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Chemodynamics: Transport and Behavior of Chemicals in the Environment—A Problem in Environmental Health

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In the manufacture and use of the several thousand chemicals employed by technological societies, portions of these chemicals escape or are intentionally introduced into the environment. The behavior, fate, and to some extent the effects produced by these chemicals are a result of a complex interaction of the properties of the chemical with the various processes governing transport, degradation, sequestration, and uptake by organisms. In addition, such processes as adsorption, evaporation, partitioning, and degradation are influenced by ambient conditions of temperature, air movement, moisture, presence of other chemicals, and the concentration and properties of the subject chemicals. These influence the level and extent of exposure to these chemicals that man might receive. Study of the physicochemical properties of compounds in relation to these various processes has provided a basis for better understanding of the quantitative behavior. Such information is useful in development of predictive models on behavior and fate of the chemicals in relation to human exposure. Beyond this, it provides information that could be used to devise procedures of manufacture, use, and disposal that would minimize environmental contamination. Some of the physical principles involved in chemodynamics are presented in this review.

Introduction

During the past three decades there has been nearly an exponential increase in the amount and number of chemicals used by modern society (*1–3*). This situation is a result of the productivity of the synthetic chemist in responding to man's desire for a higher standard of living. Thus, we have a continuing increase in the production and use of drugs, food additives, pesticides, and industrial chemicals (*1, 2, 4–6*).

The types of classes of chemicals used range from simple aliphatic organic chemicals to complex polynuclear compounds to high molecular weight polymers. Also included are a variety of inorganic substances of widely different properties. Tables 1 and 2 list the production of some representatives of some of the classes of chemicals currently in use.

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The use of these chemicals has provided society with better health and a higher standard of living. However, the proliferation of chemical usage has elicited concern over the long range effect of these materials on man and his environment. The reason for this concern is the realization that many chemicals have become widespread environmental contaminants (*1, 8–12*). Thus, it is apparent that our knowledge of chemical behavior has not kept pace with the technology required to produce chemicals.

Two major categories of environmental pollutants are pesticides and industrial chemicals (*2, 13*). Pesticides have received the most attention, since they are used on food crops and are applied to large areas of the environment (*14–17*). The ubiquitous nature of chlorinated hydrocarbon pesticide residues was a major factor in demonstrating the important role of behavior of a chemical in the environment (*10, 12, 14, 15, 17–22*). However, pesticides are not unique chemicals which predispose them to become environmental contaminants. It has been amply demonstrated that many of the in-

dustrial chemicals such as polychlorobiphenyls and organohalogens have also become widely distributed (*4, 5, 11–13, 15, 21, 23*). Thus, there is potential for widespread dissemination of residues of any chemical.

The basis of concern of chemicals in the environment is whether or not the substance will effect the health and welfare of man. The effect may be a direct one, producing a lesion or deterioration of health; it may be indirect, producing a less healthful environment or restricting food production or other activities of man; or it may be a remote effect causing a deterioration of environmental quality. It is, of course, important to prevent these consequences if we are to protect the health and welfare of man. It would seem the prudent course of action to prevent health hazards in preference to having to attempt to ameliorate the effects of such exposure. However, until there is an understanding of the transport and behavior of chemicals in the environment, it is difficult to devise the appropriate methods of preventing environmental exposure. With the appropriate understanding, methods of manufacture, handling, use and disposal can be devised to abate the problem. Similarly, a knowledge of transport through food chains or by physical means permits the appropriate avoidance reaction. A number of examples could be cited to illustrate how a prior understanding of the chemodynamics of a compound could have been utilized to avoid problems such as with DDT, PCBs, mercury, vinyl chloride, and various heavy metals.

If one were to consider the path followed by a chemical from its release or escape to the site of action in an organism or population of organisms, it would be found that there are at least four major steps, namely: interaction of the chemical with the environment during its transport to the boundary of the organism; interaction with the boundary of the organism; passage through the boundary; and intracellular action of the chemical. These four steps give a means of partially relating the properties of

Table 1. Production of various types of chemicals.

Class	Representative compounds	Annual production, (millions of pounds)	Example of uses
Inorganic	Chlorine	19.7×10^3	Water purification
	Ammonia	28.6×10^3	Fertilizer
	Titanium dioxide	1.4×10^3	Pigment
Organohalogen	*Ethylene dibromide*	315.5	Gasoline additive
	Carbon tetrachloride	996.7	Specialty solvent Grain fumigant
	Hexachlorobutadiene	8.0	Solvent Heat transfer liquid
	Vinyl chloride	5088.0	Chemical intermediate
Organophosphorous	Tri(2-chloroethyl) phosphate	29.4	Flame retardant for plastics Synthetic lubricants
	Acyclic phosphorodithioate Lube oil additives [zinc di(butylhexyl)-phosphorocithioate]	68.0	Lube oil additive
Organosilicones	Silicone fluids [polydimethylsiloxane]	74.7	Release agents Antifoaming agents Polish and cosmetic ingredients
Oxygen-containing	Dioxane	14	*Specialty solvent* Inhibitor in chlorinated solvents
Nitrogen-Containing pulp	(Ethylenedinitrilo) tetraacetic acid, tetrasodium salt	64.3	Agriculture, detergents Pulp and paper processing
	Ethyleneimine	5.0	*Chemical intermediate*
Plastics	Polyethylene	7.63×10^3	Plastic
Detergents	Dodecylbenzenesulfonic acid, sodium salt	364.1	Detergents
	N,N-Dimethyldodecylamine oxide	36.1	Detergent
Hydrocarbons	Benzene	8937.1	Chemical intermediate

Table 2. Pesticide production volumes.[a]

Class	Common name	Production, 10^6 lb A. I.[b]
Insecticide	Methyl parathion	45
	Toxaphene	50
	Carbaryl	45
	Malathion	35
	Chlordane	25
	Parathion	15
	Methoxychlor	10
	Diazinon	10
	Carbofuran	8
	Disulfoton	8
	Phorate	8
Herbicide	Atrazine	90
	2,4-D	45
	MSMA-DSMA	35
	Sodium chlorate	30
	Trifluralin	25
	Propachlor	23
	Chloramben	20
	Alachlor	20
	CDAA	10
	2,4,5-T	6
Fungicide	PCP and salts	46[c]
	Dithiocarbamates	40[d]
	TCP and salts	20
	Captan	18
	PCNB	3
	Dodine	3

[a]From Lawless et al. (7).
[b]Active ingredient.
[c]Includes use as herbicide, desiccant, molluscicide, and for termite control.
[d]Includes CDEC, Ditane M-45, Ditane S-31, Ferbam, Maneb, Metham, Nabam, Niacide, Polyram, Thiram, Zineb, and Ziram.

the chemical to the ultimate action on the biota. It is with the first step, that the chemodynamics is primarily concerned with and it is the step at which preventive action can be taken. At each of the four steps, a number of different processes or reactions can occur. Certain of these processes or reactions are common in several of the steps. These processes or reactions are dependent on both the properties of the chemical as well as the property of the particular element of the system with which it may be interacting. On this basis then, the physical chemical properties of the compound permits some prediction of probable behavior and an estimate of whether the exposure received by man is likely to produce serious consequences. Table 3 attempts to identify the different processes that may be associated with the four different steps described above.

From the foregoing it can be seen that there are some general processes or reactions common to two or more of the steps.

Table 3. Processes involved in chemical action.

Steps	Processes
Interaction with the environment	Adsorption of surfaces
	Vaporization
	Photochemical breakdown
	Autochemical breakdown
	Dissolution
	Partitioning
Interaction with barrier of organisms	Adsorption
	Destructive reactions
	Rejection
Intracellular transport	Adsorption
	Metabolic binding
	Metabolism
	Partitioning
Reaction with critical site	Adsorption
	Reaction

Escape of Chemicals

In the production and use of any chemical it is nearly impossible to avoid some transfer of material into the environment (*1, 2, 8, 9, 24–26*). In theory, even in the use of a "closed" system there may be some opportunity for a chemical (or chemicals) to escape during transfer in the system. In manufacturing and use of chemicals under normal circumstances, the systems are at best only partially closed, thus affording opportunities for chemicals to escape through air and water effluent from the manufacturing plant, handling and fabrication, or use to some other sites (*4, 6, 16*). Having escaped into the environment, the chemical may be transported by water or air to afford an exposure to man and other organisms in the environment (*1, 10, 15, 22, 23, 27*).

The chemicals used as starting materials or intermediates in manufacture may end up as residues in air through vaporization (*14, 15, 24, 28–30*), in surface and underground water through contact and leaching (*18, 31–34*), by sewage effluents (*1, 4*), or in soil through adsorption (*19, 23, 29, 35–37*). All of these points of release are potential sources for widespread contamination. In light of the large scale production and use of chemicals, we therefore need a critical evaluation of the uses and properties of these chemicals in assessing their hazard to man and the environment (*1, 16, 38*).

An evaluation of the hazard from a chemical's use involves consideration of a number of factors (*1, 4, 16, 22, 31, 39–43*). These include the amount and nature of chemical being used, the manner in which it is used, the extent of transport and alteration in the environment, and the biological effect of residues on organisms including man.

Over the years, a considerable body of information has built up relating physical chemical properties and reactivity to the behavior and fate of chemicals in the environment (*10, 16, 18, 25, 44–47*). From this information, it is possible to develop models of the transport of these chemicals and various facets of their behavior.

The soil becomes the residence for a large portion of the chemical that finds its way into the environment (*17, 19, 34, 35, 48*). What happens after the chemical reaches the soil is of considerable importance in determining whether the substance will subsequently find its way into air or water, how long it will persist, and its bioavailability (*14, 15, 22, 27, 31, 36, 49, 50*). The interaction between the chemical and the various soil constituents (sorption) is quite important. It was noted very early that with nonpolar organic substances there is an inverse relationship between water solubility and the extent to which the chemical is absorbed (*38, 49, 51*). Subsequent studies of the thermodynamics of the sorption process suggested that the strength of binding for such chemicals may be related to the latent heat of solution (*16, 19–21, 41, 46, 52*). Others had pointed to the fact that there is a correlation between the partition coefficient and the sorption of the chemical by the soil organic matter (*10, 34, 36*).

Soil and sediments in water are quite complex systems consisting of clays, accompanying organic matter, and living organisms. While the initial reaction with the chemical may be physical in nature, this heterogeneous system may promote chemical reactions through catalysis through intervention of enzymes from the living organism (*12, 17, 22, 26, 53*). These reactions usually result in the reduction of the biological activity of the compound, or its sequestration, the rates of which depend both on the soil or sediment system and the properties of the compound. Some of the common reactions include hydrolysis, oxidation, reduction, and conjugation (*9, 14, 17, 38, 54, 55*). The rate at which these reactions, or decompositions, occur may give an indication of the persistence of the chemical in the aqueous or other components of the environment. There is evidence that the rate of hydrolysis of certain classes of organics in laboratory buffer systems give a good indication of the likely behavior of the compound in the natural system (*3, 12, 56–58*).

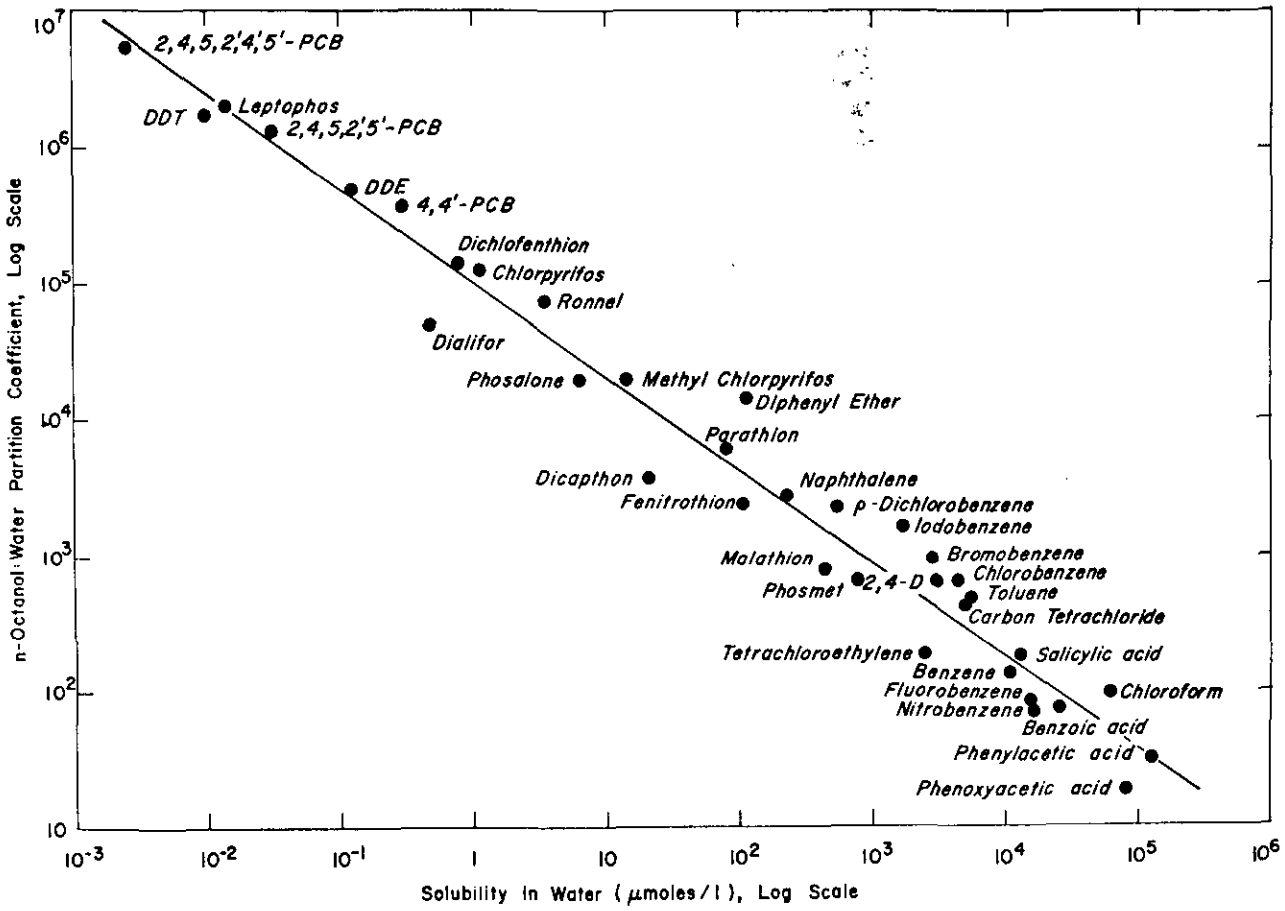


FIGURE 1. Relation between water solubility and partition coefficient of varying compounds.

Likewise, a knowledge of the vapor pressure and latent heat of vaporization allows an estimate of the rate at which the chemical may evaporate or exchange across a water/air and air/soil interface (*14, 21, 27, 28*). This provides an indication of the potential of the chemical for aerial contamination and transport.

The accumulation of certain compounds in living organisms (biomagnification) has led to problems for populations of organisms. Many of the compounds that do this have a low water solubility and a high solubility in nonpolar solvents (lipophilic). The relation between water solubility and partition coefficient for a number of compounds is seen in Figure 1 and Table 4. The partition coefficient of such compound provides a good measure of their tendency to accumulate in living organisms (*10, 47, 53*) (see Fig. 2). This coupled with a refractoriness toward reaction gives an indication not only of accumulation but transmission from one trophic level to another. The determination of the partitioning between an aqueous phase and a solvent phase can utilize a variety of organic solvents. The most desirable solvent, however, is one that more nearly resembles the adipose tissue of the living organism. Such solvents as olive oil and corn oil have been used but while they may satisfactorily represent some system the solvent failed to meet the criteria of representation and convenience is *n*-octanol (*25, 42*). Accordingly, the *n*-octanol/water partition coefficient is the more widely reported.

Table 4. Solubilities and partition coefficients of various compounds.

Compound	Solubility in water, ppm (temp, °C)	Log (*n*-octanol/H_2O partition coefficient)
Benzene	1710 (20)[k]	2.13[b]
Toluene	470 (16)[a]	2.69[b]
Fluorobenzene	1540 (30)[a]	2.27[b]
Chlorobenzene	448 (30)[a]	2.84[b]
Bromobenzene	446 (30)[a]	2.99[b]
Iodobenzene	340 (30)[a]	3.25[c]
p-Dichlorobenzene	79 (25)[a]	3.38[d]
Naphthalene	30[a]	3.37[c]
Diphenyl ether	21 (25)[d]	4.20[d]
Tetrachloroethylene	400 (25)[d]	2.60[d]
Chloroform	7950 (25)[d]	1.97[f]
Carbon tetrachloride	800[a]	2.64[g]
p,p'-DDT	0.0031[h]-0.0034[i]	6.19[j]
p,p'-DDE	0.040 (20)	5.69[j]
Benzoic acid	2700 (18)[a]	1.87[b]
Salicylic acid	1800 (20)[a]	2.26[f]
Phenylacetic acid	16600 (20)[a]	1.41[b]
Phenoxyacetic acid	12000 (10)[a]	1.26[b]
2,4-D	890 (25)[d]	2.81[b]
2,4,5,2',5'-PCB	0.010 (24)	6.11
2,4,5,2',4',5'-PCB	0.00095 (24)	6.72
4,4'-PCB	0.062 (20)	5.58
Phosalone	2.12 (20)	4.30
Methyl chlorpyrifos	4.76 (20)	4.31

[a]Data of Hodgman (*59*).
[b]Data of Fujita et al. (*60*).
[c]Data of Leo et al. (*42*).
[d]Data of Kenaga (*10*).
[e]Data of Hansch and Fujita (*61*).
[f]Data of Hansch and Anderson (*62*).
[g]Data of Macy (*63*).
[h]Data of Bowman et al. (*44*).
[i]Data of Biggar et al. (*18*).
[j]Data of O'Brien (*64*).
[k]Data of Arnold et al. (*88*).

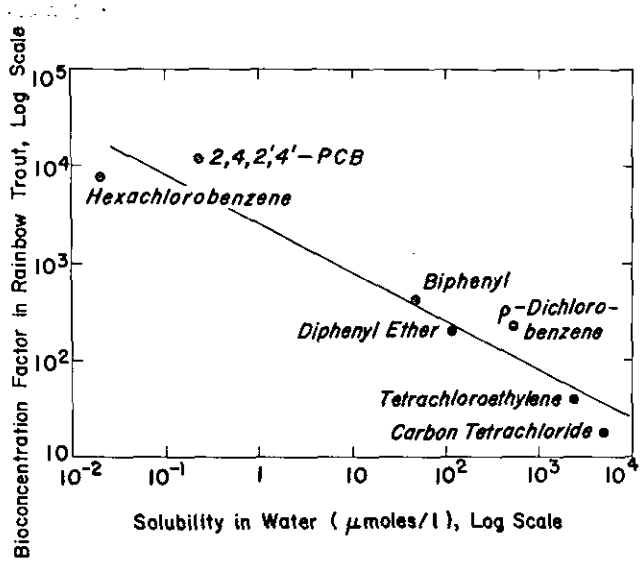
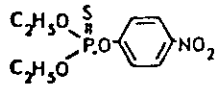
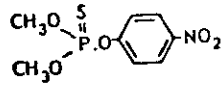
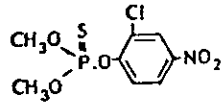
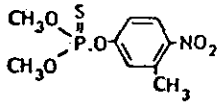
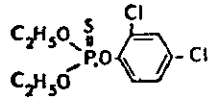
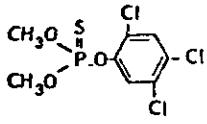
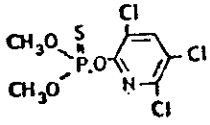
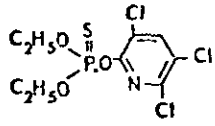


FIGURE 2. Water solubility vs. bioconcentration. Data of Neely et al. (*47*).

However, no singular physicochemical property is adequate to describe and predict the probable behavior and fate of a chemical in the environment and its likely method of transport. Rather, as has been pointed out, one needs a profile of these various characteristics in order to estimate the transport and fate of the chemicals in the environment (*1, 4, 11, 22, 23, 56*). Such a profile of some organophosphates used as pesticides is found in Table 5.

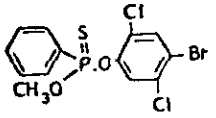
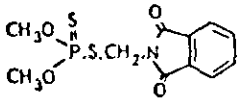
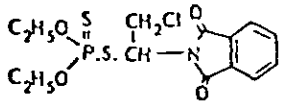
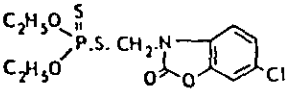
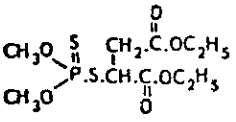
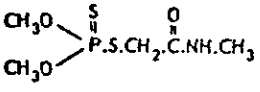
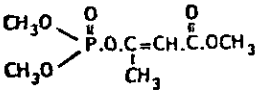
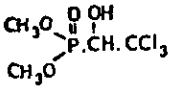
The specific properties which are required to predict such behavior are: water solubility, heats of solution, ionization constants, vapor pressures, rates of hydrolysis, and partition coefficients. The first three properties determine the degree and strength to which a chemical is adsorbed on surfaces such as soil or river sediments. This behavior will obviously determine the extent to which a chemical is transported by the aqueous environment. With chemicals subject to hydrolysis, this property will govern the persistence of chemicals in both the physical and biological environment. Vapor pressure and heat of vaporization serve as a measure of the rate of vaporization and tendency of volatilization across air/chemical as well as air/water and air/soil interfaces. Finally, partition

Table 5. Physical properties of some organophosphate compounds.

Compound	Structure	Mp, °C	Bp, °C/mm Hg	Vapor pressure mm Hg (t, °C)
Parathion		6.1[a]	113/0.05[a] 157–162/0.6[d,e]	3.78×10^{-5} (20)[f]
Methyl parathion		35–36[a]	109/0.05[a]	9.7×10^{-6} (20)[d]
Dicapthon		52–53[a,c] 51–52[g]		3.59×10^{-6} (20)[b] 2.38×10^{-5} (30)[b]
Fenitrothion			95/0.01[a] 140–145/0.4[c]	6×10^{-6} (20)[a] 5.4×10^{-5} (20)[c]
Dichlofenthion			108/0.01[a] 120–123/0.2[c]	
Ronnel		41[a] 35–37[j]	97/0.01[a]	5.29×10^{-5} (20)[b] 1.86×10^{-4} (30)[b]
Methyl chlorpyrifos		44.5–45.5[b] 45.6–46.5[i]		3.37×10^{-5} (20)[b] 1.47×10^{-4} (30)[b]
Chlorpyrifos		42–43.5[n] 41.5–43[a]		1.87×10^{-5} (25)[o] 8.87×10^{-5} (35)[o] 7.82×10^{-5} (30)[b]

ΔH_{vap}, kcal/mole	H_2O solubility, ppm (t, °C)	Octanol/H_2O partition coefficient	Hydrolysis: Half-life	Hydrolysis: pH	Hydrolysis: t, °C	ΔH_{hyd}, kcal/mole	LD_{50}, mg/kg: Oral, rat	LD_{50}, mg/kg: Dermal, rabbit
15.5	11.9 (20)[b] 11 (40)[d]	6,430[b]	26.8 days 130 days	7.4 7.4	37.5[b] 20[b]	16.31	13 (M)[c] 3.6 (F)[c]	21 (rat)[c] 6.8 (F)[c]
21	25 (20)[d] 77 (40)[d]		175 days 11 hr	1-5 1-5	20.0[a] 70.0[a]		14 (M)[c] 24 (F)[c]	67 (rat)[c]
33.4[b]	6.25 (20)[b] 35[a]	3,790[b]	5.5 days 29.0 days	7.4 7.4	37.5[b] 20[b]	17.17	400 (M)[g] 330 (F)[g]	>2000 (guinea pig)[c]
22	30[a]	2,380[b]	11.2 hr	6.0 (1:4 ethanol/H_2O)	70[h]		250[c] 250–500[g]	3000 (mice)[c] 1300 (rat)[i]
	0.245 (25)[c]	137,000[b]	48.0 hr	6.0 (1:4 ethanol/H_2O)	70[h]		270[c]	6000[g]
22.2[b]	1.08 (20)[b] 40[c]	75,300[b]	10.2 hr 10.4 hr	6.0 (1:4 ethanol/H_2O) 6.0 (1:4 ethanol/H_2O)	70[h] 70[h]		1500[c] 1740[k]	2000 (rat)[c] 1500[j]
26.0[b]	4.76 (20)[b] 4.0 (23–25)[l]	20,200[b] 9,300[c]	12.5 days 2.6 days	7.4 7.4	20[b] 37.5[b]	16.22	941[m]	
28.4	0.4 (23)[o] 2[p]	66,600[n] 128,700[b]	13.4 days 53.0 days	7.4 7.4	37.5[b] 20[b]	14.21	163 (M)[c] 135 (F)[c]	2000[c]

Table 5. Physical properties of some organophosphate compounds (continued).

Compound	Structure	Mp, °C	Bp, °C/mm Hg	Vapor pressure mm Hg (t, °C)
Leptophos		70.2–70.6[c] 71.5–72.0[g]		2.3×10^{-8} (20)[b] 1.7×10^{-7} (30)[b]
Phosmet		72–72.7[e] 71.9[g]		4.52×10^{-7} (30)[b] 9.38×10^{-7} (40)[b]
Dialifor		67–69[x]		6.2×10^{-8} (30)[b] 3.45×10^{-7} (40)[b]
Phosalone		45–48[e] 45–47[a]		
Malathion		2.85[b]	120/0.2[a] 156–157/0.7[c,d]	1.25×10^{-6} (20)[a] 4×10^{-5} (30)[d,t]
Dimethoate		43.5–45.8[c] 42–46[b]	107/0.05[a]	8.5×10^{-6} (20)[a]
Mevinphos			99–103/0.03[g] 106–107/1[k]	2.2×10^{-3} (20)[a] 5.7×10^{-3} (29)[d]
Trichlorfon		83–84[c] 78–80[k]	100/0.1[c]	7.8×10^{-6} (20)[c]

[a]Data of Mel'nikov (*65*). [b]NIEHS data (*66*). [c]Data of Spencer (*67*). [d]Data of von Rümker and [illegible] (*72*). [f]Data from Farm Chemicals Handbook (*73*). [j]Data of Hammer (*74*). [k]Data of Burchfield and [illegible] Collier and Dieter (*80*). [q]Data of Velsicol Chemical Corp. (*81*). [r]Data of Stauffer Chemical Co. (*82*)

ΔH_{vap}, kcal/mole	H_2O solubility, ppm (t, °C)	Octanol/H_2O partition coefficient	Hydrolysis Half-life	Hydrolysis pH	Hydrolysis t, °C	ΔH_{hyd}, kcal/mole	LD_{50}, mg/kg Oral, rat	LD_{50}, mg/kg Dermal, rabbit
35.3[b]	0.0047 (20)[b] 0.03 (25)[g]	2.02×10^{6}[b]	19.0 hr	6.0 (1:4 ethanol/H_2O)	70[b]		42–53[c] 90[m]	>10,000 (rat)[v] >800[p]
13.8[b]	25 (25)[a]	677[b]	1.1 hr 7.1 hr	7.4 7.4	37.5[b] 20.0[b]	19.27	230 (M)[c] 299 (F)[c]	>3160[c]
32.4	0.18[x]	49,300[b]	1.8 hr 14.0 hr	7.4 7.4	37.5[b] 20.0[b]	21.19	5–70[x] 50[m]	145[c]
	10[g] 2.15 (20)[b]	20,100[b]					120[c] 135–170 (F)[u]	1000[g] 390 (rat)[g]
17	145 (20)[a] 300 (30)[d]	781[b]	1.3 day 10.5 days	7.4 7.4	37.5[b] 20.0[b]	21.58	1375[t] 2800[g]	4100[g]
22	39,000[a] 50,000 (30)[d]	0.508[b]	0.8 hr 21 hr	9 2	70[a] 70[a]		250–265[a] 245[u]	400 (rat)[d]
16.6	High[a] Miscible[d]	30–35 days 3 days	7[a] 9[q]			5.0–6.8[c] 3.7–12.0[g]	4.7–33.8[c] 16–34[d]	
25.7	154,000 (25)[c] 120,000 (26)[u]						630(M)[c] 560 (F)[c]	>2000 (rat)[c]

[illegible] from Shell Chemical Co. (*69*). [f]Data of Bright et al. (*70*). [g]Data of Martin (*71*). [h]Data of Ruzicka et al. [i]Data of Kenaga (*76*). [m]Data of Thomson (*77*). [n]Data of Kenaga (*78*). [o]Data of Brust (*79*). [p]Data of [illegible] Inc. (*83*). [t]Data of American Cyanamid Co. (*84*). [u]Data of Zweig (*85*).

coefficients indicate the propensity for uptake and storage of chemicals in biological systems. Compounds of low water solubility are nearly always extensively adsorbed on surfaces. In biological systems, the adsorption and storage of chemicals is a function of a compound's lipophilicity as well as its water solubility. So partition coefficients, or lipophilic to hydrophilic ratios, will determine whether a compound will be stored and biomagnified.

Table 6 attempts to summarize what has been demonstrated in a number of publications on the relation of physicochemical properties to environmental behavior.

Table 6.

Physical chemical data	Related to
Solubility in water	Leaching, degree of adsorption, mobility in environment
Latent heat of solution	Adsorption, leaching, vaporization from surfaces
Partition coefficient	Bioaccumulation potential, adsorption by organic matter
Hydrolysis	Persistence in environment and biota
Ionization	Route and mechanism or adsorption or uptake, persistence, interaction with other molecular species
Vapor Pressure	Atmospheric mobility, rate of vaporization

Thus, such data provide not only a basis of predicting the transport and possible compartments of accumulation, but would also give an indication of persistence and fate of the chemical.

Quantitative Behavior of Chemicals in the Environment

Chemicals used by man represent a wide variety of classes of compounds. They are grouped according to the purpose for which they are used, e.g. pesticides for insect, weed, or fungus control, plastics, pharmaceuticals, detergents, etc. One of the main characteristics of many of the compounds is that they are generally low molecular weight organic compounds with very low water solubility; however, some inorganic compounds and organometallics are also used (*2, 26*).

In order to answer the question as to what happens to a chemical when it is introduced into the environment, one must have an understanding of the nature of the environment itself. The fundamental phases of the environment are: land (lithosphere), water (hydrosphere), air (atmosphere), and biota (biosphere). A rough estimate of the masses of the various phases yields the following: atmosphere 5.3×10^{18} kg, soil to 6-in. depth 1.1×10^{17} kg, water 1.3×10^{21} kg, animals 2.0×10^{13} kg, and plants 1.1×10^{15} kg. When a chemical is released into the environment it will be distributed (partitioned) between the various phases with the concentration in any phase being a function of the properties of both the chemical and the phase (*9, 34, 41*). Applying the simple law of Boltzmann distribution to this complex system we have the following equation:

$$N_{ij} = N_0 e^{-\epsilon_{ij}/kT} \quad (1)$$

If we assume that $N_{ij} = N_{ji}$, $N_{ij} = 0$ when $i = j$ and $N_0 = N_1 + N_2 + N_3 + N_4 + N_5$, where N_0 is the number of molecules of the chemical initially introduced and $N_1, \ldots, N_5$ are the number of molecules in respective phases of the environment. In the Eq. (1), ϵ represents the energy barrier between two phases, k represents the Boltzmann constant, and T represents the absolute temperature. To understand the behavior of a chemical in the above five components one must have a detailed knowledge of the physical and chemical properties of the chemical.

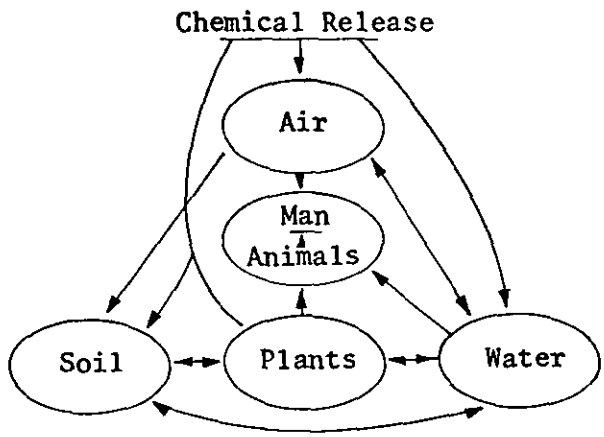


FIGURE 3. Man's exposure to a chemical through cycling of residues in the environment.

Evaporation and Transport

To illustrate the evaporation of liquids, pesticide spray application will be used. The application of sprays for pest control involves forcing the carrier

liquid under pressure through the orifices of appropriately spaced and arranged nozzles. Almost regardless of the type of nozzle, fluids, e.g., water, oil, tend to break up into droplets as they leave the orifice. The droplet size is not uniform, rather any given nozzle and orifice will tend to produce a spectrum of droplet sizes on either side of the median.

A variety of forces and properties such as surface tension, viscosity, pressure of the fluid, orifice size and geometry, shear effects, etc., influence the droplet size spectrum.

The rate of fall of a droplet or any particle is governed by Eq. (2):

$$V = 2r^2\Delta\rho g/9\eta \qquad (2)$$

where V is terminal velocity, r is radius of the droplet, $\Delta\rho$ is the difference between the density of the particle and the density of air, g is the acceleration due to gravity, and η is the viscosity of air (1.8×10^{-4} poise). Obviously then, with a given liquid, the size of the droplet becomes important in the rate at which it falls to the target area. The smaller the droplet, the slower this terminal velocity will be. If there is a wind to displace the droplet from a purely vertical line of fall, the droplet is said to "drift." It thus must follow a longer path from the nozzle to the target surface. The degree of displacement that a particle can experience is illustrated in Table 7.

is large in relation to the volume of the drop (4.18×10^{-6} cm^3). Obviously, if a drop is yet smaller, it presents a larger surface area in relation to its volume for evaporation. The relationship of evaporation to drop size is shown in Eq. (3):

$$P = P_0 e^{2\gamma V/rkT} \qquad (3)$$

This equation indicates that as the radius gets smaller, the vapor pressure increases, and hence the rate of evaporation increases.

During the fall of the droplet, evaporation will take place. This decreases the size of the droplet allowing even more extended drift.The rate of evaporation increases with temperature and, of course, reduced humidity which further exacerbates the problem.

Once a chemical is introduced in the environment, its entry into and transport through the atmosphere will depend on several factors such as the vapor pressure and the heat of vaporization of the chemical, the partition coefficient between the atmosphere and any other phase, and the air flow mass which will transport any chemical dispersed in the atmospheric phase.

The vapor pressure of the chemical will play a major role in the atmospheric transport since it re-

Table 7. Drift of naturally occurring water droplets.

Description	Droplet size, μm	Drift (at wind speed 10 mph)	
		Height 5 ft	Height 50 ft
Fog	10		14.5 miles
Mist	100	75 ft	750 ft
Avg. particle size of mist under Niagara Falls	217.3	21.5 ft	210 ft
Drizzle	300	8 ft 4 in.	83 ft
Light rain	590	2 ft 2 in.	21.5 ft
Moderate rain	800	1 ft 3 in.	12.0 ft

Every substance has a tendency to change from solid to liquid to vapor due to the motion of the molecules making up that substance. The tendency of a liquid to pass into gaseous state or vaporize is indicated by its vapor pressure and is materially influenced by the amount of energy required to accomplish this procedure. The liquid droplet emerging from the spary nozzle now presents a large surface from which the various components of the droplet can evaporate. Thus, for example, the area of a particle of 200 μm diameter (a not uncommon size for sprays) is 0.001256 cm^2. However, this

lated to the proportional amount of chemical in the gas phase (*14, 28, 32*). The vapor pressure P of a pesticide is related to the temperature T by the well-known Clausius-Clapeyron equation (4),

$$\frac{d(\ln P)}{dT} = \frac{\Delta H}{RT^2} \qquad (4)$$

where R is the gas constant and ΔH is the heat of vaporization. The quantity ΔH regulates the amount of chemical converted into vapor phases at

a given heat flux. The vapor pressure of organic chemicals vary over a wide range from the highly volatile substances such as fluorocarbons, chloroform, and vinyl chloride through the moderately volatile compounds like parathion, to the low volatile materials such as DDT, PCBs, and polymers (*1, 23, 48*). An expression relating vapor pressure to quantity evaporating is found in the Langmuir equation (5):

$$Q = \beta P\,(M/2\pi RT)^{\frac{1}{2}} \qquad (5)$$

where β is an evaporation constant of a chemical under a given atmospheric condition.

In the atmospheric phase, the kinetic motion of molecules as well as eddy current will cause their distribution. The molecules will distribute vertically like a column of gases having a concentration gradient. The heavier molecules will have the highest concentration at the bottom and the lighter ones on the top, and the pressure P (or concentration) of a chemical will be governed by the barometric formula (6):

$$P = P_o e^{-mgx/RT} \qquad (6)$$

where x is the height at which pressure is sought, P_o is the pressure at some reference point, and m is the mass of the gaseous molecule.

The presence of suspended dust or aerosol particles may result in sorption of some of the vapors and consequently will increase the partition function of the chemical between the atmospheric phase and other elements of the environment. The sorbed chemical may then be transported some distance with the particulate. This may explain the finding of pesticides where they have never been used (*13, 15, 27, 30*). Since the vaporization of a chemical from a surface is related to its diffusion in the air, air currents can increase the rate of vaporization.

Many chemicals in an aqueous system will evaporate simultaneously with the water; in other words, codistill (*44*). Vapor loss of a pesticide from the soil system, for example, is accelerated by the presence of moisture. This has been shown with such diverse materials as 2,4-D esters, thiolcarbamates, triazines, *N*-phenylcarbamates, and the organochlorine insecticide aldrin (*24, 46, 51*).

Although vapor pressure of a chemical to a great extent determines the entry of the chemical in the atmosphere, caution must be exercised in interpreting the data. The vapor pressure of a chemical can give a good estimate of air transport as long as the chemical is in the free state or is evaporating from an inert surface. However, when the chemical is bound to surface, the vapor pressure cannot be used as an index for vapor transport. It must be pointed out that while studying the vapor loss of a soil surface other factors which may control the release of the chemical may include temperature, initial concentration of the chemical, moisture, and pH.

Solution Behavior

The major factors contributing to the partitioning of a chemical into the aquatic environment are its water solubility (*17, 18, 33, 34*) and the latent heat of solution (*16, 41, 46*). Many organic compounds in use today evidence a hydrophobic character having water solubilities in the parts per million (ppm) or even parts per billion (ppb) range. This makes exact determinations of their solubilities quite difficult.

The alkalinity or acidity of the solution is thought to influence the stability and the solubility of certain pesticides. For example, the solubility of triazine molecules (a class of pesticides) usually increases with lowering pH and is attributed to protonation of nitrogen with the formation of cationic species. The presence of salts in an aqueous solution of pesticide may cause ion-association or ion-pair formation.

As would be expected, temperature significantly influences the behavior of organic chemicals in aqueous solution. Though the exact mechanisms of the solubilization of some of the sparingly soluble chemicals is not known, solubility usually increases with temperature. The question still remains whether or not they form ideal solutions. However, by substituting the solubility of the compound at two temperatures in the Van't Hoff equation, an enthalpy of solution value ΔH can be obtained. The enthalpy value may be used as an approximate index of the tendency of a chemical to transport to the aqueous phase from the solid state, or dissolve. The ΔH values thus derived for a solution approximate the heat of adsorption for a physical-type adsorption.

Thiolcarbamate herbicides show reversal in the effect of temperature on solubility; solubility decreases with an increase in temperature. It has been suggested that this behavior is due to hydrogen-bond formation between water and the thiolcarbamates.

Other factors which may contribute to the transport and the persistence of chemicals in an aquatic environment are the presence of clay or soil particles or proteins and lipids, and the effects of ultraviolet or other high-energy radiations causing a decomposition of the molecule. The presence in water of soil particles of any nature (soil, clay, sand, or biocolloid) will reduce the concentration of dissolved chemical by adsorption. The extent of adsorption will depend on the nature of the suspended particles and the temperature.

Soil Behavior

The two major processes controlling the behavior of chemicals in a soil matrix are adsorption and leaching–diffusion (*32–34, 38, 48*). A change in the moisture content of the soil-chemical system and of temperature will greatly influence both processes.

A soil matrix represents a heterogeneous mixture of various constituents, namely organic matter, sand, clays, and inorganic salts. These sometimes present a large surface area with a number of sites on which adsorption can occur. Although the bulk of the adsorption may be from solution, adsorption to a certain extent also occurs from the chemicals present in the vapor state.

The equilibrium in a chemical-soil system can be represented by Eq. (7):

$$P(H_2O)_x + S(H_2O)_y \rightleftharpoons P(H_2O)_zS \qquad (7)$$

where P and S represent the compound and soil matrix, respectively. With sufficient water present, both the chemical molecule and the soil matrix will be in the hydrated form. The symbols x, y, and z denote the hydration numbers of the chemical, the soil, and the complex, respectively. The equilibrium constant K^E for the reaction is:

$$K^E = \frac{[P(H_2O)_zS]}{[P(H_2O)_x]\,[S(H_2O)_y]} \qquad (8)$$

Here the quantities in brackets represent the activities of the compound. An exact determination of K^E is difficult since an estimate of the exact volume occupied by the adsorbed species is nearly unattainable. Usually the adsorption data for a soil-chemical system are represented with a Freundlich isotherm:

$$x/m = KC^n \qquad (9)$$

where x/m is the amount of chemical sorbed per weight of the absorbent, C is the equilibrium concentration of the chemical, and K and n are constants. For a dilute solution of many compounds, the value of n approaches unity. The constant n throws much light on the nature of the adsorption, whereas K represents the extent of adsorption and is related to the free-energy changes in the adsorption.

The adsorption also depends upon the nature of the chemical under investigation. Inorganic salts and organic cations adsorb on the clay portion of the soil through an exchange reaction. Most neutral organic molecules follow a physical type adsorption, and the amount of chemical sorbed in many cases follows an inverse relation to its solubility (*35, 36*).

Adsorption of chemicals from aqueous solution is in most instances an exothermic process. Usually a lowering in temperature means an increase in the adsorption. In general, for neutral adsorption of neutral organic compounds, the heat of adsorption is in the range of only a few kilocalories per mole, indicating a physical type adsorption or in some cases weak hydrogen bonding between adsorbate and the surface. Formation of a chemical bond or chemisorption has rarely been observed in neutral pesticide-soil system (*20, 37*). For most of the neutral organic molecules the adsorption is of the physical type, in which there is first the formation of a monolayer on the surface followed by a build-up of multilayers. Hence, by analogy to the adsorption of gases on solids, the heat of adsorption for aqueous solution of a pesticide should be in the range of heat of solution.

Transport in Soil

Another important process which controls the transport of a chemical in a soil matrix is its movement with water, a process termed leaching (*12, 33, 34, 52*). The leaching may take place in three directions: downward, since this is the usual direction of water movement, but the lateral movement of the chemical in the soil with water and even upward movement are sometimes significant. The upward movement, which is a result of mass transfer of water upward under the influence of evaporation from the surface, may concentrate a chemical at the soil surface, thus effectively removing it from the root zone.

The movement of water downward in soil is thought to be in the form of film and is produced by combined effects of capillary and gravitational forces. The chemicals are usually applied to the surface of the soil; as water arriving at the surface penetrates, it encounters the chemical, dissolving and carrying the chemical with it as it percolates through the soil.

The displacement of the chemical under rapid percolation of water is predominantly with the bulk of the water solution. Counteracting this downward movement is the tendency of isodiametric diffusion of the chemical in solution. Where the water percolation is rapid, the bulk movement of the chemical will be in the direction of water flow, but as water percolation becomes slower and slower, diffusion becomes a greater factor in determining the distribution of chemical. In other words, there is a dynamic equilibrium between the free chemical and the chemical in the adsorbed phase as the chemical is carried through the soil profile by the movement and the adsorbed phase. As a consequence, a chemical which is tightly adsorbed should be leached

slowly, and vice versa (*37*). Thus, the ΔH of solution gives an indication of a chemical's mobility in leaching.

In practice the important factors controlling leaching are water solubility of the chemical, adsorption, soil type, and moisture and percolation velocity. A highly soluble chemical having a low enthalpy of adsorption will be leached soon because of its tendency to go into solution. As a consequence the amount of chemical carried in the soil will be proportional to the amount of water available to dissolve the chemical. Temperature will play an important role in the leaching since it affects the solubility.

The behavior of chemicals described in the foregoing has dealt primarily with the different components of subsystem of the total environment. What is desired is a more comprehensive picture of the movement and behavior in the total environment system taking into account the interactions of the different subsystems. Perhaps the most intensive attempt to model behavior of a pesticide in the total environment has been done with DDT. Harrison et al. (*86*), provided one of the early detailed models of the behavior of this chemical in an attempt to estimate transport through various trophic levels and possible persistence of the chemical. Woodwell (*30*), in assessing a global model for transport and persistence of DDT, found the concentration much lower in certain compartments than would be predicted on the basis of the model utilizing the parameters available to him. The most recent attempt to give a quantitative description or model of the circulation of DDT was done by Kramer (*87*). He pointed out that rates of degradation, transfer, and adsorption by plankton are critical factors in such a model. Recent monitoring data would appear to suggest the rate of disappearance of DDT may be more rapid in the general environment than had been previously estimated. Others have given some attention to modeling behavior of pesticides other than the organochlorines in the atmosphere, soil, and water. As yet, insufficient data has been accumulated to facilitate further development of these models.

Summary and Conclusions

Quantities of chemicals in ever growing numbers are being manufactured and used and in the process escape into the environment. As a result of this environmental contamination, man is being exposed to low quantities of many of these chemicals either directly or through his food chain. In many instances, little is known about the long-term consequences of such exposure at the low levels experienced. However, prudence would indicate that, in so far as possible, further reduction or prevention of this exposure is to be sought rather than attempting to deal with the health problem that may arise from it.

A body of knowledge is emerging and indicates a relationship between the properties of the chemical and the transport and behavior in the environment. In many instances quantitative data and usable mathematical relationship has been developed. On this basis it is felt that we are rapidly approaching the time where transport, behavior, and persistence of a chemical in the environment can be predicted from the properties of the chemical, method of use, and rate of degradation. Such predictions will be useful in evaluating possible exposure to man and the level at which this exposure may occur. Also, it would serve as a basis for designing systems of handling, use, and disposal to minimize health and environmental impacts.

The indirect impact of these chemicals on man is another area meriting attention. The alteration of biologically mediated geochemical cycles or modification of biota diversity indices can be of consequence to man's health and well being. There is reason to believe that chemicals in the environment acting singly or in concert may bring about alterations of these factors with a consequence to man.

It would seem, therefore, that the area of transport, behavior, and persistence of chemicals in the environment, i.e. chemodynamics, warrants further attention and research.

Further research on the relationship between the properties of the chemical, characteristics of environmental compartments (e.g., soil, air, and water) the transport, behavior, and persistence of the material in relation to exposure to man is necessary. Concomitantly, efforts should go forward to develop appropriate models of this behavior so as to be able to assess exposure levels and devise the appropriate protective measures.

Development of a program for inventorying the chemicals in the environment, both as to kinds and quantities, would lead to the knowledge necessary for development of the appropriate monitoring programs.

Assessment of direct, latent, and indirect effects of environmental chemicals on man and the environmental processes of consequence to man's health as these chemicals move from source to ultimate sink is the ultimate goal.

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REFERENCES

1. Brian, R., and Rideal, E. K. Chemicals and Health. Report of Panel on Chemicals and Health, Pres. Sci. Advisory Committee, Office of Science and Technology, National Science Foundation, 1973.
2. Cook, G. A. Survey of Modern Industrial Chemistry. Ann Arbor Sci. Pub., Ann Arbor, Michigan, 1975.
3. Moolemaar, R. J. Environmental impact of chemicals. In: Chemicals, Human Health, and the Environment—A Collection of Dow Scientific Papers, Vol. 1. Dow Chemical Co., Midland, Mich., 1975.
4. Epstein, S. S., and Shafner, H. Estimation of exposure levels to target systems. In: Principles for Evaluating Chemicals in the Environment. National Academy of Sciences, Washington, D. C., 1975, pp. 45-81.
5. Kent, J. A. Reigels Industrial Chemistry. Reinhold, New York, 1962.
6. Sittig, M. Pollution Control in the Organic Chemical Industry. Noyes Data Corp., Park Ridge, New Jersey, 1974.
7. Lawless, et al. The pollution potential in pesticide manufacturing. Pesticide Study Series 5. EPA Technical Studies Report, June 1972.
8. Epstein, S. S., and Shafner, H. Chemical mutagens in the human environment. Nature 219: 385 (1968).
9. Hampel, D. A., and Haeley, G. G., Eds. Encyclopedia of Chemistry, 3rd. ed. Van Nostrand-Reinhold, New York, 1973, pp. 366-368.
10. Kenaga, E. E. Partitioning and uptake of pesticides in biological systems. In: Environmental Dynamics of Pesticides. R. Haque and V. H. Freed, Eds., Plenum Press, New York, 1975, p. 217.
11. Moolenaar, R. J. Environmental impact of chemicals. In: Conference Report: Early Warning Systems for Toxic Substances. OTS/EPA, 1975, p. 167.
12. Gould, R., Ed. Organic Pesticides in the Environment (Adv. Chem. Ser. 60), American Chemical Society, Washington, D. C., 1966.
13. Howard, P. H. Establishing environmental priorities for synthetic organic chemicals: focusing on the next PCB's. In: Conference Report: Early Warning Systems for Toxic Substances. OTS/EPA, 1975, p. 51.
14. Cliath, M. M., and Spencer, W. F. Dissipation of pesticides from soil by volatilization of degradation products. I. Lindane and DDT. Environ. Sci. Technol. 6: 910 (1972).
15. Cohen, J. M., and Pinkerton, C. Widespread translocation of pesticides by air transport and rain-out. In: Organic Pesticides in the Environment (Adv. Chem. Ser. 60), American Chemical Society, Washington, D. C., 1966, p. 63.
16. Haque, R., and Ash, N. Factors afflicting the behavior of chemicals in the environment. In: Surviving in Toxic Environments. M. A. Q. Khan, and J. P. Bederka, Eds., Academic Press, New York, 1974, p. 357.
17. Guenzi, W. D., Ed. Pesticides in Soil and Water. Soil Science Society of America, Madison, Wisconsin, 1974.
18. Biggar, J. W., Dutt, G. R., and Riggs, R. L. Predicting and measuring the solubility of *p,p*-DDT in water. Bull. Environ. Contam. Toxicol. 2: 90 (1967).
19. Freed, V. H., and Haque, R. Adsorption, movement, and distribution of pesticides in soils. In: Pesticide Formulations. W. van Valkenburg Ed., Dekker, New York, 1973, p. 441.
20. Haque, R., and Coshow, W. R. Adsorption of isocil and bromacil from aqueous solution onto some mineral surfaces. Environ. Sci. Technol. 5: 139 (1971).
21. Hartley, F. S. Evaporation of pesticides. In: Pesticidal Formulations Research, Physical and Colloidal (Adv. Chem. Ser. 86). American Chemical Society, Washington, D. C., 1969, p. 115.
22. Metcalf, F. L., Sahgha, G. K., and Kapoor, I. P. Model ecosystem for the evaluation of pesticides biodegradability and ecological magnification. Environ. Sci. Technol. 5: 708 (1971).
23. Lovelock, J. E. Natural halocarbons in the air and in sea. Nature 256: 193 (1975).
24. Hamaker, J. W., and Kerlinger, H. O. Vapor pressure of pesticides. In: Pesticidal Formulations Research (Adv. Chem. Ser. 86), American Chemical Society, Washington, D. C. 1969, p. 39.
25. Hansch, C. A quantitative approach to biochemical structure-activity relationships. Accts. Chem. Res. 2: 232 (1969).
26. Environmental Protection Agency. Papers of a Seminar on Early Warning Systems for Toxic Substances. Conference Report, Office of Toxic Substances, EPA, 1975.
27. Lloyd-Jones, C. T. Evaporation of DDT. Nature 229: 65 (1971).
28. Freed, V. H., Haque, R., and Schmedding, D. Vaporization and environmental contamination by DDT. Chemosphere 1: 61 (1972).
29. Haque, R., Schmedding, D., and Freed, V. H. Solubility, adsorption, and vapor behavior of the PCB Aroclor 1254. Environ. Sci. Technol. 8: 139 (1974).
30. Woodwell, F. M., Craig, P. P., and Johnson, H. A. DDT in the biosphere: Where does it go? Science 174: 11019 (1971).
31. Crosby, D. G., and Moilanen, K. W. Vapor phase decomposition of pesticides. Paper presented at 163rd Natl. Meeting. American Chemical Society, Washington, D. C., 1972.
32. Ehlres, W., et al. Lindane diffusion in soils. I. Theoretical considerations and mechanism of movement. Soil Sci. Soc. Amer. Proc. 33: 501 (1969).
33. Gardner, W. R., and Brooks, R. H. A descriptive theory of leaching. Soil Sci. 95: 295 (1957).
34. Hamaker, J. W. The Interpretation of soil leaching experiments. In: Environmental Dynamics of Pesticides. R. Haque and V. H. Freed, Eds., Plenum Press, New York, 1975, p. 115.
35. Lambert, S. M. Functional relationship between sorption in soil and chemicals structure. J. Agr. Food Chem. 15: 572 (1967).
36. Lambert, S. M. Omega (Ω), a useful index of soil sorption equilibria. J. Agr. Food Chem. 16: 340 (1968).
37. Lindstrom, F. T., Haque, R., and Coshow, W. R. A new model for the kinetics of adsorption-desorption processes. J. Phys. Chem. 74: 495 (1970).
38. Bailey, R. W., and White, J. L. Review of adsorption and desorption of organic pesticides by soil colloids, with implications concerning pesticides bioactivity. J. Agr. Food Chem. 12: 324 (1964).
39. Albert, A. Selective Toxicity, 4th ed. Methuen, London, 1968.
40. Gillett, J. W., et al. Evaluation of human health hazards on the use of dichlorvos, especially in resin strips. Residue Revs. 44: 115 (1972).
41. Haque, R., and Freed, V. H. Behavior of pesticides in the environment: environmental chemodynamics. Residue Revs. 52: 89 (1974).

42. Leo, A., Hansch, C., and Elkins, D. Partition coefficients and their uses. Chem. Rev. 71: 525 (1971).
43. Trim, A. R., and Alexander, A. E. Selective Toxicity in Anti-metabolites. Academic Press, New York, 1949.
44. Bowman, M. C., Acree, F., and Corbett, M. K. Solubility of carbon-14 DDT in water. J. Agr. Food Chem. 8: 406 (1960).
45. Brian, R., and Rideal, E. K. On the action of plant growth regulators. Biochem. Biophys. Acta 9: 1 (1952).
46. Freed, V. H., Haque, R., and Vernetti, J. Thermodynamic properties of some carbamates and thiolcarbamates in aqueous solution. J. Agr. Food Chem. 15: 1121 (1967).
47. Neely, W. B., Branson, D. R., and Blau, G. E. Partition coefficent to measure bioconcentration potential of organic chemicals in fish. Environ. Sci. Technol. 8: 1113 (1974).
48. Helling, C. S., and Turner, B. C. Pesticide mobility: determination by soil thin-layer chromatography. Science 162: 562 (1968).
49. Hurle, K. B., and Freed, V. H. Effect of electrolytes on the solubility of some 1,3,5-triazines and substituted ureas and their adsorption on soil. Weeds 12: 1 (1972).
50. Weber, W. J., and Gould, J. P. Sorption of organic pesticides from aqueous solution. Adv. Chem. Ser. 60: 280 (1966).
51. Guenzi, W. D., and Beard, W. E. Volatilization of lindane and DDT from soils. Soil Sci. Soc. Amer. Proc. 34: 443 (1970).
52. Sherburne, H. R., and Freed, V. H. Adsorption of 3(*p*-chlorophenyl)-1,1-dimethyl urea as a function of soil constituents. J. Agr. Food Chem. 2: 937 (1954).
53. Albert, A. Selective Toxicity, 4th ed. Methuen, London, 1968.
54. Nash, R. G., and Woolson, E. A. Persistence of chlorinated hydrocarbon insecticides in soils. Science 157: 924 (1967).
55. Ward, R. M., and Weber, J. B. Aqueous solubility of alkylamino-*s*-triazines as a function of pH and molecular structure. J. Agr. Food Chem. 16: 959 (1968).
56. Albert, A. Relation between molecular structure and biological activity-stages in evolution of current concepts. In: Annual Review of Pharmacology. Vol. 11. Annual Reviews, Inc. Palo Alto, California. 1971.
57. Boyer, A. C. Vinyl phosphate insecticide sorption to proteins and its effect on cholinesterase I_{50} values. J. Agr. Food Chem. 15: 282 (1967).
58. Ketelaar, J. A. A. Chemical Constitution—An Introduction to the Theory of the Chemical Bond. Elsevier Publishing Co., New York, 1953.
59. Hodgman, C. R., Ed. Handbook of Chemistry and Physics, 34th Ed., Chemical Rubber Publishing Co., Cleveland, 1952.
60. Fujita, R., Iwasa, J., and Hansch, C. A new substituent constant, π, derived from partition coefficients. J. Amer. Chem. Soc. 86: 5175 (1964).
61. Hansch, C., and Fujita, T. ρ-σ-π Analysis. A method for the correlation of biological activity and chemical structure. J. Amer. Chem. Soc. 86: 1616 (1964).
62. Hansch, C., and Anderson, S. M. The effect of intramolecular hydrophobic bonding on partition coefficients. J. Org. Chem. 32: 2583 (1967)
63. Macy, R. Partition coefficients of fifty compounds between olive oil and water at 20°. J. Ind. Hyg. Toxicol. 30: 140 (1948).
64. O'Brien, R. D. Nonenzymic effects of pesticides on membranes. In: Environmental Dynamics of Pesticides. R. Haque, and V. H. Freed, Eds., Plenum Press, New York, 1975, p. 336.
65. Mel'nikov, N. N. Chemistry of Pesticides. (Translated from Russian) by R. L. Busbey (1968); published as Res. Rev. 36: (1971).
66. National Institute of Environmental Health Sciences Grant No. ES 00040-10 Annual Progress Report (1975).
67. Spencer, E. Y. Guide to the Chemicals used in Crop Protection. 6th ed. Research Branch, Agriculture Canada, 1973.
68. von Rümker, R., and Horay, F. Basic information on thirty-five pesticide chemicals. Pesticide Manual. Part II. U. S. Agency for International Development, 1972.
69. Anonymous. Summary of basic Data for Shell Technical Ethyl Parathion. Shell Technical Bulletin ACD 66-102 (Rev. 7-67).
70. Bright, N. F. H., J. C. Cuthill, and N. H. Woodbury. The vapor pressure of parathion and related compounds. J. Sci. Food Agr. 1: 344 (1950).
71. Martin, H., Ed. Pesticide Manual. British Crop Production Council, Clarks Farm, Doreley, Ombersley, Worchester, England, 1971.
72. Ruzicka, J. H., Thomson, J., and Wheals, B. B. The gas chromatographic determination of organophosphorus pesticides. Part II. A comparative study of hydrolysis rates. J. Chromatog. 31: 37 (1967).
73. Farm Chemicals Handbook. Pesticide Dictionary, Meister Publishing Co., Willoughby, Ohio, 1975.
74. Hammer, O. H. Dow ET-14. A new organic phosphorus insecticide. Down to Earth. 12(1): 2 (1956).
75. Burchfield, H. P., and Johnson, D. E. Guide to the Analysis of Pesticide Residues. Vol. II. U. S. HEW, Washington, D. C., 1965.
76. Kenaga, E. E. Some physical, chemical, and insecticidal properties of some *O,O*-dialkyl *O*-(3,5,6-trichloro-2-pyridyl) phosphates and phosphorothioates. Bull. World Health Org. 44: 225 (1971).
77. Thomson, W. T. Agricultural Chemicals, Book I. Insecticides. Thomson Publications, Indianapolis, Indiana, 1972.
78. Kenaga, E. E. Evaluation of the safety of chlorpyrifos to birds in areas treated for insect control. Res. Rev. 50: 1 (1974).
79. Brust, H. F. A summary of chemical and physical properties of Dursban. Down to Earth 22(3): 21 (1966).
80. Collier, B. L., and Dieter, C. E. Dursban—a new insecticide for cinch bug and sod webworm control in St. Augustine grass. Down to Earth 21(3): 3 (1965).
81. Velsicol Chemical Corp. Phosvel insecticide. Velsicol General Bulletin, #09-070-601A, Chicago, Ill., 1972.
82. Stauffer Chemical Co. Imidan insecticide. Stauffer Technical Bulletin #A10426, Richmond,Calif., 1972.
83. Hercules Inc. Torak organophosphate pesticide (dialifor). Summary of Toxicological Investigations. Hercules Tech. Bull. T121, Agricultural Chemicals Synthetics Department, Hercules, Inc., Wilmington, Del., 1973.
84. American Cyanamid Co. Malathion Manual for Insecticide Formulators. American Cyanamid Tech. Bull., Princeton, N. J., 1962.
85. Zweig, G. Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives. Vol. II. Insecticides, Academic Press, New York, 1964.
86. Harrison, H. L., et al. Systems study of DDT transport. Science 170: 503 (1970).
87. Kramer, J. Model of the circulation of DDT on earth. Atm–si eric Sci. 7: 241 (1973).
88. Arnold, D. S., et al. Solubility of benzene in water. Chem. Eng. Data Ser. 3: 253 (1958).