatus	eastern chipmunk
Tenebrio sp.	mealworm
Terrapene sp.	box turtle
Thamnophis sirtalis	garter snake
Tinca tinca	tench
Tivela stultorum	pismo clam
Trachinotus carolinus	pompano
Tyto alba	barn owl
Ulva spp.	sea lettuce
Volsella demissa	Atlantic ribbed mussel

4. Discussion of Biological Effects Tests

4.1. Ecological Effects Tests. Releases of hazardous chemical substances into the environment during manufacturing, processing, distribution, use, or disposal, whether accidental or planned, can have an adverse impact on both natural and man-modified ecosystems and their components. The societal costs may include degradation of the environment; losses in sport and commercial fisheries,

shellfish populations, and wildlife resources; losses in agriculture; losses in tourism and property values; and other adverse impacts.

Testing for such effects requires the selection of indicators (i.e., indicative parameters) that provide for wide taxonomic representation and include a range of biological processes. Ideally, testing at levels of ecological organization above the individual species would provide information more directly related to ecological consequences of the release of a hazardous chemical. However, the development and standardization of such tests are difficult because of the complexity of the species interactions that characterize ecosystems. A major thrust for the future therefore will be the development of test methods to address interactions such as those that occur between predator and prey, among competitors for habitat or food, and between disease and host organisms. As methods such as microcosm studies and other laboratory model systems are developed, they may help to address these ecological testing needs.

Laboratory testing below the level of the organism is also potentially useful. It is generally rapid and readily amenable to standardization. Because many cellular and subcellular functions are common to a wide range of organisms, they have the potential of being applicable to many sets of ecological circumstances.

However, most ecological effects tests currently in use employ single-species test populations of vertebrates, invertebrates, or plants. Individual species represent an intermediate level of biological organization between subcellar functions and community/ecosystem interactions. Many single-species tests are considered state-of-the-art and have correlated well with actual ecological effects of chemicals.

The following criteria can be used to select tests:

- The test results are significant and useful for risk assessment.
- The test applies to a wide range of chemical substances or categories of chemical substances.
- The test is cost-effective in terms of personnel, time, and facilities.
- The test is adequately sensitive for detection of the subject effect.

Confidence in extrapolation from simple test to ecologically significant impacts depends not only on the appropriate kinds of tests but also on the selection of appropriate organisms to be used in those tests. Organisms useful for assessment testing should have characteristics such as the following:

- The organism is representative of an ecologically important group (in terms of taxonomy, trophic level, or realized niche).
- The organism occupies a position within a food chain leading to humans or other important species.
- The organism is widely available, is amenable to laboratory testing, is easily maintained, and is genetically stable so that uniform populations can be tested.
- There is adequate background data on the organism (its physiology, genetics, taxonomy, and role in the natural environment are well understood) so that data from these tests can be adequately interpreted in terms of actual environmental impacts.

4.2. Plant Effects Tests. All organisms require energy to perform vital functions and use the radiant energy of sunlight as their ultimate source of energy. Green plants use this energy directly through the process of photosynthesis when suitable inorganic carbon and nutrients are present. The sun's energy is converted into chemical energy, which is stored in plants in the form of sugars, starches, and other organic chemicals to be used by the plants themselves or by other organisms as energy sources.

Photosynthesis is the source of virtually all atmospheric oxygen. Plants also synthesize vitamins, amino acids, and other metabolically active compounds essential to many organisms. In this context, the maintenance of the biosphere depends on the normal functioning of green plants. Data from the tests in this section are expected to provide preliminary indications of the effects of chemical substances on the following groups of plants: blue-green algae, diatoms, green algae, monocotyledons, and dicotyledons.

Blue-green algae make up one of the two groups of organisms capable of converting atmospheric nitrogen into forms that can be utilized by all living organisms. Diatoms and unicellular green algae are responsible for most of the world's photosynthesis and are the primary food energy base for most

organisms inhabiting aquatic environments. They are therefore necessary for all aquatic life and for human food taken from freshwater and marine environments (e.g., fish).

Algal inhibition. Testing for inhibition or stimulation of the growth of algae indicates the extent to which a test chemical can affect primary producers in lakes, streams, estuaries, and oceans. It can also generally indicate phytotoxicity or stimulation of plant growth. Substances that drastically inhibit growth at or near concentrations expected in the environment may reduce aquatic productivity. Even those substances that inhibit algal growth only partially, or that stimulate growth, at or near concentrations expected in the environment might shift relative algal populations so that undesirable species could increase. If diatoms or green algae grow less in the presence of the chemical than do blue-green algae, for example, a bloom of the less desirable blue-green species could develop.

Algae are often selected to represent aquatic primary productivity because they constitute the major mechanism for fixation of energy in most aquatic locations. Techniques for culturing and measuring them are simpler and less expensive than those for larger plants or for attached organisms (e.g., periphyton). The parameters recommended to measure potential effects on algae are inhibition of dry weight increase and changes in cell size. There are other potential effects that are not recommended. Lethality, for example, is commonly measured for other organisms, but it is difficult to determine for microscopic organisms and for nonmotile organisms. Inhibition of photosynthesis and/or respiration could be measured, but the balance between photosynthesis and respiration is accumulated as growth. In addition, growth represents the product that is important in the food chain and is therefore more directly relevant to assessment.

Uncertainties in using these data in assessment center on whether the selected species are adequate indicators of the potential for stimulation or toxicity to nonselected algal species, on whether the benefits of algae to the food chain can be accurately predicted from changes in dry weight and cell size, and on whether there are significant interactive effects (such as competition) that are affected at lower concentrations of the chemical substance than is any individual species.

4.3. Animal Effects Tests. The potential of a chemical to produce adverse ecological effects can be indicated by the results of preliminary testing of "representative" animals. Preliminary tests and test organisms should be selected on the basis of taxonomic, ecological, toxicological, and chemical exposure criteria. Test schemes should reflect those ecological hazards that a specific chemical substance may cause. Test responses-death, reproductive and/or behavioral dysfunction, and impairment of growth and development-are important factors for hazard assessment.

4.3.1. INVERTEBRATES. Toxicity of a chemical substance to invertebrates is an important factor in preliminary assessment of impact on ecosystems. Invertebrates have broad ecological roles and show various sensitivities to chemicals.

4.3.1.A. Aquatic Invertebrates. A number of aquatic invertebrates for acute tests are listed below:

Marine and Estuarine Invertebrates

copepods: *Acartia tonsa, Acartia clausi*
shrimp: *Penaeus setiferus, P. duorarum*
grass shrimp: *Palaemonetes pugio, P. intermedius, P. vulgaris*
sand shrimp: *Crangon septemspinosa*
mysid shrimp: *Mysidopsis bahia*
blue crab: *Callinectes sapidus*
green crab: *Carcinus maenas*
oyster: *Crassostrea virginica, C. gigas*
polychaetes: *Capitella capitata*

Freshwater Invertebrates

daphnids: *Daphnia magna, D. pulex, D. pulicaria*
amphipods: *Gammarus lacustris, G. fasciatus,* or *G. pseudolimnaeus*
crayfish: *Oronectes* sp., *Cambarus* sp., *Procambarus* sp.

stoneflies: *Pteronarcys* sp.
mayflies: *Baetis* sp. or *Ephemerella* sp.
mayflies: *Hexagenia limbata* or *H. bilinata*
midges: *Chironomus* sp.
snails: *Physa integra, P. heterostropha, Amnicola limosa*
planaria: *Dugesia tigrina*

4.3.1.B. Terrestrial Invertebrates. The ecological role and suitability for toxicity testing of a number of terrestrial invertebrates are discussed below.

Phylum Annelida

Class. Oligochaeta (Earthworms). Family Lumbricidae: *Lumbricus terrestris* (common earthworm).

Ecological Role. Earthworms occur in upper soil levels and feed on decaying organic matter. They are particularly important as soil mixers, aerators, and drainers and serve as food for many insectivores (robins, woodcock, mice, and shrews).

Suitability for Toxicity Testing. The diversity and wide distribution of worms make them desirable test species. Earthworms are particularly valuable because of their role in soil ecosystems, their part use, and their ease of maintenance.

Earthworms are important in the later stages of soil formation and in maintaining soil structure and fertility. They contribute in many ways, such as by incorporating decaying organic matter into soil, turning it over and mixing it with other soil fractions, and helping to improve soil aeration, drainage, and moisture-holding capacity. Earthworms have been reported to move as much as 250 tons of soil and organic matter per hectare annually. Certain species, particularly *Lumbricus terrestris,* pull organic matter down into the soil, fragment it, and mix it with mineral particles.

Earthworms are eaten by many vertebrates, including birds, poultry, and pigs. Ecologically they are near the bottom of the terrestrial trophic food chains and have a tendency to concentrate compounds such as organochlorine insecticides and PCBs in their tissues. These chemicals seldom harm the worms directly but can either kill vertebrates that eat the worms or be taken up into their tissues, thus indirectly affecting other animals higher in terrestrial food chains.

Earthworms have a number of characteristics that identify them as one of the most suitable soil animals to be used as a key bioindicator organism for testing for pollution by soil chemicals. In addition to their importance and key role in soil fertility, they are common in the great majority of soils and also in organic matter, they are large in size and easy to handle, they can be collected and identified readily, and they are known to be affected by, and to take up into their tissues, a number of organic and inorganic chemicals.

Earthworms are easily bred quite rapidly and in large numbers in the laboratory for toxicity testing, and their longevity makes it unlikely that many worms would die during the period of a toxicity test in untreated media. Several species are available commercially from fish bait breeders. Because of these characteristics, and because the earthworm is such a typical and important member of the soil fauna, it has been selected as a key indicator organism for the ecotoxicological testing of the toxicity of industrial chemicals by many national pesticide registration authorities and by international organizations such as the OECD, FAO, EU and others (2658).

Phylum Mollusca

Class. Gastropoda (pulmonate snails): *Helix aspersa.*

Ecological Role. Terrestrial snails and slugs are primary consumers and eat a varied diet of plant materials. They are a food source for larger insectivores.

Suitability for Toxicity Testing. Helix sp. is a very widely distributed snail and is abundant in certain moist habitats.

Phylum Arthropoda

Class Arachnida. Members of this class are spiders, mites and ticks, scorpions, and harvestmen.

Ecological Role. Mites and ticks are parasitic on plants and animals, deriving their substance directly from the fluids of their hosts. Spiders are carnivorous invertebrates whose food consists entirely of small animals, primarily insects. All arachnids are potential food sources for insectivores.

Suitability for Toxicity Testing. Mites and ticks are easily maintained under controlled conditions. Spiders are excellent test subjects because they are predators on many insects; they are relatively easy to maintain, if not to breed; and their web building provides a very useful experimental tool.

Class Insecta, order Orthoptera. This order includes many large and well-known insects-crickets, grasshoppers, roaches, locusts, and praying mantids. Toxicological research has been done on wide-ranging and easily obtainable species: *Periplaneta americana*, the common cockroach; *Gryllus pennsylvanicus*, the field cricket; *Schistocera gregaria* ; and *Locusta migratoria*, locusts; *Mantis* sp., *Stagmomantis* sp., and *Tenodera* sp., mantids.

Ecological Role. Crickets and cockroaches are omnivorous insects and will feed on many kinds of organic matter. Locusts and grasshoppers are vegetarians and can occur in very large numbers, sometimes defoliating the countryside. Praying mantis are predators and feed primarily on insects. All of these species are possible food items for insectivorous invertebrates and vertebrates.

Suitability for Toxicity Testing. The insects in this order are easily maintained and very abundant. Praying mantis, being strictly carnivorous and relying heavily on insects for food, might accumulate certain chemicals or be more heavily exposed to target animals.

Orders Hemiptera, Homoptera. Hemipterans are true bugs, the homopterans are closely associated with the bugs.

Ecological Role. Hemipterans and homopterans are feeders on organic fluids, primarily plant juices. They can be destructive agricultural pests. These insect groups are food for insectivorous invertebrates and vertebrates. Aphids or plantlice are a large group of Homopterans and frequent pests on vegetation. The herbivorous aphid species are good selections for use in studies of environmental contaminants that may accumulate or deposit on vegetation.

Order Coleoptera. Beetles that have been used in research are frequently pest species, though not exclusively. Included are ground beetles *(Harpalus*, *Agonum*, *Feronia),* lady beetles (Hippodamia, Coleomegilla), and flour beetles *(Tribolium).*

Ecological Role. Some beetles are pests on agricultural crops, and others are predacious ground-dwelling species (e.g., *Harpalus*). Others feed on fungi and carrion. All beetles are potential food for insectivorous invertebrates and vertebrates.

Order Lepidoptera. Butterflies and moths are conspicuous and well-known insects.

Ecological Role. The larvae of butterflies and moths, often severe agricultural pests, are economically much more important than the adults, some of which never feed. They frequently supply food for insectivorous predators.

Order Diptera. The "flies" are a well-known group of insects and one of the larger orders. Mosquitoes, stable flies, house flies, and blow flies are pests of humans and other animals.

Ecological Role. Many adult dipterans are vectors of disease and nuisance pests of other animals. However, they also can represent staple foods for insectivorous predators (i.e., bats, swallows, frogs). Aquatic larvae are frequently major food sources for fish in quiet waters. The double association of some forms (e.g., mosquitoes) with aquatic and terrestrial systems at different times during their life cycles may make them particularly suitable subjects in experiments in which land-water transfer of a substance is to be studied.

Order Hymenoptera. The hymenopterans include ants, sawflies, ichneumons, chalcids, wasps, and bees.

Ecological Role. Many hymenopterans are important as pollinators and as parasites on

Table 26. Comparison between Field- and Laboratory-Cultured Populations for Marine Pollution Studies (1717).

Field Population	Laboratory Population
A. Disadvantages	
1. Careful handling needed during collection and transportation	1. Genetic drift from wild conditions
2. Seasonal variation in mortality and in healthy condition	
3. Variations in size and life stages	
4. Seasonal changes in population abundance	
5. Various physiological states due to zonation	
B. Advantages	
1. Natural population realistic	1. Close to the normal physiological state; capable of growing and reproducing in captivity
	2. Ages known
	3. Available throughout the year
	4. Biochemical comparison possible between laboratory and suspected polluted populations
	5. Useful for chronic toxicity tests

other insects. They feed on pollen and plant juices, and many feed on other liquid foods.

Class Crustacea. Wen Yuh Lee (1717) recommends three laboratory-cultured crustaceans for use in marine pollution studies because they are characterized by wide distribution, a short life cycle and high reproductive potential and are representative of the plankton and benthos in coastal waters and the intertidal zone. The recommended crustaceans are *Acartia tonsa* (a planktonic copepod), *Sphaeroma quadridentatum* (an isopod), and *Amphitoc valida* (an amphipod).

The selection of specific organisms should further be based on vulnerability to marine pollutants in a critical life state (usually the larval or temporary planktonic stage), commercial or biological value, availability and ease of collection, ease of rearing and maintaining in the laboratory, and existing knowledge on ecological requirements (927). Laboratory-bred populations show several advantages in a long-term toxicity study. One of the most important is that the cultured population is able to grow and reproduce in the laboratory and is available whenever either a test is to be undertaken to determine the toxicity of products (e.g., oils) or to rank products such as dispersants in toxicity. The advantages and disadvantages of natural and laboratory cultured populations are summarized in Table 26.

Crustacean Life Cycle. Aquatic invertebrates are the most common food chain links between phytoplankton and desirable species of fish and shellfish. The extent to which chemical substances affect reproduction and growth of aquatic invertebrates is important because healthy stocks of fish and shellfish are dependent on adequate sources of food. A life cycle test is desirable for assessment because it gives a better estimate of total hazard than, for example, an acute toxicity test.

Freshwater Crustacean: Daphnia. One of the most widely performed and economical life cycle tests used *Daphnia,* a freshwater zooplankton. Daphnids have a planktonic existence, have a short life cycle, and can be easily cultured. They have been widely used in toxicological testing and are sensitive to toxicants. Although no invertebrate life cycle tests have been completely standardized, the *Daphnia* life cycle test has been used extensively

by many researchers. Reproduction and life cycle tests on *Daphnia* begin with newborn daphnids, which are exposed to a chemical substance in culture for approximately three or four weeks. Reproductive impact of the chemical substance is evaluated by comparing the number of young produced by the organisms exposed to a chemical substance with the number produced by controls. Chronic lethal effects are evaluated by observing survival of the daphnids initially exposed throughout their life cycle.

Marine crustacean: mysid shrimp. Mysidopsis bahia is an excellent species for life cycle tests for *marine invertebrates* because of its sensitivity to known toxic chemicals, its ease of culturing, its short life cycle, and its importance in near-shore marine food webs.

4.3.2. VERTEBRATES

The term "toxicity test" covers a wide and increasing range of types of investigations. With fish, such tests can include

(a) The study of the toxic properties of fish (that is, fish toxicology).
(b) The use of fish for detecting the presence of, or determining concentrations of, metals, toxins, and hormones, for example, in solution (i.e., bioassay and tests for screening for the presence or absence of some defined response).
(c) Laboratory and field tests of selective piscicides.
(d) Basic toxicological research into the metabolism and detoxification of substances by this class of animal.
(e) Tests to compare the relative lethal toxicities of different substances, under some fixed but arbitrary set of conditions, to one or more species of fish.
(f) Tests to compare the lethal toxicity of a given substance to a single species of fish under a range of test conditions (e.g., pH, dissolved oxygen, hardness) to determine the effects of environmental conditions on toxicity.
(g) Simple, but unscientifically based, laboratory tests made under fixed conditions to assess arbitrarily for some administrative convenience the acceptability of a substance or effluent.
(h) Laboratory tests of the effects of a substance on survival, growth, reproduction, and so on, in fish.
(i) Laboratory and field tests of the effects of a waste (or of a chemical for use in agriculture) on fishes, on fish populations, and, where these exist, on fisheries.
(j) The laboratory use of fish to monitor aqueous wastes for harmful effects.
(k) The laboratory use of fish to monitor waters being abstracted from rivers for drinking, food processing, irrigation, and so on, for harmful effects.
(l) The use of fish in cages to monitor river water for aqueous domestic and industrial wastes for harmful effects.

Toxicity studies are conveniently classified on the basis of the duration of exposure (as shown in Table 27), which of course automatically reflects the concentration of the poison. In a full investigation these tests would typically follow each other in the order given, should the substance under effect and the nature of exposure warrant it. Special studies are made for carcinogenic,

Table 27. Broad Scheme of Toxicity Testing

Type of Test	Information Sought
(a) Acute	The lowest concentration having effect within a few days of continuous exposure. The effect is related to the breakdown of physiological systems, and typically death is the response sought.
(b) Subchronic	The highest concentration having no effect within perhaps one-tenth of the normal average life span. Used to determine the mode of action and functional and physiological changes.
(c) Chronic	The highest concentration having no effect over the lifetime of the animal.

teratogenic, and mutagenic effects. Rainbow trout *(Salmo gairdneri)* and bluegill sunfish *(Lepomis macrochirus)* are suggested as standard test species. These two fish, one a cold water species and the other a warm water species, have generally been the most sensitive to most previously tested chemical substances. The choice of species may depend on the geographical area of expected chemical release and on the available testing facilities. If salt water exposure is probable, testing a marine species is advised. Even though marine species generally are no more sensitive than freshwater species, toxi c effects can be significantly modified by water chemistry.

4.3.2.A. Fish Embryo-Juvenile Test. Objectives: The objective of this test is to give preliminary indication of potential effects of a chemical on fish. Chemical substances can have significant chronic effects on individual fish at concentrations 2 to 500 times lower than LC_{50} values. When long-term exposure is probable, data on chronic effects contribute to assessment. Differences in sensitivities between a chronic and embryo-juvenile test are generally small or negligible, whereas differences in cost are great. The embryo-juvenile test is usually an excellent, cost-effective substitute for a chronic fish study.

Test Description. In an embryo-juvenile test, fish eggs and fry hatched from these eggs are exposed to a chemical at several concentrations for a few weeks. Effects on hatchability of eggs and on growth and survival of fry are determined by comparing responses at each concentration with the control.

4.3.2.B. Fish Bioconcentration Test. Objectives: Bioconcentration, the uptake of a compound from water into living tissue, affects the movement, distribution, and toxicity of chemical substances in the environment. A substance that bioconcentrates may affect life far removed from the initial points of environmental release and may alter ecological processes at concentrations much lower than predicted from acute and subacute results. Bioconcentration is the first step in the process of food chain biomagnification. Results of bioconcentration studies are useful in assessing risk to the environment, especially when the substance is highly lipid soluble (e.g., the octanol/water partition coefficient is greater than 1000), is poorly soluble in water, and does not undergo rapid chemical or biological transformation.

4.3.2.C. Test Description

Fish. Fish are exposed to the chemical substance in water for 28 days or until their tissue concentration reaches steady state. After steady state or 28 days, fish are placed in uncontaminated water for 7 days. During the exposure (1-28 days or steady state) and depuration (1-7 days) periods, fish are sacrificed periodically and the concentration of chemical substance in their tissues is measured. The bioconcentration factor, the relative uptake rate, and the depuration rate constants are estimated from these data. The most commonly tested species are fathead minnow *(Pimephales promelas)* and bluegill sunfish *(Lepomis macrochirus).*

Amphibians and Reptiles: Anurana. The aquatic forms of frogs and toads, the tadpoles have been widely used to study developmental biology. Common species in North America and Europe are:

Rana catesbiana: bullfrog
Rana clamitans: green frog
Rana palustris: pickerel frog
Rana pipiens: leopard frog
Rana sylvatica: woodfrog
Hyla crucifer: spring peeper
Hyla versicolor: treefrog
Bufo americanus: American toad
Bufo fowleri: Fowler's toad
Rana esculenta: edible frog
Rana temporaria: common frog
Bufo bufo: common toad

Anurans are carnivorous animals that feed on a great variety of invertebrate species, particularly

insects. Many larger predators utilize them as a food source. Birds, snakes, turtles, and mammals feed on the adults, and the tadpoles provide food for predators associated with aquatic habitats.

Chelonia. Turtles are basically omnivorous reptiles and are important elements in the aquatic systems. They are predators on all types of invertebrates, and some species are avid consumers of aquatic vegetation.

Birds. Birds are a fairly large vertebrate group. They are very important in the world ecosystem. They are primary and secondary consumers, feeding on plants, invertebrates, and vertebrates alike. They in turn are food for mammalian predators (including humans), a few amphibians and reptiles, and a few species of birds. Many avian species are good indicators of environmental quality.

A toxicity test recommended by EPA (1464) is the *Quail Dietary Test.* The objective of a quail dietary test is to give preliminary indication of possible effects of a chemical substance on terrestrial birds. This test is designed to determine the concentration of a substance in food that will be lethal to 50 percent of a test population as well as to observe behavioral, neurological, and physiological effects. The test is appropriate for a chemical that might be found in or on terrestrial bird food. The bobwhite quail *(Colinus virginianus)* is an appropriate test species because it is easily and economically reared, is widely available, and is generally more sensitive to many hazardous chemicals than other common test species.

4.4. In Vitro Toxicity Assays. In vitro tests are considered useful for screening vast numbers of chemicals, detecting pollution in the environment, evaluating synergistic and antagonistic interactions between combinations of chemicals, and formulating computer-derived predictions based on quantitative structure-activity relationships (QSARs).

4.4.1. THE NEUTRAL RED ASSAY (NR ASSAY) USING GOLDFISH GF-SCALE (GFS) CELLS. *In vivo* acute lethal toxicity tests with fish are frequently used to investigate the effects of xenobiotics on aquatic biota, but their usefulness is limited by the small number of species that can be economically and conveniently studied. *In vitro* cytotoxicity assays using cultured fish cells have been developed in order to obtain toxicological data through simple, rapid, reproducible, and economical test methods, while at the same time responding to social concerns about reducing the number of test animals.

The bacterial Microtox test of *Photobacterium phosphoreum* (2681), the immobilization test of *Tetrahymena pyriformis* (2682), the bacterial growth inhibition test of *E. coli* (2683), and the cytotoxicity assays using established fish cell lines (2684, 2685, 2686, 2687) have been developed for predicting the acute toxicity of aquatic pollutants to fish. The neutral red assay (NR assay) was initially developed for use with mammalian cells and was later adapted for cytotoxicity studies with fish cells. GFS cells, a fibroblastic cell line derived from the scale of the goldfish, and their NR_{50} values were significantly correlated with *in vivo* acute toxicity to 10 aquatic species.

NR_{50} values refer to the dye "neutral red" and represent the 50% decrease of absorbance of the extracted dye neutral red from the test cultures compared to the absorbance of neutral red extracted from the control cultures. Pesticides have been conveniently classified according to their NR_{50} values as follows:

I: highly cytotoxic	$NR_{50} \leq 10$ mg/l	
II: moderately cytotoxic	NR_{50} between 10 and 100 mg/l	
III: relatively low cytotoxic	$NR_{50} > 100$ mg/l	(2680)

4.4.2. RUBISCO-TEST (SCHNABL). The inhibition of toxicants on the enzymatic activity of Ribulose-P2-Carboxylase in protoplasts is investigated in this microtest. This enzyme is responsible for the CO_2 uptake by the protoplasts (2698).

4.4.3. OXYGEN TEST (SCHNABL). The effect of toxicants on the oxygen consumption of protoplasts is determined in this test (2698).

GLOSSARY

acaricide (miticide) a material used primarily in the control of plant-feeding -mites (acarids), especially spider mites.

actinomycetes a group of branching filamentous bacteria, reproducing by terminal spores. They are common in the soil. Selected strains are used for production of certain antibiotics.

adjuvant an ingredient that, when added to a formulation, aids the action of the toxicant. The term includes such materials as wetting agents, spreaders, emulsifiers, dispersing agents, foaming adjuvants, foam suppressants, penetrants, and correctives.

algicide a chemical intended for the control of algae.

alkaloid a physiologically active, usually naturally occurring nitrogenous compound alkaline in reaction. Many are characteristic of specific plants, i.e., nicotine in tobacco.

anesthetic a chemical that induces insensibility to pain, such as chloroform or diethyl ether. Vinyl chloride is also an anesthetic.

anthelmintic a material used for the control of internal worms (helminths) parasitic in humans and animals.

antibiotic any of certain chemical substances that are produced by microorganisms such as bacteria and fungi (molds) and that have the capacity to inhibit the growth of, or destroy, bacteria and certain fungi that cause animal and plant diseases.

anticoagulant rodenticide a rodenticide that kills rats by inducing uncontrolled internal bleeding; an example is Warfarin.

approximate fatal concentration the geometric mean between the largest concentration allowing survival for 48 hr and the smallest concentration that was fatal in this time for practically all fish.

avicide a substance to control pest birds.

$BCF_{vegetation}$ The bioconcentration factor for vegetation is defined as the ratio of the concentration in aboveground parts (mg of compound/kg of dry plant) to the concentration in soil (mg of compound/kg of dry soil) (Travis, C. C., and Arms, A. D., "Bioconcentration of organics in beef, milk, and vegetation," *Environ. Sci. Technol.,* 22 (3), 1988. (2644).

benthic referring to aquatic organisms growing in close association with the substrate.

benthos (benthon) aquatic microorganisms capable of growing in close association with the substrate.

BFT The biotransfer factor is useful in risk assessment, because chemical exposure to cattle and cows may occur through both food and water pathways. The biotransfer factors for beef, B_b, and milk, B_m, are defined as follows:

B_b = concentration in beef (mg/kg)/daily intake of organic (mg/d)

B_m = concentration in milk (mg/kg)/daily intake of organic (mg/d)

where measured concentrations of organics in beef or milk fat are converted to a fresh-meat or whole-milk base, assuming meat is 25% fat and whole milk is 3.68% fat.

bioaccumulation (bioconcentration) the process by which chemical substances are accumulated in living organisms.

- direct bio-accumulation
    1. The process by which a chemical substance accumulates in organisms by direct uptake from the ambient medium through oral, percutaneous, or respiratory routes.

2. The increase in concentration of test material in or on test organisms (or specified tissues thereof) relative to the concentration of test material in the ambient environment (e.g., water) as a result of partitioning, sorption, or binding.

- indirect bio-accumulation: the process by which a chemical substance accumulates in living organisms through uptake via the food chain.

bioaccumulation factor the ratio of the concentration of the test chemical in the test animal to the concentration in the test environment (e.g., water) at steady state (apparent plateau) or the ratio of the uptake rate constant (k_1) to the depuration rate constant (k_2).

bio-accumulation factor (BAF) equilibrium ratio of the organic chemical concentration resulting from the water and food routes to the water concentration; that is,

$$\text{Lipid-based BAF} = \frac{\mu\text{ g chemical/kg lipid}}{\mu\text{ g Chemical/l water}} = \text{l/kg}$$

bioconcentration factor (BCF) concentration resulting from the water concentration only.

biodegradability the ability of an organic substance to undergo biodegradation.

biodegradation molecular degradation of an organic substance, resulting from the complex action of living organisms.

biomagnification a process by which chemicals in organisms at one trophic level are concentrated to a level higher than in organisms at the preceding (lower) trophic level.

bird repellent a substance that drives away birds or discourages them from roosting.

bloom a concentrated growth or aggregation of plankton, sufficiently dense as to be readily visible.

blue-green algae the group Myxophyceae, characterized by simplicity of structure and reproduction, with cells in a slimy matrix and containing no starch, nucleus, or plastids and with a blue pigment in addition to the green chlorophyll.

cancer a malignant tumor anywhere in the body of a person or animal. Its origin is usually in the several types of epithelial tissue, and it invades any of the surrounding structures. The characteristic of metastasis, or seeding to other organs of the body, is positive to this diagnosis. Leukemia can be regarded as a cancer of the blood.

carbamate insecticides carbamates are esters of carbamic acid, and like the organophosphorus compounds, they inhibit chlorinesterase. Carbamic acid: $H_2N\text{-}COOH$.

carcinogen a highly controversial term, applied generally to any substance that produces cancer, as well as to highly specific chemicals suspected of being the cause of cancer development in any one of many target organs of the body in test animals or human beings. The words "cancer suspect agent" have been used by U.S. authorities to cover this possibility. However, NIOSH has broadened this terminology to include any agent reported in the literature to cause or to be suspected of causing *tumor* development, *malignant* or *benign* (see *oncogenic*). Examples include some mineral oils, vinyl chloride, benzene, beta-naphthylamine, hydrazine, and nickel.

chelating agents (chelates) agents that are readily soluble in water and have found wide use in many areas through their control of metal ions. These chelants (chelated metal ions) are used in the fields of textiles, water treatment, industrial cleaners, photography, pulp and paper, agriculture, and so on. In agriculture, both macronutrients and micronutrients are essential for proper plant growth. In some areas, the intensification of agricultural practices has resulted in depletion of available micronutrients. In order to achieve adequate agricultural production, it is necessary to add micronutrients to these soils. A chelated micronutrient is made by reacting a metallic salt with one of the chelating agents, forming a protective glove around the metal and retarding the normal soil chemistry reactions that tie up that metal. Thus it is more available to the plants.

chemosterilants compounds that sterilize insects to prevent reproduction.

chlorinated organic pesticides the organochlorine chemicals from one of the three principal families, including aldrin, benzene hexachloride, chlordane, DDT, endosulfan, heptachlor, lindane, methoxychlor, toxaphene, and so on.

cholinesterase a body enzyme that is necessary for proper nerve function and is destroyed or damaged by organic phosphates or carbamates taken into the body by any path of entry.

cholinesterase-inhibiting pesticides a class of pesticides having related pharmacological effects, including aldicarb, carbaryl, carbofuran, chlorpyrifos, parathion, etc.

cohort a group of individuals selected for scientific study of toxicology or epidemiology.

compatibility the ability of two or more substances to mix without objectionable changes in their physical or chemical properties.

contact herbicide a herbicide that kills primarily by contact with plant tissues rather than by translocation (systemic herbicides).

contact insecticide a chemical causing the death of an insect with which it comes in contact. Ingestion is not necessary.

controls the most important factor in any statistically meaningful experiment. The nature, number, and reproducibility of results with the controls determine the accuracy and significance of the conclusions drawn from the experimental cohort results.

coupling agent a solvent that has the ability to solubilize or to increase the solubility of one material in another.

critical range the range of concentrations in mg/l below which all fish lived for 24 hr and above which all died. Mortality is given as a fraction indicating the death rate (e.g., $^3/_4$).

cyclodiene insecticides mainly aldrin, chlordane, dieldrin, endrin, heptachlor, endosulfan, and toxaphene. The cyclodienes are characterized by their endomethylene bridge structure.

defoliant a preparation intended to cause leaves to drop from crop plants such as cotton, soybeans, and tomatoes, usually to facilitate harvest.

desiccant a preparation intended for artificially speeding the drying of crop plant parts such as cotton leaves and potato vines.

disinfectant (1) a substance that destroys harmful bacteria, viruses and the like and makes them inactive. (2) a substance that destroys infesting organisms such as insects, mites, rats, weeds, and other organisms multicellular in nature.

dispersant a material that reduces the cohesiveness of like particles, either solid or liquid.

encapsulated pesticides pesticides enclosed in tiny capsules of such material as to control release of the chemical and extend the period of diffusion.

epidemiology discipline that attempts to evaluate the health of a defined human population and to determine cause-and-effect relationships for disease distribution. Factors such as age, sex, and ethnicity are its parameters. It is the study of the distribution and determinants of disease and injuries in human populations. Examples of epidemiological studies include those that associated a lower incidence of dental caries with fluoridated drinking water and a higher incidence of lung cancer with cigarette smoking.

eradicant fungicide a fungicide used to destroy ("burn out") fungi that have already developed and produced a disease condition.

food chain accumulation BAF/BCF is a measure of the tendency of a chemical to accumulate in an organism from both food and water exposures. BAF/BCF 1 indicates that food chain accumulation has occurred.

fumigant a substance or mixture of substances that produces gas, vapor, fumes, or smoke intended to destroy insects, bacteria, or rodents.

fungus (fungi) all non-chlorophyll-bearing thallophytes (i.e., all non-chlorophyll-bearing plants of a lower order than mosses and liverworts) as, for example, rusts, smuts, mildews, and molds. Many cause destructive plant diseases. The simpler forms are one-celled; the higher forms are branching filaments.

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green algae organisms belonging to the class *Chlorophyceae* and characterized by photosynthetic pigments similar in color to those of the higher green plants. The storage food is starch.

hematology examination of the blood.

herbicide a chemical intended for killing plants or interrupting their normal growth.

Herbicides are used in five general ways:

1. pre-planting: applied after the soil has been prepared but before seeding.
2. pre-emergence (contact): nonresidual dosages are used after seeding but before emergence of the crop seedlings.

3. pre-emergence (residual): applied at time of seeding or just prior to crop emergence; it kills weed seeds and germinating seedlings.
4. post-emergence: applied after emergence of a crop.
5. sterilant (nonselective): used to effect a complete kill of all treated plant life.

histopathology microscopic examination of tissue.

inoculum the inoculum is a combination of microorganisms that, in degradability experiments, is added to the test system in order to obtain degradation of the compounds under investigation (substrate).

insecticides the various insecticides fall into six general categories according to the way they affect insects:

1. stomach: toxic quantities are ingested by the insect.
2. contact: kills upon contact with an external portion of the body.
3. residual contact: remains toxic to insects for long periods after application.
4. fumigant: possesses sufficient natural or induced vapor pressure to produce lethal concentrations.
5. repellent: does not kill but is distasteful enough to insects to keep them away from treated areas.
6. systemic: capable of being absorbed into the plant system where it makes plant parts insecticidal.

Various classes of insecticides, according to their composition, and examples of each, include:

- inorganics: calcium and lead arsenates, sodium fluoride, sulfur, and cryolite.
- botanicals: pyrethrum, nicotine, rotenone.
- chlorinated hydrocarbons: DDT, BHC, lindane, methoxychlor, aldrin, dieldrin, heptachlor, toxaphene, endrin.
- organic phosphates: parathion, diazinon, malathion, ronnel.
- carbamates: sevin, zectran

isomer a chemical the molecules of which contain the same number and kind of atoms as another chemical but arranged differently; e.g., normal (straight-chain) octylalcohol and its isomer, isooctyl alcohol. Stereoisomers are those isomers in which the same number and kind of atoms are arranged in an identical manner except for their relative position in space; e.g., endrin is a stereoisomer of dieldrin.

juvenile hormone a hormone produced by an insect in the process of its immature development that maintains its nymphal or larval form.

larvicide a substance intended to kill especially the larvae of certain insect pests such as mosquitoes.

leaching downward movement of a material in solution through soil.

LC_{50} (lethal concentration fifty) a calculated concentration that, when administered by the respiratory route, is expected to kill 50% of the population of experimental animals. Ambient concentration is expressed in milligrams per liter.

LD_{50} (lethal dose fifty) a calculated dose of a chemical substance that is expected to kill 50% of a population of experimental animals exposed through a route other than respiration. Dose concentration is expressed in milligrams per kilogram of body weight.

maximum acceptable toxicant concentration (MATC) the geometric mean of the lowest concentration producing a statistically significant effect and the highest concentration producing no such effect on survival, growth, or fecundity in any life stage in a life cycle or partial life cycle, or early life stage test. It is used as a threshold for toxic effects in exposures of indefinite duration but does not correspond to any particular level or type of effect on any particular life stage.

median tolerance limit (TL_m) has been accepted by most biologists to designate the concentration of toxicant or substance at which 50% of the test organisms survive. In some cases and for certain special reasons, the LC_{10} or LC_{90} might be used. The LC_{90} might be requested by a conservation agency negotiating with an industry in an area where an important fishery exists and where the agency wants to establish waste concentrations that will definitely not harm the fish. The LC_{10} might be requested by a conservation agency that is buying toxicants designed to remove undesirable species of fish from fishing lakes.

metabolism process by which all natural and synthetic chemicals ingested or inhaled by the living body, either animal or vegetable, are continually subjected to chemical transformation in the

organism into other products by myriad chemical reactions, such as synthesis and oxidative transformation in the organs of the body. Many of these primary and intermediate products find their way to body excretions through lung exhalation, urine, feces, or other expirations. The tracing of these routes is important for specific chemicals and their possible relation to disease. Isotope-tagged materials are used for these research studies. These studies are often called *pharmacokinetic and metabolism research* .

metastasis in medicine, the shifting of pathogenic cells of a disease, such as a malignant tumor, from one part or organ of the body to another unrelated to it.

mite mites are tiny organisms closely related to ticks in the group *Acarina.* They have eight legs as do spiders, except newly hatched mites, which have only six. Some mites, such as the chicken mite and the chigger, are parasitic on higher animals. A large family of mites is known as the spider mites from their habit of spinning a web on undersides of leaves where they feed.

mold any fungus, exclusive of the bacteria and yeasts, that is of concern because of its growth on foods or other products used by humans; fungus with conspicuous profuse or wooly growth (mycelium or spore masses). Occurs most commonly on damp or decaying matter and on the surfaces of plant tissues.

molluscicide a compound used to control snails that are intermediate hosts of parasites of medical importance.

mothproofer a substance that, when used to treat woolens and other materials liable to attack from fabric pests, protects the material from insect attack.

mutagenesis alteration of the genetic material of a cell in such a manner that the alteration is transmitted to subsequent generations of cells. A particular case is where a genetic change can be passed from parent to offspring.

mutation a sudden variation in some *inheritable* characteristic of an individual animal or plant, as distinguished from a variation resulting from generations of gradual change. It is an effect attributed to an action prior to conception of the embryo. It has been correlated with increased incidence of chromosome breaks in the reproductive cells, male or female.

necrosis destruction of cells.

nematocide a material, often a soil fumigant, used to control nematodes infesting roots of crop plants; an example is ethylene dibromide.

nematode a member of a large group (phylum *Nematoda*) also known as threadworms, roundworms, etc. Some larger kinds are internal parasites of humans and other animals. Nematodes injurious to plants, sometimes called eelworms, are microscopic, slender, wormlike organisms in the soil, feeding on or within plant roots or even plant stems, leaves, and flowers.

NR_{50} values values that refer to the dye "Neutral Red" and represent the 50% decrease in absorbance of the extracted dye "neutral red" from the test cultures compared to the absorbance of neutral red extracted from the control cultures. Pesticides have been conveniently classified according to their NR_{50} values as follows:

I: highly cytotoxic	NR_{50} ≥10 mg/l
II: moderately cytotoxic	NR_{50} between 10 and 100 mg/l
III: relatively low in cytotoxicity	NR_{50} >62;100 mg/l

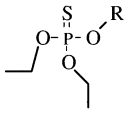
nymph the early stage in the development of insects that have no larval stage. It is the stage between egg and adult during which growth occurs in such insects as cockroaches, grasshoppers, aphids, and termites.

organochlorine insecticides the principal pesticides included under organochlorines are the *bis* -chlorophenyls (e.g., DDT) and the cyclodienes (aldrin, etc.) with 50% chlorine content or more. These insecticides are characterized by their persistence in the environment.

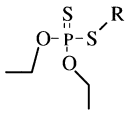
organophosphorus pesticides anticholinesterase chemicals that damage or destroy cholinesterase, the enzyme required for nerve functions in the animal body. Use of some of these pesticides may involve danger for the applicator. Examples of the leading series are as follows, where R represents some organic radical:

- phosphate: dicrotophos

- phosphorothioate: parathion



- phosphorodithioate: phorate



organotin fungicides Several tin-based organic fungicides are commercially available, such as triphenyltin acetate, triphenyltin hydroxide, and tricyclohexyltin hydroxide.

oxidation pond an enclosure for sewage designed to promote the intensive growth of algae. These organisms release oxygen, which stimulates the transformation of the wastes into inoffensive products.

pathogen any microorganism that can cause disease. Most pathogens are parasites, but there are a few exceptions.

photosynthesis process of manufacture, by algae and other plants, of sugar and other carbohydrates from organic raw materials with the aid of light and chlorophyll.

phytoplankton plant microorganisms, such as certain algae, living unattached in the water. Contrasting term: **zooplankton** .

phytotoxicity degree to which a material is injurious (poisonous) to vegetation. It is specific for particular kinds or types of plants.

plant growth regulator a preparation that in minute amounts alters the behavior of ornamental or crop plants or the produce thereof through physiological (hormone) rather than physical action. It may act to accelerate or retard growth, to prolong or break a dormant condition, to promote rooting, or in other ways.

post-emergence herbicide a chemical applied as an herbicide to the foliage of weeds after the crop has emerged from the soil.

protozoa unicellular animals, including the ciliates and nonchlorophyllous flagellates.

quaternary ammonium compounds organic nitrogen compounds in which the molecular structure includes a central nitrogen atom joined to four organic groups as well as an acid group of some sort. Nitrogen forms such pentavalent compounds, as is shown in the simplest example, ammonium chloride (NH_4Cl). When the hydrogen atoms are replaced by organic radicals, the compound is known as a quaternary ammonium compound, an example is tetramethyl ammonium chloride. These compounds are in contrast to trivalent nitrogen compounds, wherein the nitrogen combines with only three hydrogen atoms, as in ammonia, or these are replaced by one to three radicals, as in the carbamate structure.

red algae a class of algae *(Rhodophyceae)* most members of which are marine. They contain a red pigment in addition to chlorophyll.

reentry time the period of time immediately following the application of a pesticide to a field when unprotected workers should not enter.

rodent a member of the animal group (order *Rodentia*) to which rats, mice, gophers, and porcupines belong.

rodenticide a preparation intended for the control of rodents (rats, mice, etc.) and closely related animals (such as rabbits).

saprophytic utilizing dead organic matter as nutrients; the saprophytes include some plants and certain bacteria and molds.

sensitization an increased reaction on the second or subsequent exposure to a compound, it results from an immunological mechanism.

spray drift the movement of airborne spray particles from the intended area of application.

surface-active agent (surfactant) a substance that reduces the interfacial tension of two boundary lines. These materials are classified as nonionic, anionic, or cationic. Most emulsifying agents are of the nonionic type; they do not ionize. Wetting agents and detergents are primarily anionic; they become ionized in solution, the negative molecule exerting primary influence.

synergist a material that exhibits synergism. The joint action of different agents such that the total effect is greater than the sum of the independent effects.

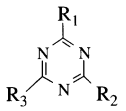
systemic pesticide a pesticide that is translocated to other parts of a plant or animal than those to which the material is applied.

toxicology is the science that attempts to determine the harmful effects of materials on human populations by testing animals. It is the science that prescribes limits of safety for chemical agents. For example, the study that reported tumor development in animals when they were fed saccharin at high dosage levels was a toxicological study. Toxicology, the prospective science, warns of the potential danger to humans of a given chemical substance, and epidemiology, the retrospective science, considers a given population exposed to the chemical and determines that indeed this is or is not a hazardous case.

trademark a word, letter, device, or symbol used in connection with merchandise and pointing distinctly to the origin or ownership of the article to which it is applied. A tradename is actually a trademarked name.

translocation distribution of a chemical from the point of absorption (plant leaves or stems, sometimes roots) to other leaves, buds, and root tips. Translocation also occurs in animals treated with certain pesticides.

triazine herbicides those materials (including atrazine, simazine, and so on) that are based on a symmetrical triazine structure, where R_1, R_2, and R_3 are a variety of attached radicals:



weed any plant that grows where it is not wanted.

wetting agent a substance that appreciably lowers the interfacial tension between a liquid and a solid and increases the tendency of the liquid to make complete contact with the surface of the solid.

wood preservative there are three main classes of wood preservatives: toxic oils (e.g., creosote) that evaporate slowly and are relatively insoluble in water; salts that are injected as water solutions into the wood; and preservatives consisting of a small percentage of highly toxic chemicals in a solvent or mixture of solvents other than water. The waterborne types are simple to apply, but they are subject to leaching, they are more or less poisonous to warm-blooded animals, and some are corrosive to iron.

zooplankton protozoa and other animal microorganisms living unattached in water.

ABBREVIATIONS

abs. perc. limit: absolute perception limit
A.C.: activated carbon
A.S.: bench scale activated sludge, fill and draw operations
ASC: activated sludge, continuous feed and effluent discharge
ASCF: activated sludge, fed slowly during aeration period
atm: atmosphere
avg: average
BCF- bioconcentration factor
BOD_5: biological oxygen demand after 5 days at 20°C
bp: boiling point
CA: chemical analysis for the test material
cal: calorie
CAN: chemical analysis to indicate nitrogen transformation
cu ft: cubic foot
cu m: cubic meter (m^3 in equations)
°C: degree centrigrade (Celsius)
CO_2: carbon dioxide used to follow oxidation results
COD: chemical oxygen demand
conc.: concentration
d: day
det. lim.: detection limit
DO: dissolved oxygen
dyn. dil.: dynamic dilution
EC: electron capture
EC: effective concentration
EC_{50}: effect concentration for 50% of the organisms exposed
effl.: effluent
EIR: eye irritation reactivity
°F: degree Fahrenheit
F: flow-through bioassay
6 f abs. app.: six-fold absorber apparatus
fp: freezing point or fusion point
FT: flow-through bioassay
g: gram
GC-EC: gas chromatography-electron capture
GC-FID: gas chromatography-flame ionization detection
geom.: geometric
glc: ground level concentration
h: hour
HC. cons.: hydrocarbon consumption
HCs: hydrocarbons
hr: hour
95%ile: 95 percentile
I.D.: internal diameter
i.m.: intramuscular
infl.: influent

inh.: inhibitory or toxic action noted
inhal.: via inhalation
i.p.: intraperitoneal
I.R.: infrared
i.v.: intravenous
kcal: kilocalorie
kg: kilogram
km: kilometer
LC_{50}: lethal concentration for 50% of the organisms exposed
LD_{50}: lethal dose for 50% of the organisms exposed
liq.: liquid
m: meter
m: month
MATC: maximum acceptable toxicant concentration
max: maximum
mg: milligram
min: minute
min.: minimum
MLD: median lethal dose = LD_{50}
mm: mm Hg
mp: melting point
mph: miles per hour
m : micron
mw: molecular weight
n: normality
nat: natural acclimation in surface water
NEN: Nederlandse Norm (Dutch standard test method)
NFG: nonflocculant growth activated sludge
NOEC: no observed effect concentration
NOD: nitrogenous oxygen demand
NOLC: No observed lethal concentration
NO ox: nitric oxide oxidation
n.s.i.: no specific isomer. This means that in the literature, no reference has been made to a specific isomer. It does not necessarily mean that the stated information is valid for all isomers.
O.I.: odor index
or.: oral
O.U.: odor units
P: plant treatment system for mixed wastes, including the test chemical
p.m.: particulate matter
PMS: photoionization mass spectrometer
p.p.: pour point
ppm: parts per million
ppb: parts per billion
R: renewal bioassay
R.C.R.: relative chemical reactivity
RD_{50}: concentration associated with 50% decrease in respiratory rate
Resp: special respirometer
RW: river water oxidation substrate
S: static bioassay
sat. conc.: saturation concentration in air
sat. vap.: saturated vapor
S.C.: subcutaneous
scf: standard cubic foot
Sd: seed material
sel. strain: selected strain, pure culture of organisms
sew: municipal sewage

sew. dil: sewage dilution oxidation substrate
sp. gr.: specific gravity
SPM: suspended particulate matter
std. dil. sewage: the standard dilution technique has been used with normal sewage as seed material
STP: standard temperature and pressure
solub.: maximum solubility in water
$t_{1/2}$: half life
TF: trickling filter
THCE: total hydrocarbon emissions
theor.: theoretical
ThOD: theoretical oxygen demand
TL_m: median threshold limit
T.O.C.: total organic carbon
TOD: total oxygen demand
T.O.N.: threshold odor number
TSP: total suspended particulates
UVS: spectrophotometry with ultraviolet light
vd: relative vapor density; that of air = 1
VLS: spectrophotometry with visible light
vp: vapor pressure
vs: versus
w: week
W: Warburg respirometer
y: year
yr: year