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EVALUATION OF HAZARDS OF PESTICIDES USED IN FOREST SPRAYING
TO THE AQUATIC ENVIRONMENT

by

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ABSTRACT

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A 6-compartment equilibrium model and a 3-compartment kinetic model (MacKay 1979) were used to assess the hazards of forest spraying with pesticides to the aquatic environment. The models are based on physico-chemical properties and typical application rates of pesticides. Estimated concentrations and laboratory toxicity data are compared with those of fenitrothion, used extensively in forest spraying. Expected environmental effects of other pesticides are then assessed relative to the known environmental effects of fenitrothion.

Key words: Forest spraying, pesticides, fenitrothion, hazard assessment

RÉSUMÉ

Zitko, V., and D. W. McLeese. 1980. Evaluation of hazards of pesticides used in forest spraying to the aquatic environment. Can. Tech. Rep. Fish. Aquat. Sci. 985, iii + 21 p.

Nous avons évalué les dangers pour le milieu aquatique de l'épandage de pesticides sur les forêts à l'aide d'un modèle statique à six compartiments et d'un modèle cinétique à trois compartiments (MacKay 1979). Ces modèles se servent des propriétés physico-chimiques des pesticides et des doses typiques d'épandage. Les concentrations estimatives et les données toxicologiques de laboratoire sont comparées à celles du fénitrothion, qui est très utilisé sur les forêts. Les effets prévus des autres pesticides sur l'environnement sont ensuite estimés, compte tenu des effets connus de fénitrothion.

INTRODUCTION

The assessment of potential effects of a new pesticide on the aquatic environment relies on judgment derived from the consideration of the pesticide's acute toxicity to some species of aquatic fauna, usually fish, potential for accumulation, and persistence. Acute toxicity data are generally available from the literature and have to be reported by the proponent in applications for registration submitted during the last few years. Potential for accumulation is usually estimated from the octanol/water partition coefficient of the pesticide (Kow) or from its solubility in water. There are no standard tests for persistence and the estimates are at best semiquantitative or purely judgmental.

In addition to these three factors, the rate of volatilization, characterized by the Henry's constant (H) and the extent of adsorption on soil or sediment, characterized by the adsorption coefficient (Koc), have been used increasingly in the last few years in considering the movement of chemicals in the environment (see for example Zitko 1980).

In assessing the potential effects of a pesticide, the values of these five factors are considered individually, usually are compared with those of a previously used pesticide with known environmental effects. The anticipated environmental effects of the new pesticide are then estimated qualitatively.

This report describes an attempt to combine the quantitative parameters, H, Koc, Kow, and the application rate, and to calculate "expected environmental concentration" (EEC) in air, water, soil and vegetation, and fish, in a hypothetical ecosystem. The EEC's are then compared with those of a pesticide with known environmental effects in the same system.

The hypothetical ecosystem is chosen quite arbitrarily and does not attempt to reflect any specific situation (Fig. 1). The initial assessment is made on the basis of the equilibrium distribution of the pesticides in the system. Additionally, nonequilibrium distributions and kinetics may be considered. The uncertainty in calculating EEC's under these conditions increases considerably

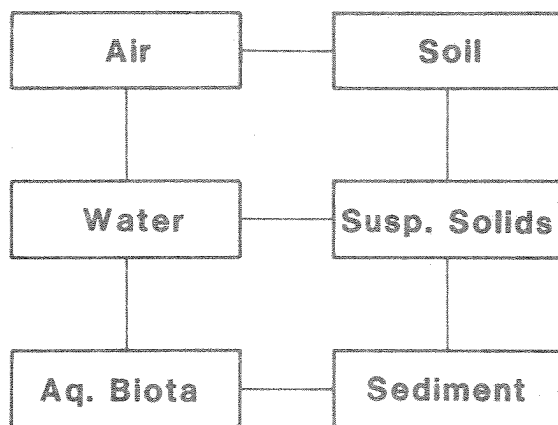


Fig. 1. A six-compartment hypothetical model.

because of the difficulties in estimating the intercompartmental transfer rates, and the rates of degradation and advection out of the system.

MODELLING THE BEHAVIOR OF CHEMICALS IN THE AQUATIC ENVIRONMENT

The status of modelling, with particular emphasis on pesticides has been discussed (Robinson 1975; Hassett and Lee 1975). Robinson described a two-compartment model and a trophic chain model; Hassett and Lee provided a critique of two DDT models and stressed the need for more consideration of the mechanisms and kinetics governing the transport of pesticides in the environment. These aspects were addressed by Smith et al. (1977), who considered volatilization, adsorption, chemical transformation, and biodegradation as well as methods for the determination of the respective equilibrium or rate constants. A nine-compartment model was designed. The aquatic compartments were river, pond, eutrophic and oligotrophic lakes. This model was examined with 11 organic chemicals (Smith et al. 1978). The results provide quantitative data on what one would expect intuitively. The results with methyl parathion, based on parameters listed in Table 1, are given in Table 2.

Emphasis on the movement of chemicals through the food web and attempts to model the influence of toxic effects are included in the work of Eschenroeder et al. (1978). This is an interesting approach that will undoubtedly be refined further.

An equilibrium distribution model was developed recently for assessment purposes by McCall et al. (1980). The model uses Henry's constant, adsorption coefficient, and bioconcentration factor and calculates the equilibrium distribution of chemicals among a number of compartments.

The hazard assessment of forest spraying presented in this report is based on the fugacity model of MacKay (1979), described in more detail below.

Table 1. Properties, equilibrium, and rate constants of parathion-methyl (Smith et al. 1978).

Molecular weight	263
Vapor pressure (20°C)	9.1E-3 torr
Solubility in water	50 µg/mL or 2.1E-4 M
Adsorption coefficient	50
Volatilization rate	6E-5 K°
Hydrolysis rate constant	9E-8 1/s
Photolysis rate constant	2.7E-7 1/s
Biodegradation rate constant	1.7E-7 µg/cellxh

Table 2. Predicted environmental fate of parathion-methyl (Smith et al. 1978).

Compartment	Half-life (h)	Steady state concentration		
		Solution ($\mu\text{g/mL}$)	Susp. solids ($\mu\text{g/g}$)	Sediment ($\mu\text{g/g}$)
River	0.6	0.989	49.46	49.1
Pond	27.3	0.012	0.6	0.6
Eutrophic lake	28.3	0.06	3.0	0.5
Oligotrophic lake	151.6	0.098	4.9	1.4

FUGACITY MODEL

FUGACITY (F)

Fugacity can be interpreted as the "escaping tendency" of a chemical from a phase (MacKay 1979) and its dimension is a unit of pressure (atm). In equilibrium, the fugacities of the chemical in all compartments are equal. For example, if the distribution of DDT between fish and water reached equilibrium, the fugacities (but not concentrations) of DDT in water and in fish are equal.

FUGACITY CAPACITY (Z)

Fugacity is related to concentration by fugacity capacity ($C = Z \cdot F$, where C = concentration, Z = fugacity capacity, and F = fugacity). At equal fugacities, compartments with higher fugacity capacities will have higher concentrations of the chemical. In the above example, the equilibrium concentration of DDT in fish is much higher than the concentration in water since the fugacity capacity of fish is much higher than that of water.

ESTIMATION OF FUGACITY CAPACITY

Fugacity capacity can be estimated from H , K_{oc} , and K_{ow} .

The fugacity capacity of the atmosphere is $1/RT$ (R = gas constant, T = temperature in $^{\circ}\text{K}$; at 20°C $1/RT = 40 \text{ mol/m}^3 \cdot \text{atm}$). The fugacity capacity of water is $1/H$. One additional factor, the concentration of suspended matter ($S, \text{g/m}^3$), affects the fugacity capacity of adsorbed chemicals, and the fugacity capacity is $10^{-6}KS/H$. Two additional factors, the fraction of lipid (Y) and the volume fraction of biota (volume of fish/volume of water) are needed to estimate the fugacity capacity of a chemical in biota (BYK_{ow}/H).

The derivation of these relationships is described in the Appendix.

HENRY'S CONSTANT (H)

This constant is the air/water distribution coefficient. The model uses H with the dimension $\text{atm} \cdot \text{m}^3/\text{mol}$. If not available, H may be estimated by dividing the vapor pressure of the chemical in atm by its solubility in mol/m^3 . The values of H range from about 0.7 for oxygen to less than 3×10^{-7} , which is the value for water. Higher values of H mean higher volatility.

ADSORPTION COEFFICIENT (K_{oc})

This is the solids/water distribution coefficient, where solids may be soil, sediment or suspended solids. K_{oc} is expressed on an organic carbon basis ($K_{oc} = 100K/\text{org. carbon } \%$) and has to be converted into the respective K values before calculating the fugacity capacity.

There is some confusion in reporting K_{oc} (or K) values in the literature. The "adsorbed" and "dissolved" concentrations must be in the same "type of units," either ppm, such as $\mu\text{g/g}$ and $\mu\text{g/mL}$ or mg/L , or ppb, such as ng/g and ng/mL or $\mu\text{g/L}$.

The value of K_{oc} can be estimated from solubility in water. A frequently used relationship is

$$\log(K_{oc}) = 3.64 - 0.55 \log(S)$$

where S = solubility in water, mg/L (Kenaga 1980).

In this work, the organic carbon content of soil and sediment was assumed to be 10 and 1%, respectively. The "soil" compartment includes vegetation, hence the higher value.

OCTANOL/WATER PARTITION COEFFICIENT (K_{ow})

The values of K_{ow} range over many orders of magnitude, consequently $\log(K_{ow})$ values are usually reported. Values of $\log(K_{ow}) > 4.5$ indicate a considerable potential uptake of the chemical by aquatic fauna. The toxicity of chemicals also generally increases with increasing $\log(K_{ow})$, but there are many exceptions when a highly specific toxic action is involved. The values of $\log(K_{ow})$ may be estimated from solubility in water by using, for example, the relationship

$$\log(K_{ow}) = 5.00 - 0.67 \log(S)$$

where S = solubility in water $\mu\text{mol/L}$ (Chiou et al. 1977).

PARAMETERS OF MODEL CHEMICALS

A number of representative pesticides have been selected for assessment by the fugacity model. Several typical hydrocarbons and nonylphenol have been included as representative of ingredients of pesticide formulations. The parameters were either obtained directly from the literature or estimated by various relationships and are summarized in Table 3.

Table 3. Properties of model compounds.

Compound	Mol. wt.	log(Kow)	Water solub. (mg/L)	Koc	H (atm. m ³ /mol)
Naphthalene	128	3.37	30	1100	4.4E-4
Dodecane	170	6.11	0.0037	95000	7.1
Methylnaphthalene	142	3.48	26	730	3.6E-4
Dimethyl " "	156	4.17	2.7	2500	1.5E-3
Trimethyl " "	170	4.28	2.0	3000	7.0E-4
Nonylphenol	220	4.10	5.0	1800	1.0E-4
DDT	352	6.19	0.0031	105000	3.9E-5
Fenitrothion	277	2.33	27	710	9.3E-7
Aminocarb	208	1.74	110	40	2.8E-6
Trichlorfon	256	0	12%	7	2.2E-11
Phosphamidon	299	0	Miscible	1	2.2E-11
Permethrin	390	5.13	0.28	5300	4.0E-5
Carbaryl	201	3.46	40	600	3.9E-6
Chlorpyrifos	350	4.97	0.4	12000	8.6E-6
Chlorpyrifos-methyl	323	4.27	4	2000	4.5E-6
Endrin	378	5.34	0.18	19000	1.6E-6
Parathion-methyl	263	3.43	51	710	1.0E-7

There are often considerable discrepancies in the values of Kow, water solubility, Koc, and H, reported in the literature. The values in Table 3 are accurate probably within 1.0-1.5 order of magnitude.

STRUCTURE OF EQUILIBRIUM DISTRIBUTION MODEL

A preliminary assessment of the equilibrium distribution of the chemicals was performed on a six-compartment model (Fig. 1). Connecting lines between compartments indicate the routes of movement of the chemical. It is assumed that there is no direct transfer of the chemical between some compartments. At equilibrium, this assumption does not affect the distribution of the chemical. The distribution depends on the properties of the chemical, size of the compartments.

COMPARTMENT SIZE

The choice of the compartment size, and particularly the ratio between the soil and the water compartment, is quite arbitrary. The area of 1 km² was chosen as a base and the compartment sizes are listed in Table 4.

BIOTA

An attempt was made to choose realistic values. About two-thirds of streams in New Brunswick drain soils overlying sedimentary formations and one-third drain thin soils overlying igneous rock formations. Few lakes occur in areas with sedimentary deposits (Smith 1952, 1963). Standing crops of fish and yield of trout to anglers from New Brunswick and Nova Scotia are low. In contrast, ponds in Prince Edward Island, with drainage areas in carboniferous sandstone have high productivity (Table 5).

A lake near Fredericton, N.B., was poisoned to eliminate goldfish and the standing crop of fish was 73 kg/ha (Hooper and Gilbert 1978). However, the production of trout (0.3 kg/ha) was low. Hooper

(1977) estimated the production of five reservoirs of the Saint John River in northwestern N.B. to be 0.6-1.95 kg/ha/yr and for five reservoirs of the Musquash River in south central N.B. to be 0.49-1.1 kg/ha/yr. It is assumed the figures represent production of trout and the figures are in general agreement with those for annual yield of trout to anglers (Table 5).

The standing crop of mixed fish of 19-40 kg/ha (Smith 1952) seems to be a reasonable estimate for the productivity of New Brunswick lakes. It is assumed from this estimate that the average standing crop of fish is 30 kg/ha and, completely arbitrarily, that the standing crop of biota is 100 times this value (300 kg/ha). At an average depth of 5 m, the concentration of biota is then 6E-2 kg/m³. Assuming further that the specific weight of biota is 1 kg/dm³, the volume fraction of biota is 6E-5. This value was rounded off to 5E-5.

EQUILIBRIUM CONCENTRATION OF PESTICIDES AND FORMULATION INGREDIENTS

Equilibrium concentrations are calculated on the assumption that the distribution of chemicals, applied at a rate typical for forest spraying, takes place without degradative or advective losses from the system. This is a crude oversimplification. On the other hand, the hazard assessment is performed on a comparative basis and draws attention to similarities and differences among chemicals. Neglecting degradation and advection may make the assessment more conservative.

Equilibrium concentrations are calculated as outlined in the Appendix by calculating the equilibrium fugacity, which is the same in all compartments and, subsequently, the equilibrium concentrations in each compartment. The equilibrium concentrations are obtained by multiplying the equilibrium fugacity by the respective fugacity capacities.

Table 4. Size of compartments in the equilibrium distribution model (Fig. 1).

Compartment	Dimensions, m	Volume, m ³	Remarks
Air	1000*1000*1000	1E9	The height of the air column was set at 1000 m
Soil	800*800*0.2	1E5	Includes vegetation, arbitrary choice of a 20-cm layer
Water	200*200*5	2E5	
Sediment	200*200*0.05	2E3	
Suspended solids		2 g/m ³	Smith (1952)
Biota		5E-5 m ³ /m ³ of water	

Table 5. Standing crops of fish and yield of trout to anglers from New Brunswick and Nova Scotia lakes and for Prince Edward Island ponds (from Smith 1952, 1963).

Category	Area	Production (kg/ha)
Standing crop mixed fish	6 N.B. lakes (poisoned)	19-40
Annual yield of trout to anglers	8 Charlotte Co., N.B. lakes 1941, 1947	Average 0.65 0.09-2.4
Annual yield of trout to anglers	4 N.S. lakes 1945-47	0.1-4.2
Standing crop brook trout	P.E.I. ponds 1948-49	50-125
Annual yield of trout to anglers	P.E.I. ponds 1943-49	25-50

Typical application rates of pesticides in forest spraying (Table 6) were chosen for calculations. The application rates of the hydrocarbons were calculated from the usual dilution ratios of aminocarb or fenitrothion formulations by the pesticide diluent 585, assumed to consist of dodecane. Representative concentrations of naphthalenes in fuel oil were used to calculate the input of these compounds.

Fugacity capacities of the compartments listed in Table 4 are summarized in Table 7.

The values of fugacity capacities are strongly affected by the value of H, and it is important that this value is determined as accurately as possible. Koc influences the fugacity capacities only in compartments containing solids (suspended solids, sediment, and soil). Kow affects the fugacity capacity of aquatic biota.

EEC's are given in Table 8.

EVALUATION OF EXPECTED EQUILIBRIUM CONCENTRATIONS

The model is hypothetical and represents an attempt to carry the assessment of potential effects of pesticides one step further from qualitative judgment of application rates, physico-chemical

constants and toxicity of pesticides. The equilibrium model assumes no degradation and no transport out of the system. In addition, the time needed to reach the equilibrium is not known. In forest spraying, the pesticide is injected into the air compartment and, almost immediately, a part of it (50-80%) reaches the surfaces of the soil and water compartments. Mixing in these compartments may take a long time and the "transient" concentrations may differ considerably from the equilibrium concentrations. In addition, EEC's are affected by the accuracy of the physico-chemical constants and other model parameters.

With these limitations in mind, two quantitative and several qualitative indicators can be used for the assessment of pesticides, based on the equilibrium model.

LETHALITY INDEX

Lethality (as 96-h LC50) is the most accurately determinable measure of toxicity and a lethality index, derived by dividing EEC's in water by the respective LC50's, appears to be a useful measure of risk.

Lethality data for freshwater fish, freshwater invertebrates (excluding insects) and marine invertebrates (Table 9) and the range of lethality indices (Table 10) are listed for each compound. It

Table 6. Application rate.

Compound	mol/km ²	g/km ²
Naphthalene	4.14	530
Dodecane	590	100000
Methylnaphthalene	25	3500
Dimethyl " "	26	4100
Trimethyl " "	24	4100
DDT	318	112000
	159	56000
	80	28000
Fenitrothion	101	28000
	76	21000
Aminocarb	41	8600
Nonylphenol	78	17200
Trichlorfon	109	28000
Phosphamidon	30	9000
	58	17400
Permethrin	4.87	1900
Endrin		
Carbaryl	139	28000
Chlorpyrifos	23	
Chlorpyrifos-methyl	23	7300
Parathion-methyl	106	28000

Table 7. Fugacity capacity of the model compartments.

Compound	Fugacity capacity (mol/m ³ atm)				
	Water	Susp. solids	Sediment	Aq. biota	Soil
Naphthalene	0.2E4	0.5E-1	0.5E6	0.8E0	0.5E6
Dodecane	0.1E0	0.3E-3	0.3E4	0.9E0	0.3E4
Methylnaphthalene	0.3E4	0.4E-1	0.4E6	0.4E2	0.4E6
Dimethyl " "	0.7E3	0.3E-1	0.3E6	0.5E2	0.3E6
Trimethyl " "	0.1E4	0.9E-1	0.9E6	0.1E3	0.9E6
DDT	0.3E5	0.5E2	0.5E9	0.2E6	0.5E9
Fenitrothion	0.1E7	0.2E2	0.2E9	0.1E4	0.2E9
Aminocarb	0.4E6	0.3E0	0.3E7	0.1E3	0.3E7
Nonylphenol	0.1E5	0.4E0	0.4E7	0.6E3	0.4E7
Trichlorfon	0.5E11	0.6E4	0.6E11	0.2E6	0.6E11
Phosphamidon	0.5E11	0.9E3	0.9E10	0.2E6	0.9E10
Permethrin	0.2E5	0.3E1	0.3E8	0.2E5	0.3E8
Carbaryl	0.3E6	0.3E1	0.3E8	0.4E4	0.3E8
Chlorpyrifos	0.1E6	0.3E2	0.3E9	0.5E5	0.3E9
Chlorpyrifos-methyl	0.2E6	0.9E1	0.9E8	0.2E5	0.9E8
Endrin	0.6E6	0.2E3	0.2E10	0.7E6	0.2E10
Parathion-methyl	0.1E6	0.1E3	0.1E10	0.1E6	0.1E10

Table 8. Expected equilibrium concentrations (EEC) for model given in Fig. 1.

Compound	Input mol/km ²	Concentration (ppm)					
		Air	Water	Sus. solids	Sediment	Aq. biota	Soil
Naphthalene	4.1	0.2E-6	0.1E-4	0.1E-3	0.1E-2	0.3E-2	0.1E-2
Methylnaphthalene	25	0.2E-5	0.1E-3	0.9E-3	0.9E-2	0.4E-1	0.9E-2
Dimethyl " "	26	0.2E-5	0.4E-4	0.9E-3	0.9E-2	0.5E-1	0.9E-2
Trimethyl " "	24	0.1E-5	0.5E-4	0.1E-2	0.1E-1	0.9E-1	0.1E-1
Dodecane	590	0.1E-3	0.4E-6	0.3E-3	0.3E-2	0.5E-1	0.3E-2
Nonylphenol	78	0.2E-5	0.4E-3	0.8E-2	0.8E-1	0.5E0	0.8E-1
DDT	318	0.8E-7	0.5E-4	0.5E-1	0.5E0	0.8E1	0.5E0
	159	0.4E-7	0.3E-4	0.3E-1	0.3E0	0.4E1	0.3E0
	80	0.2E-7	0.1E-4	0.1E-1	0.1E0	0.2E1	0.1E0
Fenitrothion	101	0.7E-6	0.2E-2	0.1E-1	0.1E0	0.4E-1	0.1E0
	76	0.5E-7	0.1E-2	0.1E-1	0.1E0	0.3E-1	0.1E0
Aminocarb	41	0.8E-6	0.8E-2	0.3E-2	0.3E-1	0.4E-1	0.3E-1
Trichlorfon	109	0.7E-10	0.8E-1	0.6E-2	0.6E-1	0.8E-2	0.6E-1
Phosphamidon	58	0.7E-10	0.8E-1	0.8E-3	0.8E-2	0.8E-2	0.8E-2
	30	0.4E-10	0.4E-1	0.4E-3	0.4E-2	0.4E-2	0.4E-2
Permethrin	4.9	0.3E-7	0.2E-4	0.9E-3	0.9E-2	0.2E0	0.9E-2
Carbaryl	139	0.3E-6	0.2E-2	0.1E-1	0.1E0	0.6E0	0.1E0
Chlorpyrifos	23	0.1E-7	0.3E-4	0.4E-2	0.4E-1	0.3E0	0.4E-1
Chlorpyrifos-methyl	23	0.3E-7	0.2E-3	0.4E-2	0.4E-1	0.3E0	0.4E-1
Endrin	159	0.1E-7	0.2E-3	0.3E-1	0.3E0	0.3E1	0.3E0
Parathion-methyl	106	0.3E-8	0.2E-2	0.1E-1	0.1E0	0.5E0	0.1E0

Table 9. The 96-h LC50's of several non-pesticidal ingredients of pesticide formulations and several pesticides to freshwater fish, freshwater invertebrates excluding insects, and to marine invertebrates.

Compound	Species or group	96-h LC50 (mg/L)	Source
Naphthalene	4 marine invertebrates	2.0-3.8	Several authors in Neff (1979)
	Brown shrimp	2.5	
	Pink salmon fry	0.9	
	Mosquito fish	150	
Methylnaphthalene	Crab larvae, grass shrimp	1.1-1.9	In Neff (1979)
	Sheepshead minnow	2.0-3.4	
Dimethyl " "	3 marine invertebrates	0.6-2.6	In Neff (1979)
	Sheepshead minnow	5.1(24-h LC50)	
Trimethyl " "	Marine polychaete	20	In Neff (1979)
Dodecane	-	-	-
Carbaryl	12 freshwater fish	0.75-20.0	Several authors in Pimentel (1971)
	2 marine invertebrates	0.02-0.08	
Parathion-methyl	11 freshwater fish	3.0-9.0	Several authors in Pimentel (1971)
	3 <i>Daphnia</i> sp.	0.006-0.008	
	3 marine invertebrates	0.01-0.04(24-h LC50)	
Nonylphenol	Juvenile Atlantic salmon	0.9	McLeese et al. (1980b)
	Fingerling rainbow and brown trout	0.15-0.23	Sundaram and Hopewell (1977)
	Freshwater clam	1.7	McLeese et al. (1980b)
	Lobster and shrimp	0.2-0.3	McLeese et al. (1980b)
DDT	4 freshwater fish	0.01-0.08	Johnson (1968)
	Brown shrimp	0.003-0.01	Portmann and Wilson (1971)
	Cockle	>10	" " " "
	Crangon shrimp	0.0004	McLeese and Metcalfe (1980)
Trichlorfon	Rainbow trout	3.2 (48-h LC50)	In Pimental (1971)
	Fathead minnow	180	
	2 <i>Daphnia</i> sp.	0.00018-0.008 (48-h LC50)	
	Freshwater amphipod	0.06	
Permethrin	Salmon	0.009, 0.012	Zitko et al. (1977, 1979)
	Trout	0.135	Coates and O'Donnell-Jeffrey (1979)
	Freshwater fish	0.004-0.008	Lindén et al. (1979)
	Freshwater fish	0.01-0.015	Jolly et al. (1978)
	Freshwater crayfish	0.0004-0.0006	" " " "
	Lobster	0.0007	McLeese et al. (1980b)
	Crangon shrimp	0.0003	" " " "
Aminocarb	Salmon	8.7	McLeese et al. (1980b)
	Crangon shrimp	0.1	" " " "
	Freshwater clam	>1.0	" " " "
	Freshwater crayfish	33.0	Sundaram and Szeto (1979)
Fenitrothion	Salmon	1.0	Wildish et al. (1971)
	Lobster	0.001	McLeese (1974a)
	Freshwater crayfish	0.01-0.03	McLeese (1976)
Chlorpyrifos	4 freshwater fish	0.0006-0.014	In Pimentel (1971)
	Mosquito fish	0.280	"
	Freshwater invertebrates	0.0001-0.002	"
Chlorpyrifos-methyl	-	-	-
Phosphamidon	Trout	8 (48-h LC50)	In Pimentel (1971)
	Freshwater invertebrates	0.004 (48-h LC50)	"
	Marine shrimp	0.44 (48-h LC50)	Butler (1964)
	Spiny lobster	0.3	Suarez et al. (1972)
	Lobster	0.05	McLeese (1974b)

Table 9 (cont'd).

Compound	Species or group	96-h LC50 (mg/L)	Source
Endrin	4 freshwater fish	0.0002-0.003	In Pimentel (1971)
	6 freshwater fish	0.0003-0.0018	Johnson (1968)
	Freshwater crayfish	0.0032 (immature)	Grant (1976)
	2 amphipods	0.0013-0.003	"
	Glass shrimp	0.0033	"
	2 <i>Daphnia</i> sp.	0.02-0.045	"
	Crangon shrimp	0.0006	McLeese et al. (1980a)

Table 10. Lethality index (expected equilibrium concentration divided by 96-h LC50) and bioconcentration (expected equilibrium concentration in aquatic biota divided by the respective concentration in water).

Compound	Lethality index		Remarks	Bioconcentration
	Max.	Min.		
Naphthalene	0.1E-4	0.7E-7	Very low risk	3E2
Methylnaphthalene	0.3E-4	0.9E-4	" " "	4E2
Dimethyl " "	0.7E-4	0.8E-5	" " "	1E3
Trimethyl " "	0.2E-4	-	" " "	2E3
Dodecane	-	-	" " "	1E5
Nonylphenol	0.3E-2	0.2E-5	Low risk	1E3
DDT	0.1	0.3E-3	Risk	2E5
Fenitrothion	2.0	0.1E-2	Very high risk	2E1
Aminocarb	0.8E-1	0.9E-3	Risk	5E0
Trichlorfon	500	0.4E-3	Very high risk	1E-1
Phosphamidon	10	0.5E-2	" " "	1E-1
Permethrin	0.7E-1	0.1E-3	Risk	1E4
Carbaryl	0.1	0.1E-3	"	3E2
Chlorpyrifos	0.3	0.2E-2	"	1E4
Chlorpyrifos-methyl	-	-	"	2E3
Endrin	1	0.7E-1	Very high risk	2E4
Parathion-methyl	0.2	0.2E-3	Risk	2E2

is understood that the ranges might be increased if the lethality data bases were extended. Aquatic invertebrates were more sensitive to the pesticides than freshwater fish. However, for endrin, freshwater fish and a marine invertebrate were equally sensitive.

The maximum lethality index for each of the compounds was chosen as the initial measure of risk. Judging from the maximum lethality indices, six compounds have small indices indicating low hazard potential. These compounds are the non-pesticidal ingredients of the pesticide formulations. Seven pesticides have indices of about 0.1-0.3, indicating high hazard potential and four pesticides with indices of 1-500 have extremely high hazard potential.

Symons (1977) devised a hazard index for fenitrothion as the ratio of the concentration of fenitrothion observed in the environment to the concentration causing a 50% response in the laboratory. For an application rate of 210 g fenitrothion/ha, the estimated hazard index for salmon mortality was 0.6E-3 to 0.13E-2. Presumably, 24- to ~48-h LC50 data were used. No mortality was predicted and no confirmed mortality was observed in the field.

Our estimates of the lethality index for fenitrothion were 0.1E-2 to 0.2E-2 for salmon, 0.3E-1 to 0.2 for freshwater crayfish and 1 to 2 for lobsters. No mortality among salmon, and probably no serious mortality among crayfish, is predicted. Greater than 50% mortality would be expected among lobsters if the expected environmental concentration should occur in sea water.

ACCUMULATION IN AQUATIC BIOTA

The bioconcentration factors, obtained by dividing the expected equilibrium concentrations in aquatic biota by the respective concentrations in water, are another useful quantitative index (Table 10).

OTHER FACTORS

Additional factors may be considered qualitatively. High concentration in air indicates that the compound may leave the system by advection from this compartment. On the other hand, a high concentration in sediment points out the tendency of the compound to remain in the system. Chemical structure of the compound gives good qualitative indications of the degradation pathways. Persistent pesticides, difficult to degrade or metabolize, such

as DDT or endrin are extremes and are not likely to be used again on a large scale. Compounds converted readily into nontoxic products by a relatively nonspecific chemical reaction such as hydrolysis or oxidation appear less hazardous than compounds whose degradation products either resemble the parent compounds in toxicity, or are formed only by relatively specific chemical reactions. For example, the degradation of permethrin by hydrolysis yields two nontoxic products compared to the parent compound. In contrast, the hydrolysis products of fenitrothion (3-methyl-4-nitrophenol) and of carbaryl (1-naphthol) are approximately as toxic to fish as are the parent compounds.

HAZARD ASSESSMENT

Based on the quantitative (Table 8) and qualitative factors, the relative hazard assessment of pesticides and other ingredients of pesticide formulations is outlined in Table 11.

The ranking depends also on the application rates of the pesticides (Table 6). For example, an increase in application rate for one of the pesticides would result in an increase in EEC, increased lethality index and relative lethality index.

KINETIC MODEL

In addition to parameters considered in the equilibrium model, parameters for the kinetic model include degradation and transfer rate constants. Since the values of these constants are at the moment largely conjectural, there is little advantage in considering a multi-compartment model. The discussion will be limited to a system of three compartments: air, water, and sediment (Fig. 2). As the equilibrium model indicates, aquatic biota contains only a small fraction of the chemical

Table 11. Ranking of pesticides and formulation ingredients in order of increasing hazard to the aquatic environment.

Compound	Relative (Lethal. index) (Bioconc.)	Other factors	Overall rank
Naphthalene	7E-5		1
Methylnaphthalene	3E-4		2
Trimethyl " "	1E-3		3
Dodecane	-		4
Aminocarb	1E-3		5
Dimethylnaphthalene	2E-3		6
Nonylphenol	7E-2		7
Carbaryl	7E-1	Degrade toxic	8
Fenitrothion	1	" "	9
Parathion-methyl	1		10
Trichlorfon	1		11
Phosphamidon	3		12
Permethrin	2E1	Degrade non-toxic	13
Chlorpyrifos	7E1		14
Chlorpyrifos-methyl	-		15
DDT	5E2	Non-degradable	16
Endrin	5E2	"	17

Following the idea of Symons (1977) for using fenitrothion as a benchmark pesticide, the maximum lethality index and bioconcentration factor for fenitrothion were assigned a value of unity. The lethality index and bioconcentration factor for each of the other compounds were adjusted accordingly. The relative lethality index multiplied by the relative bioconcentration factor provides the initial measure for ranking the compounds in terms of risk. The ranking may be modified by consideration of other factors.

Nonylphenol is the most hazardous of the non-pesticidal ingredients of the pesticide formulations, ranking two before fenitrothion. Carbaryl, parathion-methyl and trichlorfon are rated about as hazardous as fenitrothion. Phosphamidon, permethrin, chlorpyrifos and chlorpyrifos-methyl are more hazardous. The pesticides with the highest risk are DDT and endrin. Endrin has never been proposed for forest spraying operations.

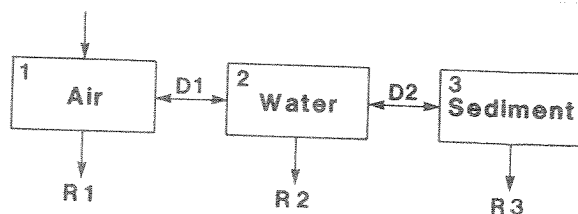


Fig. 2. A kinetic, 3-compartment model.

applied to the system. Consequently, the concentration of the chemical in aquatic biota can be assumed to be determined by the concentration of the chemical in water, without affecting it.

DEGRADATION RATE CONSTANTS

Degradation is assumed to follow first order kinetics and to include transport out of the system as well. The degradation rate constants are in units of 1/yr. If the concentration of a chemical decreases 50% in 1 d (half-life 1 d), the degradation rate constant $K=250$.

Estimates of K in the literature are not exceedingly accurate. In soil, the half-lives of nonpersistent, moderately persistent, and persistent pesticides are <20, 20-100, and >100 d, respectively (Rao and Davidson 1980). The data for some of the model pesticides and other, related pesticides are given in Table 12.

Table 12. Degradation rate constants of pesticides in soil under field conditions (Rao and Davidson 1980).

Pesticide	Rate constant (K, 1/yr)
Parathion	14
Parathion-methyl	17
Carbofuran	4
Carbaryl	21
Dieldrin	0.2
Endrin (aerobic)	0.5
(anaerobic)	2
Chlordane	0.2

The rate constants used in the kinetic model are presented in Table 13. The values are very rough estimates, based partly on literature data, partly on experience, and partly on maintaining relative relationships among the chemicals.

TRANSFER COEFFICIENTS

Very little is known about the rate of transfer of chemicals between compartments. As a temporary approximation for the purposes of this assessment model, the transfer coefficients were calculated from the formula, derived in the Appendix:

$$D_{ij} = A L_i L_j / (L_i + L_j)$$

where D_{ij} = transfer coefficient (mol/yr*atm) between compartments i and j

A = contact area (m^2)

L = transport rate constant equal to $D*Z/r$,

where D = diffusion coefficient (m^2/yr)

Z = fugacity capacity

r = thickness of diffusion layer (m).

The diffusion coefficient is determined primarily by the size of the molecule. Since all the benchmark chemicals are approximately of the same size, it was assumed that the diffusion coefficients are the same, $1.6E-2$, $3E-6$, and $160 m^2/yr$, in water, sediment, and air, respectively. The values of diffusion coefficients in water and air were estimated according to Little (1977). The diffusion coefficient in sediment was chosen arbitrarily to be 5000 smaller than that in water. This factor may be far too high since

Table 13. Degradation rate constants (1/yr) used in the kinetic model.

Compound	Degradation rate constant		
	Water	Sediment	Air
Naphthalene	300	50	500
Dodecane	300	100	500
Methylnaphthalene	200	50	500
Dimethyl " "	150	25	500
Trimethyl " "	100	5	500
Nonylphenol	50	10	500
DDT	5	0.5	100
Fenitrothion	200	15	250
Aminocarb	200	20	250
Trichlorfon	100	10	100
Phosphamidon	200	15	250
Permethrin	100	5	200
Carbaryl	200	20	250
Chlorpyrifos	200	15	250
Chlorpyrifos-methyl	200	15	250
Endrin	5	0.5	150
Parathion-methyl	200	15	250

studies on parathion indicated a factor of only about 50 (Gerstl et al. 1979) but, in view of the overall uncertainties, this discrepancy may not be very important. The thickness of the diffusion layer was estimated as $1E-4$, $1E-5$, and $1E-3 m$ in water, sediment, and air, respectively.

The calculated transfer coefficients are given in Table 14.

Table 14. Transfer coefficients (mol/yr*atm).

Compound	Water/sediment	Water/air
Naphthalene	4.1E9	1.2E10
Dodecane	6.3E5	6.4E5
Methylnaphthalene	3.8E9	1.8E10
Dimethyl " "	2.0E9	4.4E9
Trimethyl " "	4.0E9	6.2E9
Nonylphenol	2.7E10	5.1E10
DDT	1.9E11	1.1E11
Fenitrothion	1.7E12	2.5E11
Aminocarb	3.6E10	2.3E11
Trichlorfon	7.2E14	2.6E11
Phosphamidon	1.1E14	2.6E11
Permethrin	9.4E10	8.5E10
Carbaryl	3.0E11	2.3E11
Chlorpyrifos	5.4E11	1.8E11
Chlorpyrifos-methyl	5.9E11	2.1E11
Endrin	3.3E12	2.4E11
Parathion-methyl	1.0E13	2.5E11

KINETIC EQUATIONS

The three-compartment kinetic model is described by a system of three first order linear differential equations with constant coefficients (see Appendix). In forest spraying the input can be assumed to be instantaneous, reducing the

differential equations to a homogeneous system. The solution is in the form

$$C = A \text{ EXP}(-A_1 t) + B \text{ EXP}(-B_1 t) + D \text{ EXP}(-D_1 t)$$

where C = concentration

t = time

A, A₁, B, B₁, D, D₁ = constants.

PREDICTED KINETIC PROFILES

NAPHTHALENE AND ALKYLNAPHTHALENES

The kinetic pattern is similar with concentration in air declining rapidly, concentration in water peaking within about 0.5-1.0 d, and concentration in sediment increasing and levelling off within approximately 2 d. The predicted concentrations are well below those that may have toxic effects. The profile of dimethylnaphthalene is given in Fig. 3.

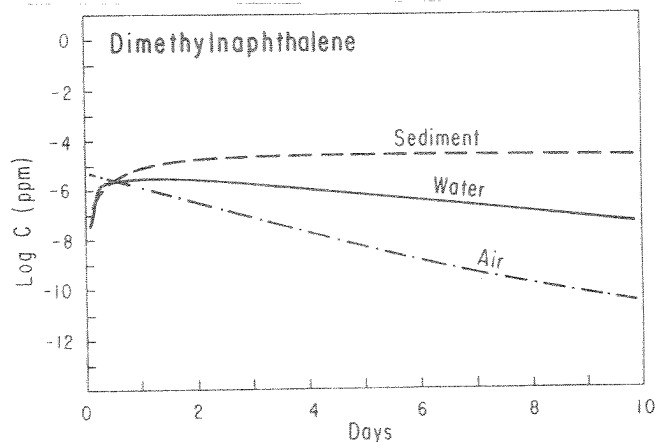


Fig. 3. Kinetic profile of dimethylnaphthalene. Degradation rate constants (1/yr): air 500, water 150, sediment 25.

DODECANE

In contrast to the naphthalenes, the highest concentration is in the air until about 5 d after the application (Fig. 4).

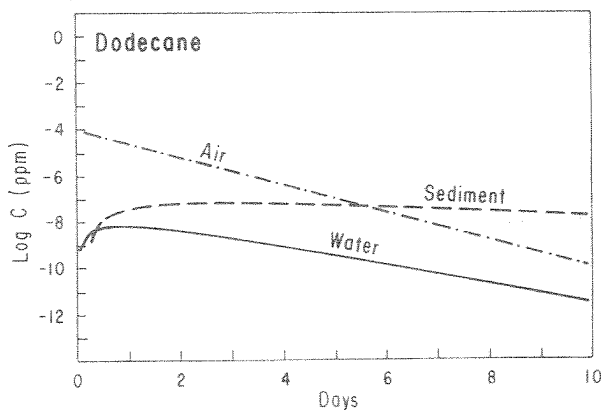


Fig. 4. Kinetic profile of dodecane. Degradation rate constants (1/yr): air 500, water 300, sediment 100.

NONYLPHENOL

The kinetics is similar to that of the naphthalenes. The concentration in water reaches a maximum after about 1 d and declines very slowly. After approximately 1 d the highest concentration is in sediment (Fig. 5). The predicted concentrations are well below toxic ones.

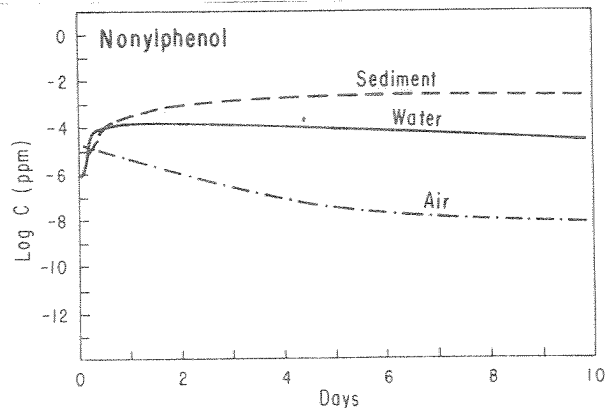


Fig. 5. Kinetic profile of nonylphenol. Degradation rate constants (1/yr): air 500, water 50, sediment 10.

DDT

Following the highest application rate (Table 5), the concentration of DDT in air decreases slowly and the concentration in water increases and levels off in the ppb range after about 1 d. The concentration in sediment increases initially quite rapidly and later more slowly, levelling off after about 10 d. After approximately 3 d the concentration in sediment reaches the 100 ppb range. Concentrations in both water and sediment are within the range of those lethal to aquatic fauna (Fig. 6).

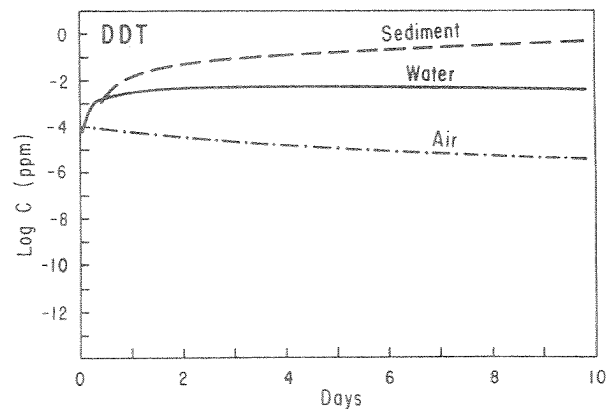


Fig. 6. Kinetic profile of DDT. Degradation rate constants (1/yr): air 100, water 5, sediment 0.5.

FENITROTHION

The concentration in air decreases steadily, in water reaches a broad maximum in the ppb range at about 1 d, and in sediment levels off in the 10 ppb range after approximately 2 d (Fig. 7). The predicted concentrations appear to be below the toxicologically significant range.

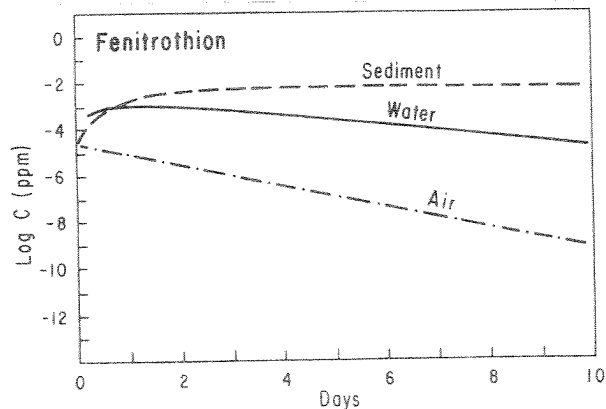


Fig. 7. Kinetic profile of fenitrothion. Degradation rate constants (1/yr): air 250, water 200, sediment 15.

AMINOCARB

The concentration in air decreases in the usual manner, and in water has a broad maximum below the ppb range. The concentration in sediment increases slowly, equalling the concentration in water after 4-5 d (Fig. 8). The concentration appears to be well below that causing toxic effects in aquatic biota.

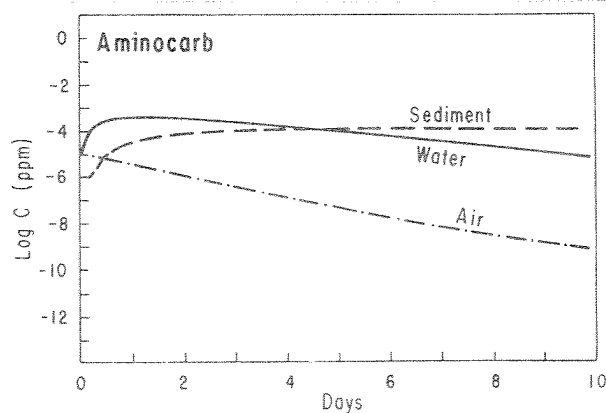


Fig. 8. Kinetic profile of aminocarb. Degradation rate constants (1/yr): air 250, water 200, sediment 20.

TRICHLORFON

The concentration of trichlorfon is highest in water and remains practically constant in the ppb range throughout 10 d after application. The concentration in sediment increases slowly but does not equal the concentration in water until about 20 d. The concentration in air has the usual pattern (Fig. 9). The concentrations appear toxicologically insignificant.

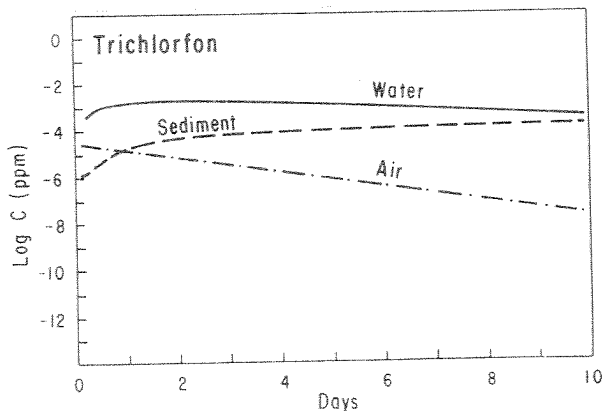


Fig. 9. Kinetic profile of trichlorfon. Degradation rate constants (1/yr): air 100, water 100, sediment 10.

PHOSPHAMIDON

The concentration profiles (Fig. 10) are similar to those of trichlorfon and also appear toxicologically insignificant.

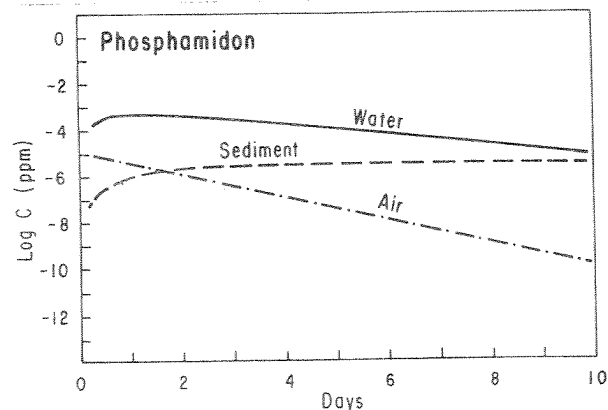


Fig. 10. Kinetic profile of phosphamidon. Degradation rate constants (1/yr): air 250, water 200, sediment 15.

CARBARYL

The concentration profiles (Fig. 11) are similar to those of fenitrothion (Fig. 7) and are probably insignificant toxicologically.

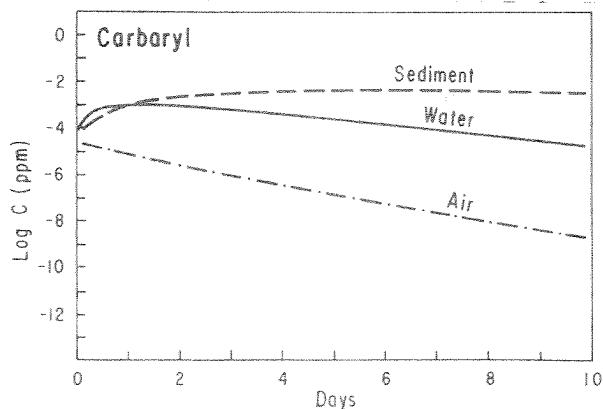


Fig. 11. Kinetic profile of carbaryl. Degradation rate constants (1/yr): air 250, water 200, sediment 20.

PERMETHRIN

The concentration profiles of permethrin (Fig. 12) have the familiar pattern of decreasing concentration in air, practically constant concentration in water in the 0.01-0.1 ppb range, and slowly increasing concentration in sediment, levelling off in the ppb range. The predicted concentration of permethrin in water appears to be just below the lethal threshold to fish, but is possibly within the range of concentrations lethal to aquatic invertebrates.

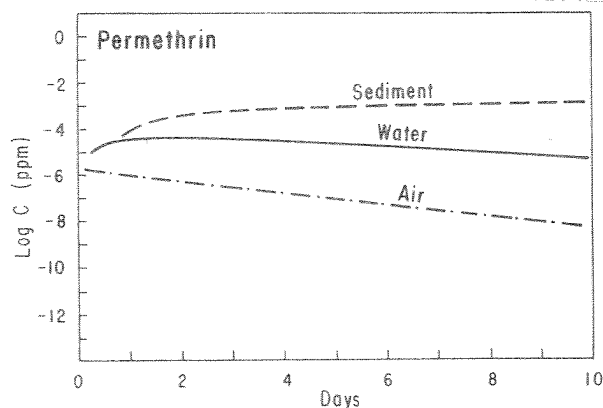


Fig. 12. Kinetic profile of permethrin. Degradation rate constants (1/yr): air 200, water 100, sediment 5.

CHLOROPYRIFOS AND CHLOROPYRIFOS-METHYL

The concentration profiles of both pesticides are similar and only that of the latter is presented (Fig. 13). The predicted concentrations are similar to those of fenitrothion and appear toxicologically insignificant.

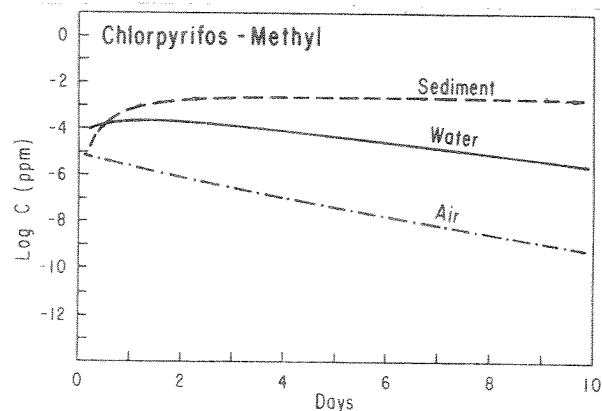


Fig. 13. Kinetic profile of chlorpyrifos-methyl. Degradation rate constants (1/yr): air 250, water 200, sediment 15.

ENDRIN

The concentration profiles are similar to those of DDT (Fig. 14) and the concentrations are within the toxicologically significant range.

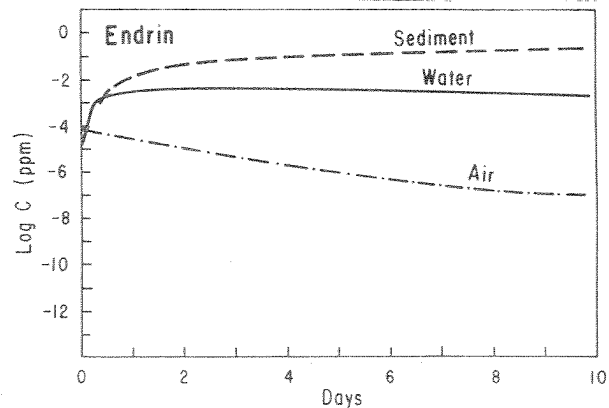


Fig. 14. Kinetic profile of endrin. Degradation rate constants (1/yr): air 150, water 5, sediment 0.5.

PARATHION-METHYL

The concentration profiles (Fig. 15) are similar to those of fenitrothion and the predicted concentrations appear toxicologically insignificant.

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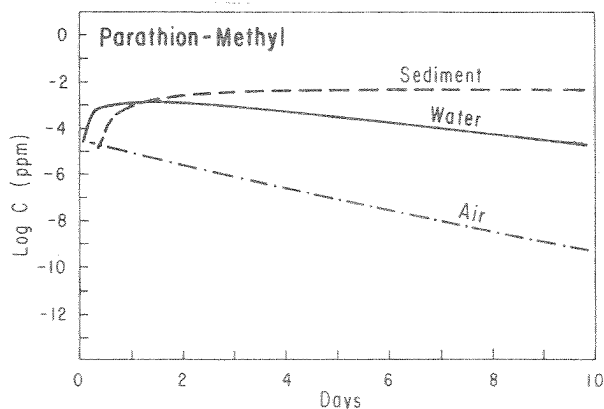


Fig. 15. Kinetic profile of parathion-methyl. Degradation rate constants (1/yr): air 250, water 200, sediment 15.

COMPARATIVE EVALUATION OF KINETIC PROFILES

The kinetic profiles of the benchmark chemicals fall into three groups:

1. Compounds with very low solubility in water ($\mu\text{g/L}$ range), very high K_{ow} ($\log(K_{ow}) = 5-6$), and a high value of H ($H > 1E-3$), such as dodecane. The concentration is highest in air for several days after application. The concentration in water peaks around 0.5-1.0 d and the concentration in sediment levels off at about the same time.

2. Compounds with low solubility in water (mg/L range), high K_{ow} ($\log(K_{ow}) > 4.5$), and intermediate to high values of H ($1E-7$ to $1E-4$). Within a few hours after application the order of concentrations is sediment > water > air and the profile depends on the persistence of the compounds. For persistent compounds (DDT, endrin) the concentration in water remains practically constant from 1-10 d after application and the concentration in sediment is increasing during this period. For less persistent compounds (organophosphates, carbamates) the concentration in water is decreasing following a maximum reached around 1 d after application.

3. Compounds with high solubility in water (g/L range), low K_{ow} ($\log(K_{ow}) < 2$), and low values of H ($H < 1E-6$) such as trichlorfon or phosphamidon. The order of concentration is water > sediment > air, and the profile depends on the persistence of the compounds.

These relationships were derived without experimentally supported data on transfer rates and with rather qualitative data on degradation rates. The results appear to make sense, but are not necessarily quantitatively correct. The accuracy will improve once the transfer and degradation processes are better characterized.

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APPENDIX
CALCULATION OF FUGACITY CAPACITIES

ATMOSPHERE

It is assumed that fugacity of a compound is equal to its partial pressure (P), which in turn may be expressed in terms of concentration by the state equation of ideal gas:

$$F = P = CRT \quad (1)$$

Consequently, for the fugacity capacity (Z),

$$Z = C/F = 1/RT = 40, \quad (2)$$

and the fugacity capacity of atmosphere is independent of the properties of the compound.

WATER

Fugacity of a compound dissolved in water is again approximated by the partial pressure of its vapor above the solution. The partial pressure is proportional to concentration (Henry's Law):

$$F = P = HC \quad (3)$$

where H = Henry's constant. The fugacity capacity is then

$$Z = C/F = 1/H \quad (4)$$

SOIL, SEDIMENT, SUSPENDED SOLIDS

The concentration of a chemical adsorbed on these substrates, C_s (g/Mg), can be expressed using the adsorption coefficient, K (m^3/Mg), concentration of the compound in water, C_w (g/m^3), and concentration of the substrate in water, S (g/m^3):

$$C_s = (1E-6)KC_wS \quad (5)$$

The factor $1E-6$ originates from converting Mg into g ($Mg = 1E6$ g). In equilibrium, fugacity of the compound in water, F_w , is equal to fugacity of adsorbed compound, F_s .

$$F_w = F_s \quad (6)$$

$$\text{From (3)} \quad F_w = HC_w \quad (7)$$

and, consequently

$$F_s = HC_w \quad (8)$$

From (5) and (8), the fugacity capacity is

$$Z = C_s/F_s = (1E-6)KS/H \quad (9)$$

BIOTA

The accumulation of an organic chemical in fish is proportional to K_{ow} (frequently also designated P in the literature).

$$K_{ow} = C_o/C_w \quad (10)$$

where C_o and C_w are equilibrium concentrations in octanol and water, respectively. Octanol simulates lipids. Assuming that the lipid content of fish is 100% and the concentration of the chemical in lipids is C_l , and that $C_l = C_o$, then the concentration of the chemical on a whole fish basis,

$$C_f = YC_l \quad (11)$$

(If A and B are the weights of the lipids and other constituents, respectively, then

$$Y = A/(A+B) \quad (12)$$

$$\text{and} \quad C_f = AC_l/(A+B) = YC_l. \quad (13)$$

$$\text{From (10)} \quad C_o = K_{ow}C_w \quad (14)$$

$$\text{and from (11)} \quad C_f = YK_{ow}C_w \quad (15)$$

If the volume of the water compartment is V and the volume fraction of aquatic biota is B (m^3 biota/ m^3 water), then the volume of biota is BV . If the amount of the chemical in water and in biota is M_w and M_f , respectively, then the concentrations are M_w/V and M_f/BV . Substituting these values into (15)

$$M_f = BK_{ow}YM_w \quad (16)$$

or $C_f' = BK_{ow}C_w \quad (17)$

where C_f' = concentration in biota expressed per volume of the water compartment.

When the concentration of the chemical in biota is in equilibrium with that in water, the respective fugacities are equal

$$F_f = F_w \quad (18)$$

From (3) $F_f = HC_w$

and $Z = C_f'/F_f = BK_{ow}/H \quad (19)$

It has been assumed so far that the concentration in biota is proportional only to the lipid fraction Y , concentration in water C_w and to the octanol/water partition coefficient K_{ow} , neglecting the uptake efficiency. Kenaga and Goring (1980) derived the following expression for the bioconcentration factor ($BCF = C_f/C_w$) in fish

$$\log BCF = -1.495 + 0.935 \log(K_{ow}) \quad (20)$$

or $BCF = 0.032 K_{ow} \quad (21)$

The coefficient 0.032 in (21) may be interpreted as the lipid fraction Y or, better, as AY , where A is the efficiency of uptake. Assuming an average lipid fraction in fish of 0.07, then the efficiency of uptake is approximately 0.5. The exponent in (21) is sufficiently close to unity to be neglected for all practical purposes. Other expressions relating BCF and K_{ow} have been published (see for example Veith et al. (1979). The differences in BCF for a given K_{ow} are usually within one order of magnitude.

There are indications (see for example Tulp and Hutzinger 1978) that the relation between $\log BCF$ and $\log K_{ow}$ is quadratic rather than linear as given in (20), but the data are too sketchy to take this into consideration. It should be borne in mind that at very high $\log(K_{ow})$ values, BCF may be lower than that given by (20).

EQUILIBRIUM DISTRIBUTION

At equilibrium, fugacities in all compartments are equal

$$F_1 = F_2 = \dots = F_i = F \quad (22)$$

and the total amount of the chemical, M , is

$$M = \sum C_i V_i = \sum F_i Z_i V_i \quad (23)$$

where C_i , V_i , Z_i = concentration, volume, and fugacity capacity of compartment i .

After substituting (22) in (23)

$$M = F \sum Z_i V_i \quad (24)$$

and $F = M / \sum Z_i V_i \quad (25)$

The equation (25) is used to calculate the equilibrium fugacity F . Once this value is known, the concentrations and amounts of the chemical in individual compartments are calculated from (26) and (27):

$$C_i = F Z_i \quad (26)$$

$$M_i = F V_i Z_i = C_i V_i \quad (27)$$

EQUILIBRIUM DISTRIBUTION WITH DEGRADATION

Degradation processes are assumed to follow first order kinetics with rate constants K_i (1/yr). Advection from a compartment is treated as degradation. Since the system is in a steady state, fugacities are constant and input of the chemical (I) is equal to degradation and advection

$$I = \sum V_i C_i K_i = F \sum V_i Z_i K_i \quad (28)$$

$$F = I / \sum V_i Z_i K_i \quad (29)$$

$$C_i = F Z_i \quad (30)$$

$$M_i = V_i C_i \quad (31)$$

The equilibrium fugacity, F , is calculated from (29); the concentrations and amounts in individual compartments are obtained from (30) and (31), respectively.

An overall degradation constant, K_m , is defined by (32).

$$K_m = I/M = \sum V_i Z_i K_i / \sum V_i Z_i \quad (32)$$

The degradation rate constants, K_i , are generally not known with great accuracy. Rough estimates of half-lives in individual compartments can be made usually on the basis of experience or literature data. A half-life of 10 d corresponds to

$$K = (365 \ln 2)/10 = 25 \text{ (1/yr)} \quad (33)$$

NONEQUILIBRIUM DISTRIBUTION WITH DEGRADATION

The system is in steady state, fugacities are constant and, consequently, the input equals degradation, but fugacities in compartments are different and transfers between compartments take place. The transfer rates are proportional to the differences in fugacities:

$$N = D(F_i - F_j) \quad (34)$$

where D = transfer coefficient between compartments i and j
 N = transfer rate (mol/yr)

Fugacities are calculated from a system of linear equations resulting from material balances for compartments. For example, for a three-compartment system in Fig. 2 of text, the material balances are

Compartment	Transfer	Degradation	Input	
1	$D_1(F_1 - F_2) +$	$F_1 R_1^a$	$=$	I
2	$D_2(F_2 - F_3) +$	$F_2 R_2$	$=$	$D_1(F_1 - F_2)$
3	0	$F_3 R_3$	$=$	$D_2(F_2 - F_3)$

(35)

$$^a R = VZK$$

From (35) the fugacities F_1 , F_2 , and F_3 are

$$F_3 = (D_2/(D_2 + R_3))F_2 \quad (36)$$

$$F_1 = (D_1/(D_1 + R_1))F_2 + I/(D_1 + R_1) \quad (37)$$

$$F_2 = D_1 I / (D_1 + R_1)(D_1 + D_2 + R_2 - D_1^2 / (D_1 + R_1) - D_2^2 / (D_2 + R_3)) \quad (38)$$

For a large number of compartments, the analytical solution of the material balance system of equations is cumbersome and it is more convenient to obtain the solution on a computer.

The equations (36) to (38) can be used to illustrate the effects of the transfer (D_i) and degradation (R_i) coefficients on the distribution of the chemical in the system. For example, if D_2 is much larger than R_3 , then from (36) F_3 is approximately equal to F_2 and the compartments 2 and 3 are practically in equilibrium. In more concrete terms, if the transfer rate coefficient from water to sediment is high relative to the degradation coefficient, then the distribution of the chemical between water and sediment is near equilibrium. The degradation coefficient R_3 depends on the volume of the sediment (V_3), given by the model and independent of the chemical, on the fugacity capacity of the sediment, which depends on K and H of the chemical (equation (9)), and on the degradation rate constant K_3 , which again depends to a great extent on the chemical. On the other hand, if R_3 is much larger than D_2 , then F_3 will be only a fraction of F_2 .

DISTRIBUTION WITHOUT STEADY STATE

The distributions discussed above were steady state ones. Fugacities in the compartments were constants, not dependent on time. When the system is not in steady state, fugacities are functions of time and may be determined from a system of differential equations describing mass balances in the compartments during an infinitesimal time interval dt . For the three-compartment system such as Fig. 2 of text, the material balances are:

Compartment	Input	Transfer	Degradation	Accumulation	
1 (water)	$D2(F3-F1)dt$	$-D1(F1-F2)dt$	$-R1F1dt$	$dM1=V1Z1dF1$	(39)
2 (sediment)	$D1(F1-F2)dt$		$-R2F2dt$	$dM2=V2Z2dF2$	
3 (air)	$I dt$	$-D2(F3-F1)dt$	$-R3F3dt$	$dM3=V3Z3dF3$	

where M_i = amount of chemical in compartment i
 $R_i = V_i Z_i K_i$.

The resulting system of differential equations is:

$$\begin{aligned} dF1/dt &= -((D1+D2+R1)/V1Z1)F1 + D1F2/V1Z1 + D2F3/V1Z1 \\ dF2/dt &= D1F1/V2Z2 - ((D1+R2)/V2Z2)F2 \\ dF3/dt &= D2F1/V3Z3 - ((D2+R3)/V3Z3)F3 + I \end{aligned} \quad (40)$$

In forest spraying, the input can be considered instantaneous and the input term (I) can be included in the initial ($t=0$) fugacity values. It may be assumed for example that at $t=0$ all pesticide is applied to the air compartment, yielding an initial fugacity $F30=A/V3Z3$, where A = application rate, V = volume of the air compartment, and $Z = 40$ is the fugacity capacity of air. No pesticide is initially present in water and sediment, and $F10=F20=0$.

The solution of the homogeneous system obtained from the above system by excluding the term I , is:

$$\underline{F} = k1U1EXP(E1t)+k2U2EXP(E2t)+k3U3EXP(E3t)$$

where \underline{F} = fugacity vector ($F1, F2, F3$)

$E1, E2, E3$ = eigenvalues of the matrix of the coefficients (right hand side of (40))

$U1, U2, U3$ = eigenvectors corresponding to the eigenvalues

$k1, k2, k3$ = constants determined by the initial fugacity values ($F10, F20, F30$).

Eigenvalues and vectors can be calculated readily by using commercial programs such as Tektronics Mathematics Vol II. Values of the constants $k1, k2$, and $k3$ are then obtained by solving the system (40) at $t=0$ and given initial fugacity values, again by a commercial program. Fugacities are converted into concentrations by multiplication by the respective fugacity capacities.

TRANSFER COEFFICIENTS

The following approach was used to estimate the transfer coefficients: Fugacities are F_i and F_j , respectively, in compartments i and j , and F_s in the contact area between the compartments, where the equilibrium has been established (Appendix Fig. 1). The rate of transport N (mol/yr m^2) is

$$N = L_i(F_s - F_i) \quad (41)$$

$$N = L_j(F_j - F_s) \quad (42)$$

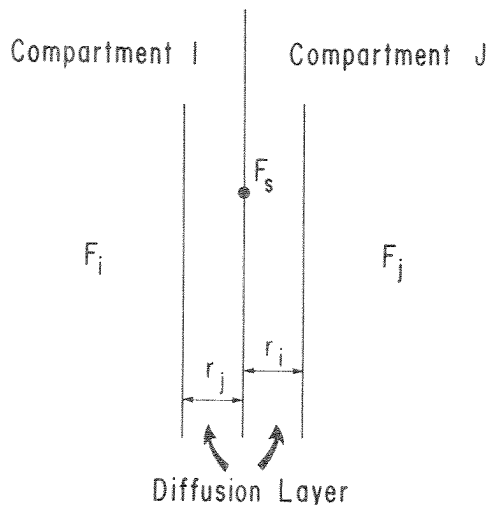
where L_i, L_j = transport rate constants (mol/yr m^2 atm). By eliminating F_s from (41) and (42)

$$N = L_i L_j (F_j - F_i) / (L_i + L_j) \quad (43)$$

and the transfer coefficient D_{ij} (mol/yr atm) is then

$$D_{ij} = A L_i L_j / (L_i + L_j) \quad (44)$$

where A = contact area between the compartments.



Appendix Fig. 1. Transfer between compartments. F_s = equilibrium fugacity at the boundary between compartments i and j .

L is related to diffusion transport in the boundary layer (Appendix Fig. 1). According to Fick's first law

$$N = D(dC/dX) \quad (45)$$

where D = diffusion coefficient
 dC/dX = concentration gradient.

By introducing fugacity, (45) becomes

$$N = DZ(dF/dX) \quad (46)$$

Assuming that $dF = F_s - F$ and that $dX = r$ (Appendix Fig. 1), then from a comparison of (41) or (42) with (46)

$$L = DZ/r \quad (47)$$

Consequently, the transfer coefficients can be calculated from diffusion coefficients, fugacity capacities, and the thicknesses of the diffusion layers. The diffusion coefficients can be estimated with reasonable accuracy for diffusion in air and in water but not for diffusion in sediment, soil or suspended matter. Similarly, there are problems with estimating the thickness of the diffusion layer. Models including transfers between compartments must be viewed with caution until the estimation of transfer coefficients is improved and confirmed experimentally. At the moment, literature data are limited to transfer coefficients between air and water, and even these appear to have considerable uncertainty.