

EXPERIMENTAL MODELS FOR STUDYING THE FATE OF PESTICIDES IN PLANTS

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Summary Experimental approaches used to study the fate of pesticides in plants have been reviewed. Since radiolabelled compounds are widely used in this work, experiments are usually done under glasshouse conditions. There is an increasing tendency, however, to do this type of work outdoors using plants grown either in pots or boxes or in small field plots. This has the advantage that the effects of the weather on degradation and volatilisation can be observed, but the use of radiolabelled compounds imposes a limitation on the scope of these studies. In future this problem might be overcome by the use of stable isotopes.

INTRODUCTION

In studies of the fate of pesticides in plants, the amount and type of information required will depend on many factors, including the end use of the pesticide and the extent to which it will be used. Consequently, various approaches have been used to study the fate of pesticides in plants.

The degradation of pesticides in plants is discussed in detail in a separate paper in the symposium and it is the purpose of this paper to review and discuss some of the experimental approaches which have been used to examine the behaviour of pesticides in plants. Such experiments are usually carried out with radiolabelled compounds with the result that most of the work reported in the literature has been done under controlled glasshouse or growth-chamber conditions. However, there is an increasing tendency to study the fate of radiolabelled pesticides in plants under more realistic outdoor conditions and the advantages and disadvantages of this approach will also be discussed.

Indoor experiments

Indoor experiments can be used to obtain data on the rate of loss of pesticides from plants under controlled conditions together with information on the identity of metabolites. Factors affecting the fate of the compound such as the plant variety and species, method of application, rate of application, pesticide formulation, temperature and humidity can also be studied in detail.

One of the simplest approaches is to apply the labelled pesticide to the foliage of the plants or to expose the plant roots or excised shoots to a solution of the compound. Treated plants may then be sampled at intervals for analysis. If

the experiment is conducted under conditions in which volatile materials can be trapped, information on the nature of any volatile products may also be obtained. Experience has shown that although good plant growth can only be maintained for a few weeks in these closed systems useful information can be obtained if a compound is metabolised rapidly to a volatile product.

An interesting example of this was reported by Harvey and Reiser (1973) in their work on the metabolism of methomyl insecticide in plants. The plants were treated with [^{14}C]-methomyl and were maintained for between 1 and 4 weeks in a closed system with air passing through into a trapping system similar to that shown in Figure 1. Any $^{14}\text{CO}_2$ evolved would be trapped in the first sodium hydroxide trap and basic volatile products would be collected in the sulphuric acid solution. Neutral products were oxidised to $^{14}\text{CO}_2$ and trapped after the combustion furnace. In the case of methomyl, labelled CO_2 was identified as a volatile product together with a neutral, volatile metabolite which was shown to be acetonitrile. If these experiments had been carried out in the open, this valuable information on the metabolic pathway would have been missed.

A review of the literature has shown that apart from isolated examples such as the work on methomyl most work on the fate of pesticides in plants has been carried out in open containers either in the glasshouse or in growth chambers under controlled conditions. In recent years, however, details of several more elaborate laboratory models have been reported in which the fate of pesticides in plants is considered alongside their fate and distribution in soil or water. A system described by Lichtenstein *et al.* (1974) is shown in Figure 2. This, together with the well-known model ecosystems described by Metcalf (1972), shown in Figure 3, has the advantage that the degradation, movement and accumulation of pesticides in soils, water and plants (and in animals in the case of the ecosystems) can all be studied in a single experiment. However, this is achieved by modifying the conditions in such a way as to make the subsequent analysis easier. For example, most model ecosystems employ sand rather than soil so that the important processes of absorption and degradation that would occur in the soil have been excluded and the effect of this on the fate of the compound could be quite considerable. However, since the main purpose of the ecosystems is to study pesticide biodegradability as a whole, and not solely in plants, a more detailed appraisal is outside the scope of this review.

Outdoor experiments

In recent years the fate of pesticides in plants has been studied under outdoor conditions and such experiments have been designed to complement indoor studies and in some cases to replace them altogether. By using outdoor conditions, the effects of weather on the fate of a compound can be observed and a more quantitative assessment of the residues of the compound and its metabolites can be made. The major limitation with outdoor experiments is that, as radiolabelled compounds are frequently used, the necessary precautions and the high costs involved tend to restrict the scope of the experiments. Nevertheless, outdoor studies are important if early information on the persistence of a new pesticide in plants is required together with some idea of the likely residue concentrations of metabolites. The ideal way to obtain this information is to carry out full scale field trials and to analyse crop samples for the parent pesticide and its metabolites but this can only be done when all of the metabolites have been identified and the necessary analytical procedures have been established.

A review of the recent literature has brought to light several reports in which the behaviour of labelled pesticides in plants has been studied outdoors and some examples are given here. For instance, Andrawes *et al.* (1971) studied the fate

of [^{14}C]-aldicarb insecticide in potatoes by applying the insecticide to furrows in field soil and sowing potatoes. A glasshouse experiment was carried out in parallel with this to provide greater quantities of metabolites for identification purposes. Golab and co-workers (Golab and Althaus, 1975; Golab *et al.*, 1975) used a similar approach in their work with isopropalin and oryzalin herbicides although in the latter case an area of field soil was isolated using galvanised pipe. Klein *et al.* (1973) and Weisgerber *et al.* (1974) used wooden boxes of soil in their work with [^{14}C]aldrin and obtained information on the relative concentrations of aldrin and its metabolites that occurred in plants. Buckland *et al.* (1973) grew wheat in pots outdoors and treated the foliage with formulated [^{14}C]-bromoxynil octanoate and this work was also carried out alongside indoor experiments in which similar treatments were made. Waring and Wolfe (1975) treated a plot of barley growing in the field with low concentrations of [^3H]-tridemorph and determined the distribution of tridemorph and its metabolites in the barley plants when they had reached maturity. In our own laboratories, the metabolism of benzoylprop-ethyl was studied using wheat grown in boxes in an outdoor wire enclosure (Beynon *et al.*, 1974). This type of experiment has been going on at Woodstock for several years and the set-up currently used is shown in Figure 4.

Plants are grown in boxes which are housed in a pit such that the soil surface in the boxes is level with the soil in the surrounding field. The whole pit is enclosed by a wire mesh fence to keep out animals and birds. The floor of the pit slopes towards a central well containing a pipe linked to a drain. This pipe can be closed and the water can be monitored for radioactivity from time to time.

The plywood boxes of size 60 x 60 x 60 cm are fitted with slats at the bottom to allow for drainage. Flaps are fitted on one side so that soil samples may be taken horizontally at different depths. The boxes are placed in light alloy trays mounted on blocks to make them level. They are filled with top-soil and allowed to settle for 1-2 months. Plants are then grown in the boxes and they can be treated with the formulated pesticide at the required time by surrounding the plants temporarily with a protective polythene cover.

This approach has been used, in conjunction with glasshouse experiments, to study the fate of several herbicides in cereals and distinct advantages and limitations of the system have become apparent. Its major advantage is that it permits the fate and persistence of a compound to be observed under outdoor conditions in a radiochemical experiment that is easy to dispose afterwards with a minimum risk of contamination. Furthermore, the metabolites formed under the conditions of the experiment are likely to occur under true field conditions. One disadvantage in practice is that, if the labelled pesticide is applied at a concentration close to that which will be employed in commercial use then the amount of metabolites formed could be small which may make identification difficult. This can be overcome by using radiochemicals with higher specific activities or by carrying out parallel indoor experiments to obtain larger quantities of metabolites. Another problem with this type of experiment is related to the interpretation of the quantitative data obtained. Although the residue levels of the pesticide and its metabolites should be close to those which will occur in the field, the small plot size and the careful way in which the radiochemical is applied to the plants can lead to somewhat higher concentrations. Nevertheless, reasonable agreement was obtained in the experiments with benzoylprop-ethyl (Beynon *et al.*, 1974). At the same time as the plants growing in boxes were treated at a rate equivalent to 1 kg/ha, wheat in a nearby field was treated at the same application rate with a commercial preparation of benzoylprop-ethyl. The results (Figure 5) show that there were similar concentrations of benzoylprop-ethyl and its metabolite benzoylprop in both sets of plants. Consequently, the other ^{14}C -containing products detected in the radiochemical samples (for which residue analytical methods were not available at the time) would be expected to occur in field samples at similar concentrations.

Such good agreement has not always been obtained, however, and there are several possible reasons for this. For example, if the crop density in the boxes is too high then a greater proportion of a spray application will be deposited onto the plants than would occur under field conditions. This can lead not only to higher residue levels but also to marked differences in the relative concentration of the pesticide and its metabolites. Despite these limitations, if these outdoor experiments are regarded as falling between glasshouse conditions and field conditions and the data are interpreted accordingly then they can be very useful.

Possible ways of overcoming the limitations which arise from the use of radiochemicals are to use either short-lived radioisotopes such as ^{32}P or to consider using stable isotopes, in particular ^{13}C . The former possibility is of limited interest only with those molecules which contain suitable elements. However, there is no reason why stable isotope labelling should not be applicable.

A range of ^{13}C enriched compounds and intermediates are now available so the synthesis of ^{13}C -labelled pesticides is possible. Regarding the analytical techniques available for ^{13}C -enriched compounds perhaps the most valuable is ^{13}C -NMR and with the present generation of instruments a spectrum should be obtained from as little as 0.5-1.0 mg of a ^{13}C -compound with 10% enrichment.

Since there are no special handling requirements as there are with radioactive materials, larger areas outdoors could be treated without hazard so more realistic applications could be made. If information were already available from conventional glasshouse metabolism experiments with ^{14}C -compound, then, with the help of ^{13}C -NMR and mass spectrometry it should be possible to obtain qualitative and quantitative information on the metabolites present in a field sample treated with the ^{13}C -labelled samples. With NMR since one would be looking only for resonances from the products containing the enriched ^{13}C , rigorous clean-up of the plant material might not be necessary. It remains to be seen whether this approach will be of any value in practice but, if successful it could be a useful way of obtaining early information on the persistence of a pesticide and its metabolites in plants.

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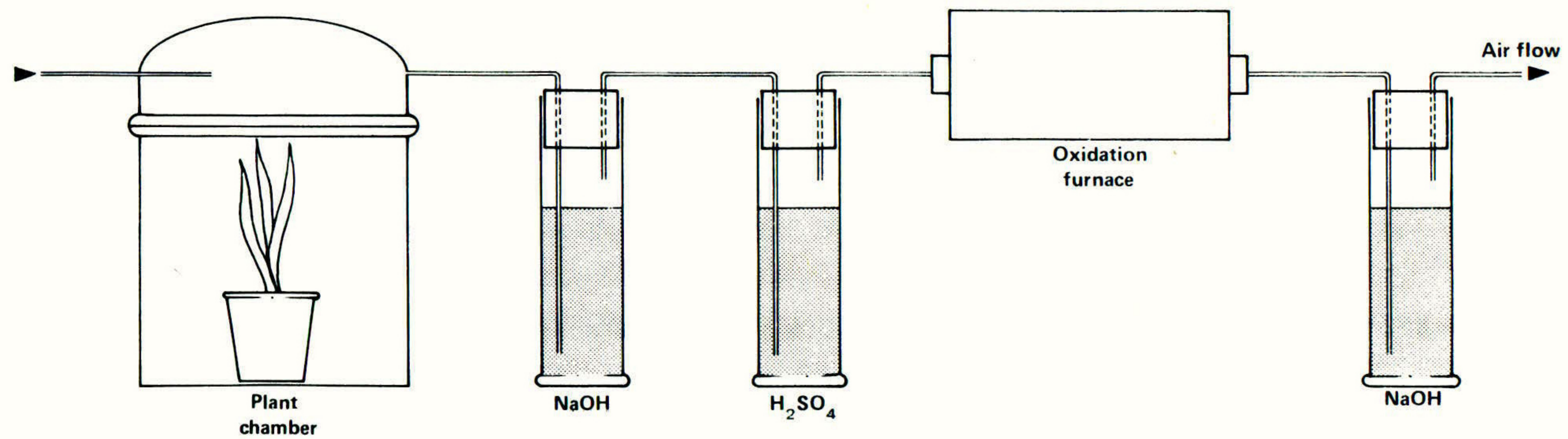


Fig 1
Closed system for plant metabolism studies
(after Harvey and Reiser, 1973)

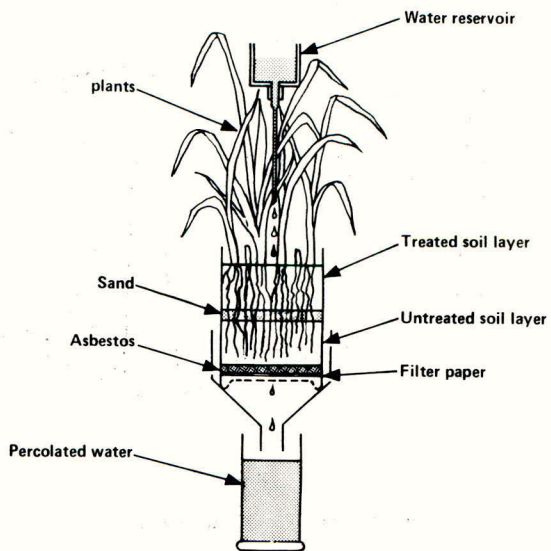


Fig 2
Model system in which plants are grown in treated soil
(after Lichtenstein *et al*, 1974)

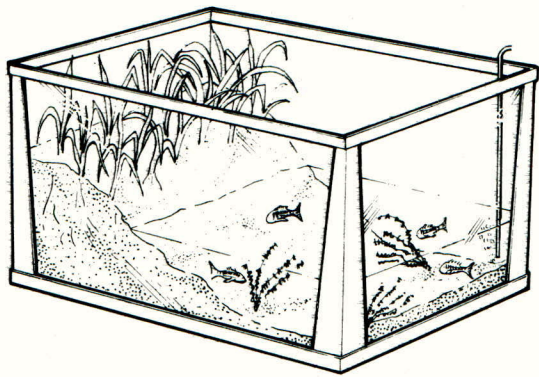


Fig 3

Schematic diagram of model eco system
(after Metcalf *et al*, 1972)

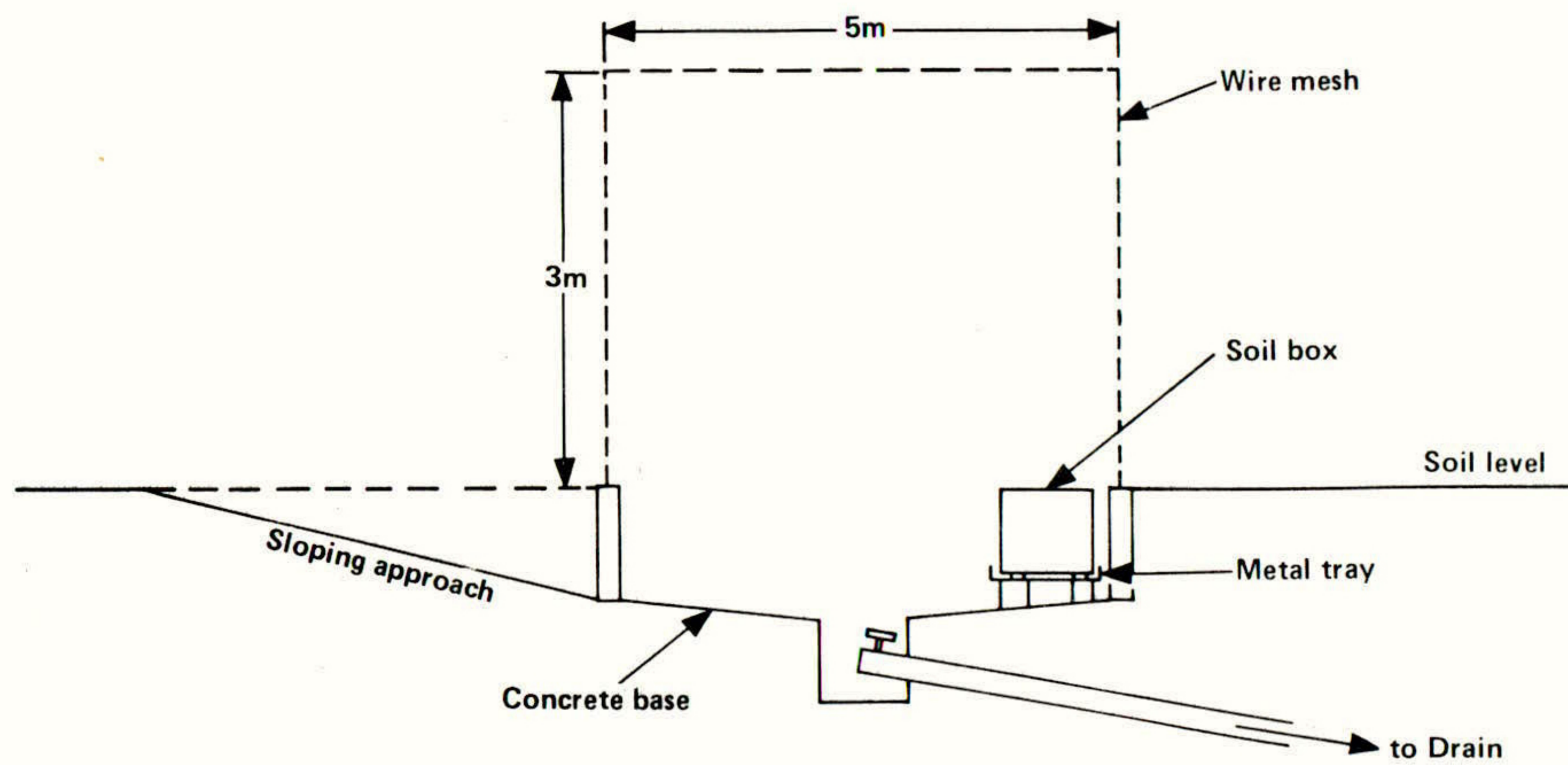
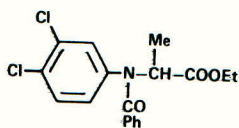


Fig 4 Diagram of outdoor enclosure for radiochemical experiments



	Radiochemical experiment (mg/kg)	Field experiment (mg/kg)
Benzoylprop ethyl	2.0	1.5
Benzoylprop	0.24	0.5
Conjugated benzoylprop	0.34	No data
Unextracted ¹⁴ C	0.37	No data

Fig 5 Concentrations of Benzoylprop ethyl and its metabolites in wheat straw

THE USE OF COMPUTATION MODELS IN STUDIES OF PESTICIDE MOVEMENT IN SOILS

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INTRODUCTION

Studying the movement of pesticides in soil is a comprehensive task. There are many hundreds of compounds including pesticides, important conversion products, and admixtures and these compounds all have their own physico-chemical properties. There is also great diversity in the conditions in which pesticides are applied. The differences in climatic conditions, soil characteristics, application techniques, and agricultural systems may be enormous. This makes it necessary to obtain the greatest possible benefit from a limited amount of experimental data. Much of the knowledge gained with a particular compound should be utilised with other compounds and knowledge from other scientific disciplines should be employed effectively. Computation models may be powerful tools in attempts to investigate pesticide movement in soils systematically.

In this review, the use of computation models in studies of pesticide behaviour in soil will be illustrated with examples. A few of the most relevant processes are then discussed separately. Finally a number of possible approaches to the setting up of mathematical models are described and compared.

PRACTICAL APPLICATIONS OF COMPUTATION MODELS

Fumigant diffusion in soil

One of the earliest applications of a computation model to the movement of pesticides in soil dealt with soil fumigation. Hemwall (1959, 1960) studied the diffusion of a fumigant with hypothetical characteristics from a line source (shank injection) in soil. The diffusion-type differential equation was converted into finite-difference equations of the explicit type, after which the concentration patterns could be obtained by computer. The resulting concentration-time products in the liquid phase at various positions in soil were used to compare the effectiveness in nematode control that could be obtained under various soil conditions. Unfortunately, insufficient data were available and some of the suppositions on the vapour-diffusion process under different soil conditions are capable of improvement. This approach was continued in studies on the behaviour of 1,3-dichloropropene and of methyl isothiocyanate (the active conversion product of metham-sodium) in soil. An essential part of the newer research in this area was the determination of missing basic data, particularly concerning the distribution of the fumigants over the phases in soil and on conversion rates (Leistra, 1972; Smelt and Leistra, 1974; Van Dijk, 1974).

The computation models were tested with measurements from experimental fumigations in the field (Leistra, 1972; Leistra et al., 1974; Smelt et al., 1974). The combination of computation models and basic data made it possible to predict the effectiveness of soil fumigation under various conditions of soil, climate, and

application (Leistra, 1972; Leistra and Smelt, 1974). One of the remarkable results was that the effectiveness of soil fumigation with metham-sodium can be expected to be higher at lower soil moisture contents in the favourable range. A survey of the application of computer models in studies on the factors determining the effectiveness of soil fumigation with 1,3-dichloropropene, metham-sodium, and methyl bromide was given recently by Siebering and Leistra (1976).

Herbicide movement in the top layer

For the effectiveness of soil-applied herbicides, behaviour near the soil surface and mobility in the top layer of soil are of great importance. At the soil surface, losses may occur by volatilisation or photodecomposition. These losses will be comparatively low if a close interaction with the soil is possible and if penetration into the soil is fast. Factors like formulation and method of application play an important part. For good activity with soil-applied herbicides, a certain degree of penetration in soil is necessary to supply sufficient amounts to the weeds. In some instances, penetration to a depth of one or a few centimetres is sufficient; in other instances such as with deep-rooting weeds, active concentrations of the herbicide should penetrate to a depth of several decimetres. With many applications in horticulture and arable farming, depth protection is needed to preclude damage to the crop. The mobility of the herbicide then has to be so low that concentrations in the root zone of the crop remain very small (Gerber and Guth, 1973).

To assess the risk of after-effects on a subsequent crop, the distribution pattern of herbicide residues in soil is important. Leaching may lower concentration-levels by spreading or even contribute substantially to removal of residues from the top layer. Knowledge of the position of residues in soil may facilitate the selection of promising alternative cultural practices.

The multiplicity of herbicide characteristics, and the differences and variability in soil and climatic conditions constitute a great problem. Computation models in combination with accurate basic data could be helpful in the systematic and more quantitative investigation of effectiveness and side-effects with soil-applied herbicides. As well as interpreting the observed differences in field performance, computation models may also be used for making predictions.

In a few instances, mathematical models have already been used in studies of herbicide movement in the top layer of soil. Dunham and Crawford (1973) calculated the distribution of atrazine near the soil surface under evaporative conditions. The conditions were defined in such a way that an analytical solution for the convection-diffusion type of differential equation could be used. In the absence of water evaporation, atrazine was calculated to penetrate slowly by diffusion from the initial distribution of 1.1 mm thickness to depths of 10 to 20 mm after 21 days. In the presence of an evaporative water flow, the downward movement was much less; at 5 mm evaporation per day a steady state was attained with atrazine being still mainly concentrated in the upper mm of soil. A similar situation may be expected in the field when the evaporative flux of water and the diffusive flux of atrazine both diminish with drying of the soil.

A numerical solution for simplified field conditions was used in a study on the movement of propyzamide in the top layer (Leistra et al., 1974). A net rainfall pattern and measured adsorption coefficients were introduced into the model. The computed and measured concentration distributions with depth were in approximate agreement, but there was a tendency to over-estimate the mobility after the first month. In most of the soils, propyzamide remained largely in the upper 2 cm and a crop may thus benefit from depth protection. In a sand soil with only 1.8% organic matter, mobility was much greater and significant concentrations were found in the 5 to 10 cm layer. As a result of the lower adsorption, concentrations in the liquid phase were comparatively high. There seem to be good possibilities for

the use of computation models in studies of herbicide effectiveness and selectivity under various conditions with respect to crop, herbicide, soil and weather.

Systemic nematicides and insecticides in the root zone

An important characteristic of soil-applied systemic nematicides/insecticides like aldicarb and oxamyl is that they are very mobile in soil. Water flow in soil will have a great influence on the distribution of the active compounds in the root zone and thus on effectiveness. This high mobility should be considered when selecting the optimum mode of application. Within a few days, aldicarb is for the greater part oxidised to aldicarb sulfoxide, the principal compound with respect to effectiveness. In soil, this sulfoxide is gradually oxidised and hydrolyzed to less active compounds (Coppedge et al., 1967). Recent experimental data indicate that for the sulfoxide under field conditions in spring, half-lives of about 4 weeks can be expected (Leistra et al., 1976). The adsorption of the sulfoxide onto soils is very weak (Bromilow, 1973), resulting in a very high mobility in soil columns during leaching experiments with artificial rainfall (Leistra et al., 1976).

In a series of preliminary computations, the effect of incorporation depth and amount of rainfall on the distribution of aldicarb-sulfoxide in the root zone was checked. The computation model simulated the application of 2.5 kg of aldicarb per ha at the beginning of April to a sandy loam soil in which a potato crop was grown. Details of the model and of some of the conditions were given by Leistra and Dekkers (1976). The aldicarb granules were assumed to be incorporated homogeneously to depths of 5 or 15 cm. Water infiltration and redistribution in soil resulted from net-rainfall patterns representative of months in spring being rather dry (15 mm/30 days), about average (35 mm/30 days), and rather wet (60 mm/30 days). Concentrations of the sulfoxide in the liquid phase at various depths in soil were computed for the first two months after application. During the first month with little rainfall on initially moist soil, the sulfoxide penetrated to a limited extent due to convection accompanied by hydrodynamic dispersion and by diffusion. For achievement of sufficiently high concentrations at depths greater than 15 cm, the deeper incorporation (15 cm) was much better under these low rainfall conditions. As a result of the withdrawal of water from soil by the developing root system of the crop, there was hardly any further downward movement during the second month. With more average rainfall conditions (35 mm/30 days) during the first month, the downward movement was such that considerable concentrations were found around a depth of 25 cm. However, the concentrations near the soil surface became rather low especially with deeper incorporation. Therefore incorporation of such mobile systemic compounds to depths greater than about 10 cm may be inadvisable. After a month with high rainfall (or sprinkler irrigation), the peaks of the sulfoxide distribution were between 15 and 25 cm. Concentrations near the soil surface (upper 5 to 10 cm) declined to low values, although they were somewhat higher for the shallow incorporation. During a second month with high rainfall, a distinct further leaching from the top layer occurred.

Under the low rainfall condition (15 mm/30 days), the pesticide distribution with depth coincided best with the distribution of root activity and the computed amounts of uptake were greatest. This may be important for the effective control of parasites via subsurface and above ground plant parts, and for the residue levels at harvest.

The material balance in soil

With present-day concern about the consequences of human activities on the environment, it is important to know the extent to which agricultural chemicals are decomposed within the domain of application. The combination of computation model and essential physico-chemical basic data can be used to make first approximations to the chances of emission of pesticides from agriculture. This would facilitate the

selection of compounds that need further investigation and the kind of experimentation needed. In protected recharge areas where drinking water is pumped, the use of pesticides is prohibited, unless there is evidence that contamination of the water in the aquifers is unlikely to occur. Two characteristics of pesticide-soil interaction are of predominant importance in this respect: the rate of decomposition and the adsorption coefficient. Decomposition within a few weeks after application usually ensures that risk of leaching to the subsoil is nil under most conditions. A fair degree of adsorption affords time for decomposition, and the chance for leaching from the root zone is accordingly decreased. Compounds that are only slowly decomposed in soil and that are mobile as well call for a more quantitative approach (Leistra and Dekkers, 1976). The conditions in which the pesticides are used will have a great influence on the possibility of leaching. Applications in autumn and winter, and application to fallow areas require extra attention in this respect (Leistra, 1976). The incorporation of the most important processes and basic data in a computation model for pesticides in soil allows first approximations of various terms of the material balance to be computed (Leistra and Frissel, 1975).

ELEMENTS OF PESTICIDE MOVEMENT IN SOILS

Soil water flow

With the quantitative description of moisture flow in soils under field conditions, the boundary conditions are frequently very complex. Water infiltration into the soil results from rather arbitrary patterns of rainfall or from the various types of irrigation. The rate of water evaporation from soil may vary significantly according to climatic conditions and the moisture status of the soil. At the lower side of the root zone, boundary conditions may differ substantially according to local conditions with features like a shallow water table or easy drainage to the subsoil. A very important sink term for the liquid in soil results from uptake by plant roots. For an accurate description of the movement of many pesticides in soil and their uptake by plants under field conditions, moisture behaviour in soil has to be tracked closely.

The flux, J_w , of liquid in soil under field conditions can best be connected to the gradient in hydraulic head H_h :

$$J_w = -K(\phi_w) dH_h/dx$$

The use of dH_h/dx as the driving force has the advantage that computations can be performed for heterogeneous soils. The hydraulic head is composed of pressure head H_p and gravitational head H_g : $H_h = H_p + H_g$. The value for the hydraulic conductivity $K(\phi_w)$ is strongly dependent on the volume fraction of liquid in soil: $K(\phi_w)$ decreases sharply when ϕ_w becomes lower. The relationship between pressure head H_p , and the volume fraction of moisture ϕ_w , is the soil moisture characteristic. Experimental relationships for hydraulic conductivity and pressure head were given by Rijtema (1969) for 20 Dutch soils. Graphical compilations of these relationships were given by Stroosnijder (1976). The computation of the separate liquid fluxes, J_w , at various positions and times is of utmost importance for the description of convective transport of dissolved substances in soil.

The conservation equation contains a transport and a consumption term:

$$\partial \phi_w / \partial t = - \partial J_w / \partial x - (\partial \phi_w / \partial t)_{\text{cons}}$$

Usually, the most important consumption term under field conditions is uptake of liquid by plant roots; the transfer of water from the liquid to the gas phase is another one. For the insertion of this term in the computations, particulars about the plants have to be known such as the distribution and activity of the root system

with position and time. the transpiration demand and the availability of the moisture at various positions in soil.

Detailed descriptions of water flow in the root zone using computation models were presented by Van Keulen (1975) and by Stroosnijder (1976). Instances of quantitative description of transient soil-water flow in computations on the movement of pesticides in soil were given by Davidson et al. (1975b). and by Leistra and Dekkers (1976).

Convective transport and hydrodynamic dispersion

Convective transport of compounds in soil is usually described with the following flux equation:

$$J_{p,conv} = J_w c_w - D_{disp} \frac{dc_w}{dx}$$

The concentration in the liquid phase, c_w , is carried along with the areic flux, J_w , of the liquid phase in soil. The spreading by hydrodynamic dispersion is described on the analogy of diffusion processes. This dispersion results from differences in flow velocity in different parts of the liquid-filled pore system (Biggar and Nielsen, 1967). Much effort is devoted to the assessment of values for the dispersion coefficient D_{disp} under conditions of unsaturated soil water flow (Frissel et al., 1974). In a range with moderate fluxes, the following relationship often gives a usable approximation: $D_{disp} = L_d J_w$, with L_d being the dispersion distance. The spreading effect of hydrodynamic dispersion is so important that it should never be neglected in computations on pesticide movement in soil.

Diffusion in the liquid and gas phases

With pesticides in soil under field conditions, diffusion nearly always plays an important part (Hamaker, 1972). The corresponding flux equations are:

$$J_{p,dif,w} = - D_{por,w} \frac{dc_w}{dx} \quad \text{and} \quad J_{p,dif,g} = - D_{por,g} \frac{dc_g}{dx}$$

The diffusion coefficients $D_{por,w}$ and $D_{por,g}$ for a compound in the liquid- and gas-filled pore systems, respectively, are complex quantities (Jackson et al., 1963). Starting from the coefficients for diffusion in water and air, a reduction has to be introduced to take into account the volume fractions ϕ_w and ϕ_g . In addition, the values of the diffusion coefficients are reduced by the geometric complexity of the phases, which is accounted for by tortuosity factors. Diffusion coefficients of pesticides in air are about 10^4 times the values in water. Diffusion in the gas phase may dominate if the partition water/air, $K_{w/g}$, is about 10^4 or lower. However, this will also strongly depend on moisture and structure status of the soil (Graham-Bryce, 1969). It is safe to check the importance of vapour diffusion for spreading in soil and for volatilization. With soil fumigants, vapour diffusion is the predominating transport mechanism in soil.

Kinetics of adsorption and desorption

As a first approximation in transport studies, an instantaneous establishment of adsorption/desorption equilibrium is usually assumed. In recent years, an increasing awareness of the importance of the kinetics of these processes (Hamaker and Thompson, 1972) has prompted closer investigation. In experiments of short duration with fast percolation of water through soil columns, the mobility of herbicides is found to be much higher than with slow percolation (Davidson and Chang, 1972; Davidson and McDougal, 1973; Davidson et al., 1975). The mobility measured with soil-layer chromatography (duration a few hours) was found to be much higher than the mobility under field conditions. With percolation of soil columns in the laboratory, the mobility of flumeturon was considerably greater than in the field (Gerber and Guth, 1975). Only part of this difference seems to be attributable to differences in

water flow. Adsorption coefficients are usually measured under slurry conditions, a system which deviates significantly from that in the field. The question is how the observations on mobility and adsorption can be quantitatively interrelated. A similar question is how the adsorption/desorption kinetics under field conditions should be described.

Because knowledge on sorption kinetics is limited, usually first-order rate equations for the continuous processes of adsorption and desorption are used:

$$d(e_b S)/dt = k_a \phi_w c_w - k_d e_b S$$

with k_a and k_d being the rate coefficients for adsorption and desorption, respectively. This equation is also presented in the following form:

$$dS/dt = k_d \left[(k_a \phi_w / (k_d e_b)) c_w - S \right]$$

At equilibrium, $dS/dt = 0$, so $S = (k_a \phi_w / (k_d e_b)) c_w = K_{s/w} c_w$. The values of k_a and k_d determine the equilibration rates, but the ratio k_a/k_d is fixed if a distribution coefficient at equilibrium, $K_{s/w}$, is assumed. The tracing of realistic values of rate constants like k_a and k_d for pesticides moving in undisturbed soil is a main challenge for model builders. Adsorption and desorption rates measured in slurry-type experiments are probably not representative of soil water systems in situ.

The physico-chemical basis of adsorption/desorption kinetics should be studied in more depth. The diffusion-controlled part lends itself very well for unravelling with computation models. This type of more fundamental work is especially needed for a better comprehension of sorption kinetics under divergent soil conditions.

The liquid phase in soil could be imagined to be divided into a mobile and a stagnant part. Sorption equilibrium with the surfaces in close contact with the mobile part of the liquid can be attained quickly. For equilibration with the less accessible sorbing sites, diffusion through the stagnant part of the liquid phase must occur, which is a comparatively slow process. The use of empirical quantities, like the ratios between the fractions occupied by the sub-phases in relation to the water flux and the geometry of the liquid-filled pores, seems to be inevitable (Van Genuchten et al., 1974; Van Genuchten et al., 1976).

The conservation equation

The various differential equations describing transport, conversion and uptake are brought together in a central conservation equations such as:

$$\partial c_m / \partial t = - \partial J_{p,conv} / \partial x - \partial J_{p,dif,w} / \partial x - \partial J_{p,dif,g} / \partial x - R_{conv} - R_{upt}$$

The amount of pesticide, c_m , per volume of soil medium changes at a rate determined by the rates of supply and discharge due to transport, and by the rates of decline due to conversion and uptake. Decisions have to be made on the type of relationships to be employed in the situation under investigation to make solution of this equation possible. Relationships are needed between the concentrations in the various phases. The rate of uptake is often related to the concentration in the liquid phase and the rate of water transpiration. A first-order rate equation describing the rate of conversion in soil could read: $R_{conv} = k_{conv} c_m$.

MODELING PROCEDURES

Analytical solutions

After describing the relevant differential equations, a choice has to be made between different solution procedures. To obtain an analytical solution, the system

has to be simplified substantially. Suppositions of frequent occurrence are: 1) the initial and boundary conditions are straightforward, 2) the soil medium is homogeneous, 3) there is a steady-state water flow at constant soil moisture content, 4) no irregular source and sink terms exist, 5) the interactions between pesticide and soil can be described with simple relationships. The system can then be schematized to arrive at equations like the following:

$$\partial c_w / \partial t = -J_w^* \partial c_w / \partial x + D_{spr}^* \partial^2 c_w / \partial x^2$$

with $J_w^* = J_w / \text{Cap}_w$ and $D_{spr}^* = D_{spr} / \text{Cap}_w$. The pesticide capacity factor of the soil is defined by $\text{Cap}_w = \phi_g / K_w / \rho_s + \phi_w + \rho_b K_s / w$.

One of the best usable analytical solutions was described by Brenner (1962). Results with this and other analytical solutions applied to the pesticide movement in soil were compared by Leistra (1973). Most of the more recently described analytical solutions involve too much simplification of some of the phenomena. Analytical solutions are especially useful for the description of systems that can be sufficiently simplified, for checking numerical solutions under simplified conditions, and for studying situations in which numerical solutions present problems.

Numerical solutions

With numerical solution procedures, the differential equations are converted into finite-difference equations (Smith, 1969). The soil system is divided into computation compartments of thickness Δx , while the time is divided into time intervals Δt . Values for the concentration of the substance are computed at specific positions and times. With numerical solutions one may start from an overall partial differential equation like:

$$\partial(\text{Cap}_w c_w) / \partial t = -\partial(J_w c_w) / \partial x + \partial(D_{spr} \partial c_w / \partial x) / \partial x - k_{conv} \text{Cap}_w c_w$$

This equation holds for a heterogeneous soil system with variable coefficients Cap_w , J_w , and D_{spr} , and conversion at a first-order rate with constant k_{conv} . A possible finite-difference solution for such an equation is given by Leistra (1973).

Characteristic of the so-called computer simulation techniques is that the computations start directly from the individual differential equations for each of the relevant processes. Starting from the situation at time t , the rates of the changes are computed. These rates are then integrated over a small time interval Δt , after which the new situation at time $t + \Delta t$ can be computed. The great flexibility and surveyability of the computer programs are convenient features when complicated soil systems under field conditions have to be simulated. The problem may be presented to the computer in languages like FORTRAN or CSMP. A number of built-in sub-routines makes CSMP specially suitable for this type of work (IBM, 1972). Detailed descriptions of the application of CSMP in studies of the transport of substances in soil were given by De Wit and Van Keulen (1972), and by Frissel and Reiniger (1974). This computer simulation approach was used in recent studies of pesticide movement in soils (Van Genuchten and Wierenga, 1974; Leistra and Frissel, 1975; Leistra and Dekkers, 1976).

CONCLUDING REMARKS

The application of computation models in studies of pesticide movement in soil is still in full development. It is only recently that computation models have been utilised to a somewhat larger degree in this research area. In several instances use is limited to the quantitative analysis of laboratory experiments but the application to pesticide behaviour under field conditions is increasing. This has been made possible by the availability of high-speed computers and the development of suitable software. There is still much work to be done in modeling pesticide behaviour in the

soil, so the development and checking of models should be continued with increased effort. Only by taking full advantage of the results from related disciplines, can sufficient progress be made.

List of symbols and units

J_w	= areic volume flux of liquid, $m^3(\text{liquid}) m^{-2}(\text{medium}) \text{day}^{-1}$
$J_{p,\text{conv}}$	= areic substance flux by convection, $\text{mmol } m^{-2}(\text{medium}) \text{day}^{-1}$
$J_{p,\text{dif},w}$	= areic substance flux by diffusion in the liquid phase, $\text{mmol } m^{-2}(\text{medium}) \text{day}^{-1}$
$J_{p,\text{dif},g}$	= areic substance flux by diffusion in the gas phase, $\text{mmol } m^{-2}(\text{medium}) \text{day}^{-1}$
L_d	= dispersion distance, $m(\text{medium})$
D_{disp}	= coefficient of hydrodynamic dispersion, $m^2(\text{liquid}) m^{-1}(\text{medium}) \text{day}^{-1}$
$D_{\text{por},w}$	= coefficient of diffusion through liquid phase, $m^2(\text{liquid}) m^{-1}(\text{medium}) \text{day}^{-1}$
$D_{\text{por},g}$	= coefficient of diffusion through gas phase, $m^2(\text{gas phase}) m^{-1}(\text{medium}) \text{day}^{-1}$
c_w	= substance concentration in liquid phase, $\text{mmol } m^{-3}(\text{liquid})$
c_g	= substance concentration in gas phase, $\text{mmol } m^{-3}(\text{gas phase})$
c_m	= substance concentration in medium, $\text{mmol } m^{-3}(\text{medium})$
S	= adsorbed substance concentration, $\text{mmol } Mg^{-1}(\text{soil})$
x	= depth in soil, $m(\text{medium})$
t	= time, day
ϕ_w	= volume fraction of liquid phase, $m^3(\text{liquid}) m^{-3}(\text{medium})$
ϕ_g	= volume fraction of gas phase, $m^3(\text{gas phase}) m^{-3}(\text{medium})$
e_b	= soil bulk density, $Mg(\text{soil}) m^{-3}(\text{medium})$
H_h	= hydraulic head, $m(\text{liquid height})$
H_p	= pressure head, $m(\text{liquid height})$
H_g	= gravitational head, $m(\text{liquid height})$
$K(\phi_w)$	= hydraulic conductivity, $m^3(\text{liquid}) m^{-1}(\text{liquid height}) m^{-1}(\text{medium}) \text{day}^{-1}$
k_a	= adsorption rate coefficient, day^{-1}
k_d	= desorption rate coefficient, day^{-1}
$K_{s/w}$	= sorption coefficient at equilibrium, $m^3(\text{liquid}) Mg^{-1}(\text{soil})$
$K_{w/g}$	= partition coefficient liquid/gas, $m^3(\text{gas phase}) m^{-3}(\text{liquid})$
k_{conv}	= conversion rate coefficient, day^{-1}

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