EXPERIMENTAL MODELS FOR STUDYING THE PERSISTENCE

OF PESTICIDES IN SOILS

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Summary  Experimental model systems for studying adsorption, leaching, photodecomposition, hydrolysis, volatilization, and degradation of pesticides in soils are discussed in this review. Adsorption processes are mainly described by the Freundlich equation. Adsorption constants are well suited to predict leaching and volatilization of pesticides in the soil environment. The methods of soil thin-layer, soil thick-layer and soil column chromatography used for determining the leaching behaviour of chemicals are discussed and compared with each other. Although all three models give comparable relative mobility data, the soil column model is prefered since it more closely simulates field conditions. Field leaching is much less pronounced than expected from laboratory results. Therefore leaching may not be a predomimant factor of pesticide disappearance in field soils. Photolysis studies with pesticides are well established in solutions, in thin films and in the vapour phase, but no suitable model is known for measuring rate of photodegradation in soil. Hydrolysis experiments carried out at various pH levels and at various temperatures yield hydrolysis rate constants. Using the rate constants and the Arrhenius equation, hydrolysis half-life periods can be calculated for each temperature. Some data indicate a possible relation between hydrolysis rates and the rate of degradation in soils. Several laboratory model systems for determining volatility of pesticides are described in the literature, but little is known of field experiments. However, from the few field data available the rate of volatilization does not seem to be of significant importance when compared to rates of degradation in soil. No representative model was established to study the rate of microbiological degradation and thus all experiments are necessarily carried out in natural soil under controlled laboratory conditions. Relatively little information is found in the literature on the degradation of pesticides under field conditions. A very successful and promising study has been made which used laboratory results to predict rates of degradation under field conditions. This latter study could be directive and its results should be confirmed by similar experiments with other pesticides.

INTRODUCTION

The persistence of a pesticide in the soil environment determines its performance and also its impact on the environment. According to Goring et al. (1975)

three important phases of pesticide degradation can be distinguished : the causes
of degradation, the pathways of degradation and the rates of degradation. But be-
sides degradative processes like chemical degradation, photodecomposition and bio-
logical breakdown, the persistence or rate of disappearance of chemicals in soils
is also influenced by dissipation effects like leaching, volatilization, plant up-
take or errosion.

Generally, the behaviour of a pesticide in the soil environment is predeter-
mined by its chemical structure which is responsible for its physico-chemical
properties, i.e. vapour pressure, water solubility, partition coefficients, hydro-
lytic, thermal and light stability etc. These properties can be influenced to
some extent by the type of formulation and the method of application to ensure
optimum performance.

The above parameters are controlled in the environment by the variable or
environmental parameters which are the soil properties and the climatic condi-
tions. Biological activity, organic matter, cation exchange capacity and reaction
(pH) of a soil are the most important properties for controlling the rate of dis-
appearance of a chemical. The climatic factors known are wind, rainfall and sun-
light, which can act as a source for photons and for heat.

The influence of each individual process cannot be measured separately under
field conditions. The disappearance of a pesticide in a field soil always depends
on the sum of these processes. Using laboratory model systems, information on the
importance of each individual factor can be obtained faster and more accurately.

The aim of the present paper is to describe laboratory model systems by which
the influence of each of the above processes or parameters on the persistence of
pesticides in soils can be measured. The various experimental techniques for car-
rying out leaching, adsorption, volatilization, photolysis, hydrolysis, and soil
degradation studies in the laboratory will be discussed and the results obtained
compared with field behaviour of pesticides whenever possible. Methods for deter-
mining water solubility, partition coefficient, dissociation constant and vapour
pressure will not be described. Furthermore, some existing relations between single
models and the possibilities of substituting one model by another will be dis-
cussed. Finally, it will be tried to indicate to what extent single factors can
contribute to the overall rate of disappearance of pesticides in the soil environ-
ment.


SOLID-LIQUID ADSORPTION


Adsorption of pesticides onto soil particles has a major influence on trans-
port processes. In addition, biological and nonbiological degradation rates are
often drastically changed following adsorption.

The most widely-used method for carrying out soil-pesticide adsorption stu-
dies is the "batch" or slurry procedure where air - or oven-dry material is sha-
ken with aqueous or 0.01 N $CaSO_4$ solutions containing graded pesticide concentra-
tions until an equilibrium is reached. According to Hance (1967) a period of 24
hours was found to be enough to reach equilibrium. Some aspects of the speed of
attainment of sorption equilibria have been discussed by Hamaker and Thompson (1972).

The aqueous suspensions are then separated by centrifugation or filtration and the equilibrium concentration in the water phase determined either by direct analysis or after extraction with an organic solvent. The use of radiolabelled compounds assures a higher accuracy than other analytical methods (Dunigan 1967). Precision in pesticide adsorption measurements is of great importance, since it depends upon the magnitude of the solution concentration change (Green and Yamane 1970). Inadequate precision can sometimes be improved by altering the soil-solution ratio in order to obtain larger concentration changes. However, there seems to be some limitation to increasing the soil-solution ratio beyond a certain extent, since the adsorption constant was found to decrease with increasing soil-water ratio (Grover and Hance 1970).

Other methods used for adsorption studies have included continuous-flow equilibrium techniques (Green and Corey, 1971 ; Grice and Hayes, 1970 and 1972 ; Grice et al., 1973) and a dialysis method (Hayes et al., 1968).

The model most frequently used to describe adsorption processes is the empirical Freundlich equation which can be written in the form

$$\frac{x}{m} = k \cdot C^{\frac{1}{n}} \qquad \text{or} \qquad \log \frac{x}{m} = \log k + \frac{1}{n} \cdot \log C$$

where $x/m$ is the amount adsorbed by unit mass of adsorbent when in equilibrium with a solution of concentration C, k and n being constants for the given system and temperature. $1/n$ gives the slope of the adsorption isotherm and is generally less than unity (0.7 - 0.9). The Freundlich adsorption constant k gives the amount of compound adsorbed by the soil in equilibrium with a solution concentration c = 1, and is commonly reported on a whole soil basis. One possible way to standardise adsorption data is to divide the constant, k, by the proportion of organic matter in the soil to obtain a Q value - the amount of pesticide adsorbed per unit mass of organic matter. An adsorption constant based on the organic carbon content $(K_{oc})$ is preferred by some authors (Hamaker and Thompson, 1972) since this quantity is determined without the additional conversion factor (1.724) used to derive soil organic matter content.

Other mathematical adsorption models known are the Langmuir equation, the Brunauer-Emmet-Teller multimolecular adsorption theory and the Gibbs adsorption isotherm. For more detailed information on the interpretation and importance of the above models, the reader is referred to papers of Bailey and White (1970), Giles (1970) and Hamaker and Thompson (1972).


LEACHING


The determination of soil leaching rates is important because the rate of leaching indicates how long a chemical is retained in the top soil where it is most subject to degradation or dissipation. This importance has been reflected in a variety of reviews (Helling, 1970; Letey and Oddson, 1972 ; Gerber and Guth, 1973 ; Hamaker, 1975).

Laboratory Studies.  Three different methods can be used to study the mobility of
a pesticide in the laboratory. Soil thin-layer chromatography (soil-TLC) original-
ly described by Helling and Turner (1968) is an adaption of the widely - used thin-
layer chromatography using soil as adsorbent and distilled water as the mobile
phase. Detection of the herbicides was first done by autoradiography (Helling and
Turner, 1968), later by bioassay (Chapman et al., 1970 ; Helling et al., 1971) and
by radiochromatographic scanning (Helling, 1971). The applicability of soil-TLC
was further shown for fungicides using 10 soil fungi and a liquefied nutrient agar
suspension as detection systems (Helling et al., 1974). A so-called masking tech-
nique which allows use of chromogenic spraying reagents after the soil colour is
masked by an appropriate sorbent was described by Helling and Thompson (1974). An
interesting transfer detection method was published by Wenzel and Dedek (1975).
After a soil TLC plate was developed with water, it was covered with a normal sili-
ca gel TLC plate and compressed for 30 minutes to transfer the compounds from the
soil to the silica gel. The compounds were then sprayed with normal spraying rea-
gents. In contrast to normal thin-layer chromatography, frontal $R_f$ values or rela-
tive $R_f$ values are used to characterize the mobility of the pesticides tested.

Soil thick-layer chromatography (soil -THLC), described by Gerber et al.,
(1970), can be considered a compromise between soil-TLC and dry column chromato-
graphy. An aluminium plate (30 cm long, 5 cm broad with a 5 mm border) is filled
with air-dried soil of particles < 2 mm. The compound to be tested is mixed with
soil and the mixture applied as a streak to the starting line of the plate. A cot-
ton cloth dipping into water gives a uniform water flow to and on the plate which
is developed using the descending technique. After the leaching process, the soil
layer is divided into 2 cm zones which are separately bioassayed using Sinapis alba
for detection of the herbicide. If the compound acts as a germination inhibitor,
Agrostis tenuis is seeded directly on the plate. Either method clearly determines
the maximum of the herbicide distribution and the distance of the maximum from the
start is called the leaching index.

Soil column chromatography (soil CC) has also found wide-spread use. A large
variety of soil columns (dismantable and undismantable ones) of different materials
have been described in the literature (Helling, 1970 ; Weber, 1971). A very useful
method is the slotted tube technique developed by Lambert et al.  (1965).

Dismantable aluminium columns are used in our laboratories and have been de-
scribed elsewhere (Guth, 1972 ; Burkhard et al., 1975). Several experimental para-
meters, like soil humidity, amount and intensity of rainfall, were evaluated in
order to establish the optimum standard conditions. It has been found with pesti-
cides from different chemical classes that neither soil humidity nor the intensity
of artificial rain (200 mm applied between 35 hours and 5 days) had a significant
influence on the penetration depth. The depth of leaching was found to be directly
proportional to the amount of rain added which should be applied dropwise by using
either peristaltic or plunger pumps to ensure a slow and constant water flux.

The presentation of soil column leaching data can be in the form of leaching
diagrams or by reporting the positions of distribution maxima, or penetration
depths. The latter are more important from the view of environmental contamination.

A step forward in standardisation of leaching experiments has been made in West
Germany where three standard soils centrally available from a government institute
are used by all pesticide manufacturers in their leaching studies. These studies,

carried out according to an official BBA-guideline (Federal Biological Institute) which was developed in collaboration between government and industrial research people, are performed in non-dismantable glass columns by only analyzing the column eluate. Thus, the model gives information only on compounds which are eluted in at least one soil, and does not allow estimation of the mobility of non-eluted pesticides.

Comparisons between mobility data obtained by the three methods described above showed that within certain limits the same relative mobility was observed (Gerber and Guth, 1973). Wu and Santelman (1975) also tested all three alternatives and found that $R_f$ values from soil-TLC and-THLC correlated well, whereas slightly greater $R_f$ values were obtained using the slotted column method. The actual working time required to conduct the studies were in the decreasing order of soil-TLC,-THLC and -CC, but although the column method was more time consuming, the conditions might be more closely related to the field situation than in the other two procedures. In Table 1 soil mobility factors of herbicides are presented to further demonstrate the good agreement between the three methods. Soil-TLC and soil-CC have been accepted by the Environmental Protection Agency for inclusion in their Guidelines for Registering Pesticides in the United States (EPA-guidelines).

In our laboratories, soil-CC is preferred since this method has the following important advantages compared with the other two procedures : 1. The water flow and thus the rate of infiltration can easily be controlled. 2. A wide choice of application method, amount and formulation of applied pesticide, and method of analysis can be used. 3. Adaptability for use with volatile pesticides. 4. Whereas soil-TLC uses only a certain soil fraction, natural soils and even intact soil cores from the field can be used. 5. The ability to carry out long-term leaching/incubation studies like the "aged residue" leaching experiments requested by EPA.

Table 1   Soil mobility of some herbicides obtained by the three described laboratory models.

| | $R_f$ values [1] | Leaching distance [2] | RMF [3] [4] |
|---|---|---|---|
| Terbutryn | - | 1 | 0.38 |
| Prometryn | 0.29 | 3.5 | 0.59 |
| Propazine | 0.35 | 5 | 0.64 |
| Alachlor | - | 7 | 0.66 |
| Ametryn | 0.39 | 7 | 0.71 |
| Atrazine | 0.44 | 10 | 1.03 |
| Monuron | 0.44 | 10 | 1.00 |
| Fluometuron | 0.46 | 11 | 1.18 |
| Bromacil | 0.69 | 16 | 1.91 |
| Picloram | 0.84 | 27 | - |

1) From Helling (1971).   2) From Gerber and Guth, (1973).
3) From Burkhard et al. (1975).   4) RMF = relative mobility factor

$$= \frac{\text{leaching distance of compound}}{\text{leaching distance of monuron}}$$

For conducting such "aged residue" leaching studies, ^{14}C-labelled pesticide is incubated with soil for one month and the aged soil residue applied to the top of a

column filled with the same soil type. Small daily amounts of artificial rain are applied to the column over a period of 9 weeks and the daily leachate monitored for radioactivity. The distribution of the radioactivity in the soil column is determined at the end of the experiment and gives information on the leaching of the pesticide and potential metabolites in soil. It seems that this type of experiment is a further approximation to real field situations since it also takes into account the degradation processes occuring in the soil environment.

Field Studies. Although the laboratory tests give reproducible and comparative results, the conditions simulated in the laboratory do not represent a normal field situation. It is therefore also necessary to obtain some information on field leaching behaviour. Mostly, field leaching of pesticides is studied together with soil disappearance in a joint experiment. For this purpose, soil samples are taken from various soil depths and analysed in the laboratory by chemical or bioassay methods. Useful equipment for soil sampling has been described by Robinson et al. (1967), Maag (1972), Schweizer and Frey (1974) and Hayden and Robbins (1975).

In the EPA-guidelines another possibility for studying field leaching is suggested which is based on the method described by Reeve and Doering (1965). Soil water is sampled at various depths by soil-water suction probes which have a porous water-permeable ceramic cup on one end.

In the field, degradation effects and frequent changes of the water flux in soil (Letey and Oddson, 1972; Osgerby, 1973 a) cause the considerably reduced leaching pattern of a pesticide when compared to laboratory results. It has been shown that even an extremely mobile compound like trichlorobenzoic acid is only moved in small quantities into deeper soil layers (Hamaker, 1975). Similar results have been reported for other pesticides, such as picloram (Bauer et al., 1972) and dinoseb (Davis et al., 1954). Leaching of fluometuron under conditions of high rainfall and a high water table was studied by La Fleur et al. (1973). They found that movement was not chromatographic and, on average, over 70 % remained in the top 23 cm after 1280 mm of natural rainfall measured over a period of one year. Similar observations were made by Gerber and Guth (1973) and Burkhard et al. (1975) when comparing fluometuron and terbutryn field leaching.

Summarizing, it can be said that laboratory leaching results can be used to compare the degree of leaching of one compound with another, but field leaching is greatly reduced and the amounts of pesticides found to reach the ground water have been extremely small. Some progress in predicting laboratory and field leaching behaviour has been made by the use of computation models (Leistra, 1973 a and 1973 b; Leistra et al., 1974 ; Osgerby, 1973 b) which will be the subject of another review.


PHOTODECOMPOSITION


There is considerable information available concerning the photolysis of pesticides in solution, in thin films and also in the vapour phase and on the experimental procedures used for such studies (Crosby, 1969 ; Crosby and Li, 1969 ; Plimmer, 1970 and 1972 ; Crosby, 1972 ; Moilanen et al., 1975). It is evident that if photochemical transformations occur in soil, this can only be on or near the soil surface where light can penetrate. Evidence concerning photodegradation in soil is infrequently recorded. Walter et al. (1970) suggested that loss of fluorodifen at the soil surface was partially the result of photolysis. Taylorson (1966) noticed an increased loss of CDEC from soil after ultraviolet radiation but could not show

that it was caused by photodecomposition. Others have shown that dieldrin (Henderson and Crosby, 1967; Robinson et al., 1966; Rosen et al., 1966) and trifluralin losses (Messersmith et al., 1971 ; Probst and Tepe, 1969 ; Wright and Warren, 1965) are rather slower and smaller from soil itself than from soil-free environments. Comes and Timmons (1965) found that the toxicity of atrazine, simazine, fenuron, monuron and diuron to oats was reduced when these herbicides were exposed on the soil surface to sunlight for 25 days when compared to non-exposed soil. Although additional work on the photodecomposition mechanisms of several pesticides on soil thin-layers was published (Nilles and Zabik, 1974 and 1975 ; Bartl and Korte, 1975), no kinetic photolysis data have appeared yet in the literature. The authors are not aware of a useful model available which would yield reproducible kinetic results and thus would allow a relative scale of photodegradability for pesticides in or on soils to be established.

## HYDROLYSIS

Although oxidative and reductive reactions are observed during degradation of pesticides in the soil environment, there is no doubt that hydrolytic breakdown can be considered the most important chemical decomposition reaction.

Hydrolysis experiments are normally carried out with the pure chemical dissolved in buffered aqueous solutions of different pH values and at different temperatures. The EPA guidelines suggest three pH levels (3, 6 and 9) to be used since pH measurements on a variety of soils have demonstrated that this range would include the majority of agriculturally important soils. In our laboratories, hydrolysis studies are conducted at pH 1, 5, 7, 9 and 13 and at temperatures of 30, 50 and $70^\circ$C. However, for hydrolytically less-stable compounds lower temperatures are used. The decrease of pesticide concentration in the aqueous solutions is followed over a certain period of time (maximum 28 days) by chemical analysis. The hydrolytic breakdown can be described by applying first order reaction kinetics. Even alkaline hydrolysis follows a pseudo first order rate law, since very dilute solutions with concentrations below 100 ppm are normally used. First order rate constants (k) are calculated for each temperature and each pH value using the equation :

$$k = \frac{\ln c_o - \ln c}{t}$$

The relationship between the rate constants and the temperature is mathematically described by the Arrhenius equation :

$$k = A \cdot e^{-E/RT}$$

With the rate constants determined at different temperatures, the activation energies E and the frequency factors A can be calculated, and from these, rate constants and half-life periods can be computed for other temperatures.

After studying the rates of hydrolysis in the pH range 1 to 13, enough information is obtained on the pH dependence of the rate constants for half-lives at pH values other than those used in the experiments to be calculated.

Table 2 summarizes a few hydrolysis data reported in the literature and from

our own studies. The hydrolysis half-lives range from a few minutes for captan to over 200 days for fluometuron and ametryn. The data further demonstrate that phosphorus acid esters, carbamates, formamidines, and carbonic acid esters are susceptible to hydrolysis, whereas s-triazine and urea herbicides show a very high hydrolytic stability.

Table 2    Hydrolysis half-life periods (in days, if not otherwise specified) of some pesticides at various pH levels.

| Compound | pH | | | | Temperature |
| | 3 | 5 | 7 | 9 | $^{o}C$ |
| --- | --- | --- | --- | --- | --- |
| Diazinon [1] | 12 h | 31 | 185 | 136 | 20 |
| Monocrotophos | - | 96 | 66 | 17 | 20 |
| Dicrotophos | - | 88 | 77 | 23 | 20 |
| Chlorodimeform [2] | > 200 | 121 | 4 | 6.6 h | 25 |
| Captan | 10 h | 10 h | 3 h | 17 min | 28 |
| 2,4-D-methyl ester [3] | - | 44 (pH 6) | - | 1.1 h | 28 |
| 2,4-D-2-propyl ester [3] | - | 710 (pH 6) | - | 17 h | 28 |
| Carbaryl [4] | - | - | 10.5 | 2.5 h | 20 |
| Terbuthylazine | - | 86 | > 200 | > 200 | 20 |
| Ametryn | - | > 200 | > 200 | > 200 | 20 |
| Fluometuron | - | > 200 | > 200 | > 200 | 20 |

1)   From Gomaa et al.  (1969).       2)   From Wolfe et al.     (1975).
3)   From Zepp  et al.  (1975).       4)   From Aly and El-Dib  (1972).


VOLATILIZATION


Vapour pressure data provide a first indication of whether evaporation losses will be of importance with a particular pesticide. Volatilization from soil however, is influenced by various other factors including the water solubility of the chemical, soil type, soil moisture, temperature and wind velocity. Comprehensive reviews on the various aspects of volatilization have been published by Hamaker (1972a) and Spencer et al. (1973).

Laboratory model systems for determining volatilization of chemicals from non-adsorbing surfaces can also be used for measuring vaporization losses from soil. Volatility studies have been carried out for example in heated wind tunnels or humidity chambers (Phillips, 1971), in simple plywood boxes (Glückel et al., 1974) and in volatilization chambers with an inlet and outlet tube and containing a pan with a fixed surface (Grover, 1974). Soil samples with defined soil moisture containing the incorporated pesticides are normally placed into a closed system and a constant, exactly measured stream of air, or better, an inert gas, such as nitrogen, is passed over the soil surfaces. The volatile pesticide is then trapped either by liquid absorption methods or by adsorption on solid media. Gas washing bottles or impingers filled with ethylene or hexylene glycol are normally used as absorption vessels. Besides solid adsorbents, like silica gel, Chromosorb 102, Florisil, Chromosorb A and W, coated solids have been used. Further details can be obtained from papers of Seiber et al. (1975) and van Dyk and Visweswariah (1975). The amounts of pesticide

absorbed in the liquid or adsorbed on the solid are then determined by chemical ana-
lysis after extraction from the sorbent. A multiclass and multiresidue method for
this purpose was described by Sherma and Shafik (1975). Recently, the use of samp-
ling tubes filled with the porous polymer Tenax-GC which are then directly attached
to a gas chromatograph has been described (Parsons and Mitzner, 1975 ; Russell,1975).

Another technique originally described by Spencer and Cliath (1969) has been
included in the EPA-guidelines as a recommended method. In this so-called transpi-
ration (gas-saturation) method, an inert gas is passed through a pesticide-treated
sand slowly enough to ensure equilibrium vapour saturation. The pesticide can be re-
moved from the carrier gas stream and determined by the above methods.

Field Studies. An accurate evaluation of pesticide volatilization losses from field
soils involves the use of equipment to trap emanating vapours, meteorological instru-
ments, and soil measurements as described by Parmele et al. (1972). Caro et al.
(1971) used these to measure dieldrin volatilization rates from field applications.
The flux rate into the air of dieldrin and heptachlor was periodically measured af-
ter incorporation of the compounds into the soil by disking, followed by planting
of corn. The vaporized pesticides were collected at several heights and the vapori-
zation rates were estimated from pesticide concentration gradients in the atmosphere
by use of vertical diffusity coefficients calculated from simultaneous water vapour
losses. This latter, extremely complex study is the only known measurement of actual
volatilization rates from soil-incorporated pesticides conducted under normal far-
ming conditions while a crop was growing. Total seasonal losses were 4.5 and 6.2 %
of the applied dieldrin and heptachlor, respectively.


DEGRADATION IN SOIL


Laboratory studies have been carried out in polyethylene bags, closed plastic
containers, glass jars closed with plastic screw caps, bottles sealed with paraffin,
open soil pots etc. Another widely-used approach is the "biometer"flask, a closed
system developed by Bartha and Pramer (1965). A rather complex open system is that
of Parr and Smith  (1969) mainly applied to metabolism studies. The latter two sys-
tems are included as recommended methods in the EPA guidelines. Also in West-Germa-
ny a guideline for studying soil persistence was issued. The same German standard
soils used for the previously mentioned soil column leaching experiments are incu-
bated with the pesticides in Erlenmeyer flasks closed with cotton wool plugs to al-
low air exchange. Best and Weber  (1974) employed an integrated system  allowing si-
multaneous monitoring of degradation, volatilization, respiration, plant uptake and
leaching processes.

It has often been observed that pesticides disappear faster in the field than
would be expected from laboratory studies. This may be due to less biological acti-
vity of the laboratory soils and has not been taken into account by many when car-
rying out laboratory persistence experiments. A method for activating the micro-
organisms of soils was described by Chisaka and Kearney (1970). The soils were kept
wet during storage and the microorganisms were activated by growing rice and retur-
ning the shoots to the soils before starting the experiments. A similar procedure is
also used in our laboratories by growing maize or wheat for one month prior to the
soil degradation study. The problems of preparation and processing of soil samples
for bio-degradation studies have been extensively discussed by Pramer and Bartha
(1972).

A model system which can to some extent estimate the influence of microorganisms on the degradation of chemicals is that requested by the EPA. In this model a pesticide is incubated with a certain soil type and the degradation studied under sterile and non-sterile conditions. However, the sterilization procedures known either destroy only a part of the microbial population or alter the chemical properties of the soil. Another un-resolved problem is the maintenance of sterile conditions for the duration of the experiment.

The rate of degradation is also effected by the concentration of a pesticide and may tend to increase with decreasing concentration which has been shown by Hamaker (1972b) when summarizing literature data for atrazine, simazine and diuron. Similar results were obtained by Hance and McKone (1971) for atrazine, linuron and picloram, but for picloram also, no significant influence was observed (Meikle et al., 1973).

In all the above systems the disappearance of pesticides is followed by analysing samples after certain time intervals either by chemical methods or bioassays (Walker, 1970 and 1973). Comparisons between results obtained by both methods showed satisfactory agreement (Guth et al., 1969 and 1970). An interesting bioassay procedure was recently published by Gerber et al. (1975). After determination of plant fresh weights, a degradation curve is determined by mathematical transformations.

Quantitatively, pesticide degradation in soil has mainly been interpreted using first order reaction kinetics and reporting half-life periods for characterising persistence. There is evidence that in many instances more complex kinetics apply and the reader is referred to the excellent reviews of Hamaker (1972b), Edwards (1972) and Goring et al. (1975).

Table 3 gives half-life periods of a few pesticides calculated by the first order rate law and shows an order of increasing stability in soil from the less stable carbamates (dioxacarb and CGA-13210) and phosphorus acid esters through the slightly persistent urea and s-triazine herbicides to the much more stable chlorinated hydrocarbon methoxychlor. It is also obvious from the table that carbamates and phosphorus esters are more stable in the acid soil, diazinon being an exception. On the contrary, the chloro-s-triazines are less stable in an acid soil environment.

Table 3    First order half-life periods (days) of some pesticides obtained in the laboratory at $22 \pm 2^{\circ}C$ following the German guidelines. Soil type : sandy loam.

| Compound | Soil 1 1.0 % Org. C pH 4.8 | Soil 2 2.2 % Org. C pH 6.5 |
|---|---|---|
| Fenitrothion | 12 | 6 |
| Diazinon | 29 | 28 |
| Methidathion | 64 | 14 |
| Dioxacarb | 28 | 2 |
| CGA-13210 [1] | 28 | 9 |
| Metobromuron | 30 | 28 |
| Simazine | 60 | 85 |
| Atrazine | 53 | 110 |
| Propazine | 64 | 124 |
| Methoxychlor | 150 | 210 |

1) 2-n-propyl-1-carboxymethyl-5 (6)-chlorobenzimidazole

Field Studies. The main objectives of field dissipation studies of pesticides are :
1. To determine the rate of dissipation of the pesticide and its significant degradation products under field conditions. 2. To determine the nature of significant degradation products in the field. 3. To determine the potential carry-over of a pesticide and its degradation products. 4. To evaluate leaching. The pesticides to be tested are applied by spraying onto or by incorporating into the soil, samples taken at various intervals with either one of the equipments described above for field leaching studies and finally the soil residues determined by chemical or biological methods.

In spite of the complexity of the field situation, a few surprisingly good attempts have been made to predict pesticide loss under field conditions. Dekker et al. (1965) used first order kinetics to calculate long-term aldrin residues which could be expected in a variety of treated fields. The amounts determined by chemical analysis were remarkably close to the calculated field residues.

Hamaker et al. (1967) statistically correlated the disappearance of picloram from 200 different soils in 18 different states and provinces of the U.S.A. and Canada with rainfall and temperature. Temperature and rainfall accounted for approx. half of the variability in loss of picloram, whereas soil factors, such as pH, organic matter content, and soil texture contributed little to the correlation. Goring and Hamaker (1971) collected additional literature results from five picloram studies under field conditions, calculated both observed and predicted half-order rate constants and showed a correlation coefficient between these of 0.87. A successful attempt to predict rates of propyzamide degradation under field conditions using laboratory data has been published by Walker (1973). The results from these and other studies are reviewed in more detail by Hamaker in another paper at this Symposium.

RELATIONS BETWEEN INDIVIDUAL MODELS

Water Solubility in Relation to Adsorption

Theoretically, it is most unlikely that such a correlation should exist since the physical processes regulating sorption and solubility are quite different. Nevertheless, it has been considered that within certain pesticide groups there exists a relationship between water solubility and extent of adsorption. This connection has been demonstrated by Bailey et al. (1968) for the substituted ureas and s-triazines excepting atrazine. However, their results with the urea herbicides are in direct contradiction to those of Yuen and Hilton (1962) and Hilton and Yuen (1963) who found that the adsorption of these compounds was inversely related to their solubilities. Hance (1965) was unable to discover any relationship at all between the solubility of phenylureas and soil adsorption, a finding which was further confirmed by the results of Talbert and Fletchall (1965), Chapman et al. (1970), Gerber et al. (1970) and Guth (1972). Harris and Warren (1964) found no solubility-sorption relationship for diquat, CIPC, DNBP, and atrazine on either organic or inorganic adsorbents. Although it is evident from the above results that no general relationship between adsorption and water solubility exists, the water solubility of a pesticide can give a first, rough indication of its adsorption and consequently its mobility in the soil environment.

Relationship between Adsorption and Mobility Data

Rhodes et al. (1970) showed that a good relationship between Freundlich ad-

sorption constants and $R_f$ values determined by soil thin-layer chromatography could be established. Further, Osgerby (1973a) observed a similar correlation between $R_f$ values and the logarithm of Q mass values. An empirical relationship between adsorption constants determined by the slurry technique and penetration depths in soil columns was reported by Guth (1972) after testing phenylureas, s-triazines and phosphorus acid esters. The conclusion was drawn that under standardized conditions on addition of 200 mm artificial rain, pesticides with k values greater than 20 would remain in the upper 2-cm soil zone, whereas those whose adsorption constant was less than 1 would leach deeper than 30 cm. Hamaker (1975) used simple chromatographic theory to correlate adsorption coefficients with $R_f$ values from soil TLC. When inserting adsorption constants into the equation developed, a good correlation between calculated and observed $R_f$ values from Helling (1971) was obtained, with the measured values being larger. This tendency would be expected since Helling made his measurements from the front of the spot, while the calculations should give the positions of the spot center. Table 4 presents mobility data and Q values from our own experiments and demonstrates the obvious correlation between adsorption and leaching. This relationship of adsorption and mobility has also been taken into account in all the computation models used for predicting leaching behaviour of pesticides in soil (Leistra, 1973 a and 1973 b ; Leistra et al., 1974 ; Osgerby, 1973 b).

Summarizing the above data, it can be said that adsorption constants can be used to estimate the mobility of pesticides on soil thin layers and also the extent of penetration of chemicals in soil columns. Substituting soil column studies by adsorption measurements would greatly reduce experimental expenditure.

Table 4    Average relative mobility factors (= RMF) in comparison to average Q mass or $K_{OM}$ values

| Compound | Q [1] (µg/g organic matter) | RMF [2] |
|---|---|---|
| Chlorobromuron | 377 | 0.28 |
| Diazinon | 332 | 0.28 |
| GS-13006 [3] | 317 | 0.28 |
| Terbutryn | 281 | 0.38 |
| Prometryn | 165 | 0.59 |
| Methidathion | 139 | 0.56 |
| Terbumeton | 122 | 0.74 |
| Ametryn | 111 | 0.71 |
| Methoprotryn | 104 | 0.66 |
| Chlorotoluron | 95 | 0.59 |
| Fluometuron | 51 | 1.18 |
| Cyanazine | 45 | 1.85 |

1) Average Q mass values obtained with three different soil types. 2) Average mobility factors relative to monuron determined in the same soil types. 3) S-(2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl) diethyl phosphorothiolothionate.

## Relations between Adsorption/Mobility and Other Parameters

There are a few papers available demonstrating the relationship between sorption and chemical structure. Lambert (1967) and Hance (1969) correlated adsorption

constants of phenylureas, s-triazines, carbamates and uracils with their parachor. The relation between Hammett constants and adsorption of phenylureas and N-phenyl-carbamates was studied by Briggs (1969). The adsorption coefficients of the latter study could also be correlated with octanol-water distribution ratios (Briggs, 1973) and, in addition, with mobility using the data of Helling (1971) and Helling et al. (1971).

## Volatilization Related to Adsorption

Adsorption coefficients, in addition to having merit in the prediction of pesticide mobility, may also be useful in estimating volatilization losses. A distribution ratio between wet soil and air can be calculated (Hamaker, 1972a) by the following equation :

$$\frac{C_{ws}}{C_{air}} = \frac{C_{water}}{C_{air}} \cdot \frac{1}{r} + K_d$$

In this equation $C_{ws}$ is the pesticide concentration in wet soil, $C_{water}/C_{air}$ is the water-air distribution ratio, r is the weight of water, and finally $K_d$ is the soil-water adsorption coefficient. This formula was applied to a number of pesticides assuming a value of 6 for r. The results summarized in the following table are taken from the EPA guidelines.

Table 5

| Compound | vapour pressure (mm Hg) | Water solubility (ppm) | Water/air concentration ratio | $K_d$ for 2 % org.C | Soil/air concentr. ratio |
|---|---|---|---|---|---|
| EPTC | $1.97 \times 10^{-2}$ | 370 | $1.84 \times 10^{3}$ | 5.66 | $1.07 \times 10^{4}$ |
| Dichlobenil | $5.5 \times 10^{-4}$ | 18 | $3.48 \times 10^{3}$ | 3.28 | $1.2 \times 10^{4}$ |
| Lindane | $3.2 \times 10^{-5}$ | 10 | $1.96 \times 10^{4}$ | 26.8 | $5.29 \times 10^{5}$ |
| DDT | $1.9 \times 10^{-7}$ | 1.2 ppb | $3.26 \times 10^{2}$ | 4860 | $1.58 \times 10^{6}$ |
| Parathion | $3.8 \times 10^{-5}$ | 20 | $3.3 \times 10^{4}$ | 209 | $6.9 \times 10^{6}$ |
| Atrazine | $8.9 \times 10^{-7}$ | 33 | $3.2 \times 10^{6}$ | 3.44 | $1.2 \times 10^{7}$ |
| Monuron | $5 \times 10^{-7}$ | 230 | $4.2 \times 10^{7}$ | 1.66 | $7.67 \times 10^{7}$ |

These estimated values clearly demonstrate that adsorption significantly reduces volatility particularly in the case of DDT and parathion.

## Chemical Hydrolysis and Soil Degradation

A first attempt to construct a model for predicting the persistence of hydrolytically sensitive herbicides in soils was reported by Furmidge and Osgerby (1967). This model was based on the use of hydrolysis rate constants and adsorption data and has been successfully applied for predicting the rate of degradation of phosphorylated atrazine and monocrotophos in soils. We are not aware of another similar and successful attempt available in the literature. However, when considering the clear pH-dependence of diazinon, thionazin and carbofuran degradation in soil

(Getzin,1968 and 1973), other literature, and our own data which are summarized in Table 6, it seems that there should be a chance for predicting soil persistence from hydrolysis rate constants, at least for hydrolytically sensitive pesticides.

Table 6    Half-life periods (days) of some pesticides obtained in the laboratory in two German standard soils in comparison to hydrolysis half-lives in aqueous buffer solutions.

| Compound | Half-life in soil at 22 $\pm$ 2$^{\circ}$C | | Hydrolysis half-lives at 25$^{\circ}$C and at pH values | | |
|---|---|---|---|---|---|
| | Soil 1 1.0 % org. C pH 4.8 | Soil 2 2.2 % org. C pH 6.5 | 5 | 7 | 9 |
| CGA - 15324 [1] | 41 | 3 | 48 | 8 | 3.1 h |
| CGA - 12223 [2] | 18 | 10 | 38 | 25 | 8 |
| CGA - 13210 [3] | 28 | 9 | 22 | 9 | 2.7 h |
| Diazinon | 29 | 29 | 31 [4] | 185 [4] | 136 [4] |
| Guthion | - | 29 [5] (pH 8.4) | - | - | 28 [6] (pH 8.6) |
| Methidathion | 64 | 14 | - | 24 | 6 |

1) ethyl (2-chloro-4-bromophenyl) S-n-propyl phosphorothioate. 2) diethyl (1-iso-propyl-5-chloro-1,2,4-triazolyl-3)phosphorothioate. 3) 2-n-propyl-1-carboxymethyl-5 (6)-chlorobenzimidazole. 4) At 20$^{\circ}$C. Data from Gomaa et al. (1969). 5) Yaron et al. (1974). 6) Heuer et al. (1974).

CONCLUSIONS

The present review has tried to show the variety of experimental model systems which are at present available for studying the behaviour of pesticides in the soil environment. All the models described are useful for measuring certain degradation effects, such as biological degradation, hydrolysis and photodecomposition, as well as the dissipation processes leaching and volatilization which are both mainly influenced by adsorption. Researchers working in the field of agrochemicals are fully aware that the soil is a heterogeneous environment in which the multitude of interactions make it extremely difficult to understand what contribution each factor makes toward the persistence of a pesticide in soil. Although we can not give a pat solution for this problem, we will at least try to estimate the relative importance of the individual factors using the experimental data reported.

Adsorption processes influence leaching and volatilization of pesticides in soils. This has been demonstrated by the mathematical equations given above correlating adsorption constants with $R_f$ values from soil thin-layer studies, penetration depths obtained from column leaching studies, partition coefficients and volatilization. There is no clear relationship available on the interaction of adsorption and degradation in soil.

Mobility data obtained by either one of the laboratory methods can be used to compare the leachability of one chemical with another whose leaching behaviour may

be known, but do not quantitatively predict leaching under field conditions. Published studies show that little, if any, of even quite mobile pesticides is leached sufficiently deep to enter the ground water. The successful simulation model for predicting the persistence of herbicides in the field (Walker, 1973) did not include terms for losses through leaching, photodecomposition or volatilization. Considering field leaching data and the results of the simulation model it seems that for many pesticides, leaching in the field is not a major factor controlling their disappearance.

Although considerable information is available concerning photodecomposition of pesticides in solution, no data on the kinetics in or on soil have been reported which would enable clear statements concerning the quantitative influence of the photolytic process on the persistence of pesticides in soils to be made.

Several examples were given of satisfactory agreement between some hydrolysis half-life periods and half-lives observed in soil degradation experiments. In addition, the hydrolysis rate was used together with the adsorption constant for successfully predicting the rate of breakdown of two hydrolytically-sensitive pestisides in soil. However, the information available is relatively limited and further work has to be done to prove that hydrolysis data can help to predict the persistence of certain pesticides in soils.

Volatilization of a pesticide can be high from a non-adsorbing surface, dependent only on its vapour pressure and its rate of movement from the evaporation surface, but it is considerably reduced when incorporated into the soil. The extent of this reduction is mainly determined by the strength of adsorption. Although considerable work has been published on volatility of pesticides, particularly of the chlorinated hydrocarbons, only one study was carried out measuring actual volatilization rates from field soil. The measured seasonal losses of dieldrin and heptachlor were 4.5 and 6.2 %, respectively. This is a relatively low loss for compounds which are known to be extremely volatile, when compared to actual rates of degradation in soil systems. Thus volatilization seems to be of significant importance only for the persistence of such pesticides which are more volatile than the chlorinated hydrocarbons.

The soil factor having one of the most profound but unpredictable influence on the decomposition of pesticides is related to soil microbes. However, there is no representative model known for studying only the microbiological stability of pesticides. Experiments therefore have to be and are carried out in natural soils under more or less controlled laboratory conditions. Each laboratory model system described can give useful information on the relative persistence of pesticides, but comparisons with data obtained with other models are not possible.

A better standardization of the experiments could help to increase the value of such persistence data. Some progress has been made to standardize model studies on a national basis in the United States and partially in Germany, but unfortunately nothing is in sight on an international level.

Relatively little information is found in the literature on the rate of disappearance of pesticides under field conditions and attempts to use laboratory data for predicting rates of dissipation in the field are even less. However, a very successful study has been made which used laboratory results to predict rates of degradation under field conditions (Walker, 1973). This must be regarded as a landmark study since it has demonstrated the validity of predicting field degradation rates from measurements of rates of degradation in the laboratory and weather data such as

temperature and rainfall. This latter study has clearly pointed out in which direction further work should be planned, and it would be desirable to confirm the above findings with other pesticides.

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