✓ AP-42 Section 9.2.2
Reference 7
Report Sect.
Reference

CHAPTER 5

Fate of pesticides in soil: predictive and practical aspects

D. J. Arnold and G. G. Briggs

INTRODUCTION

Before any novel compound is introduced into agriculture it has to undergo rigorous examination in terms of its overall safety in the environment. It is under the broad umbrella of environmental safety that the fate of the chemical in soil is

Environmental Fate of Pesticides
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examined in order to satisfy both the agrochemical company and government regulatory authorities worldwide that the product will not lead to unacceptable side effects.

Any approach to soil studies should be viewed in the context of the intended use pattern of the chemical. In this way, appropriate studies can be carried out in order to address specific needs where necessary. This approach, however, does not always meet the 'catch-all' policies of regulatory requirements. Opinions differ between particular government authorities from which has arisen increasing guideline specificity and divergence between them. This, in turn, has led to the imposition of different criteria by which pesticide behaviour is both investigated and, perhaps more significantly, interpreted.

In recent years certain pesticide regulatory requirements (for example, those involving toxicological data) have remained largely unchanged; in contrast, there has been a significant increase in requirements for information on the behaviour of pesticides in the soil environment. Two key issues have influenced this demand: (1) the potential for contamination of drinking water highlighted by the detection of certain compounds at low concentrations in ground water and (2) the search for less recalcitrance linked to an increasingly held view that persistence is an undesirable property. In both instances it is not necessarily the toxicological significance of the residue that is at issue but rather the presence of the compound *per se* at any concentration.

Methodologies for the study of pesticides in soil have developed steadily over the past 20 years or so, but how effective they are in addressing current issues is debatable. From a scientific standpoint, experiments should be designed to attempt to elucidate particular mechanisms of behaviour in soil, whether it be degradative route, adsorption or mobility, information which can be used to formulate a reasoned understanding of the behaviour of the compound in the context of environmental acceptability. Inevitably, laboratory studies provide a substantial amount of this information, but there are increasing demands to evaluate pesticides in soil both in more sophisticated laboratory systems and under actual use conditions in the field. It is easy to lose sight of the difference between laboratory and field evaluations. Laboratory studies are essential in order to provide reproducible procedures for comparative purposes. They allow manipulation of the systems in order to provide a measure of control over a particular parameter whether it be, for example, soil moisture, airflow rate or temperature. In degradation studies, laboratory data are generated principally in order to determine routes of metabolism. Conversely, field studies evaluate the net effects of all the environmental, biotic and edaphic influences on the rate of transformation and the consequent metabolites produced.

Soil is such a highly variable matrix and such is the complexity of its chemistry and biology that no amount of increased sophistication in laboratory assays can ever hope to reproduce the interactions of the pesticide, soil and climate in the field. There is, therefore, a need to return to first principles and take a closer look at the properties of the pesticide molecule itself and then to examine the influences that will affect its behaviour in the field.

MECHANISMS GOVERNING THE FATE OF PESTICIDES IN SOIL

The principal factors governing the fate of a chemical, be it xenobiotic or natural, in the field are given in Figure 1. The chemical structure defines the intrinsic properties of the compound, the soil defines the properties of the medium containing it and the climate defines the temperature, water and air fluxes. Fate is determined by the complex interactions of all three. Many reviews have been written discussing these factors (Jury *et al.*, 1987a, b; Leonard and Knisel, 1988)

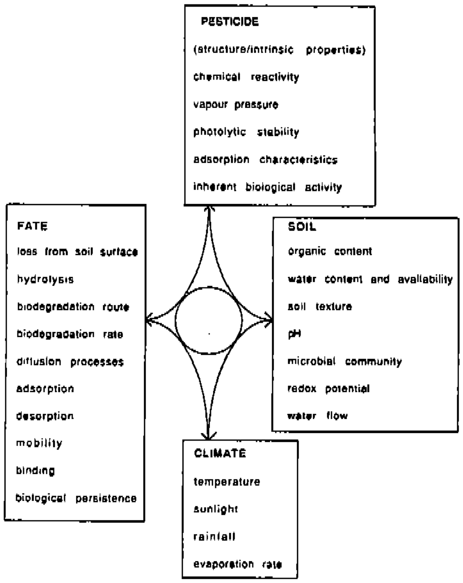


Figure 1 Factors governing the fate of pesticides in soil

and the key processes by which the fate of the chemical is defined are generally recognized to be adsorption of the chemical by the soil, volatilization of the chemical from the soil and its rate of degradation by biotic and abiotic mechanisms. These are summarized briefly below.

Adsorption

Adsorption of neutral molecules by soil is most effectively correlated with organic matter or organic carbon content of the soil. Adsorption per unit of organic carbon (K_{oc}), is relatively constant within a two- to threefold range for a particular compound in surface soils. A variety of relationships has been developed between K_{oc} and various physicochemical parameters, the most useful being with the octanol–water partition coefficient (K_{ow}). A number of log–log relationships has been defined with a range of slopes and intercepts depending on the experimental method for determining adsorption, the compounds used and the expression of the adsorption data as linear or Freundlich isotherms. All these relationships produce the same answer at $\log K_{ow} = 3$, where K_{oc} is about 500 and K_d, the soil–water partition coefficient, is about 5 for a soil with 1% organic carbon (1.75% organic matter). These values are included in several current regulatory guidelines either as triggers for further work or as indicators of preferred compound characteristics. Since the range of organic carbon in surface soils is from about 0.1% to 50%, that of K_d for such a compound in the field will be from about 0.5 to 500, a fact long recognized on herbicide labels, many of which require increased rates at organic contents up to 10% and limit use to the 1–10% range. At the low end of the range herbicide adsorption is low and depth protection of the crop may fail, whereas at the top of the range adsorption is too strong for useful biological activity.

Adsorption of neutral molecules is little affected by soil pH but this is not true for weak acids and bases where the ionized and unionized forms behave differently. By analogy with mono-cations such as ammonium and potassium, the K_d for an organic cation will be at least 100, equivalent to a neutral molecule with $\log K_{ow}$ of about 6. Such strong adsorption of the cation is effective at soil pH up to 2–3 units above the dissociation constant (pK_a) of the base. Above this pH level adsorption depends on the K_{ow} of the unionized form. K_d of di-cations is about 10000 as observed for inorganic and organic di-cations such as calcium and paraquat. Ionization of organic acids lowers $\log K_{ow}$ by 3–4 units. This alone produces a large decrease in adsorption at pH 2–3 units above the pK_a of the acid (Nicholls and Evans, 1985). A weak acid with pK_a 4 and $\log K_{ow}$ of 3 will therefore have a K_d of about 5 in a soil with 1% carbon at pH 5 but less than 0.5 at pH 7.

Mechanisms other than cation-exchange or partition-like adsorption have been proposed but not really substantiated, with the exception of the correlation of the adsorption of glyphosate with that of phosphate (Hance, 1976). The use of compounds such as the highly active sulphonylureas at very low application rates (grams rather than kilograms per hectare) may require some re-evaluation of ideas conceived for the higher rates of use.

Adsorption of aged residues appears to increase with time, leading to concepts of available and unavailable compartments (Duffy *et al.*, 1987). The nature of the unavailable compartment is not understood, but in leaching terms it can only mean that less occurs than the initial K_d would indicate.

Volatilization

Vapour losses of chemicals from soils depend on the air–soil distribution (K_{as}), the location of the chemical in the soil and the climatic factors. These factors all interact but the general features are as follows.

Volatilization from water is conveniently estimated by the Henry's Law constant (K_{aw}). In the soil–water–air system, adsorption of the pesticide by soil from the water phase lowers its concentration in the water and hence its concentration in air. The distribution of the chemical between air and wet soil is given by the air/water distribution divided by the soil/water distribution. The air–soil distribution is thus a function of water solubility, vapour pressure and soil adsorption, which can be approximately described as a function of boiling point and K_{ow} (Briggs, 1981). Vapour loss depends on the air–soil ratio, the distribution of the compound in the soil and the climatic conditions. A chemical initially below the soil surface can move to the surface under drying conditions and higher concentrations at the surface can lead to significant vapour loss (Spencer *et al.*, 1988).

Movement to the surface will depend on the soil organic matter, the K_{ow} of the compound and the water movement, so that although the physical properties can be used to describe the potential for vapour loss relatively easily (and simple laboratory experiments demonstrate it) actual losses in the field can be highly variable.

Degradation

In contrast to adsorption and vapour loss, degradation is generally a combination of both abiotic and biotic processes. The distribution and activity of soil micro-organisms will differ in laboratory and field studies and thus affect the degradation rate and possibly even the route of pesticide transformation. Under field conditions, pesticide degradation rates will vary with the influence of soil and climate as shown in Figure 1. Under constant environmental conditions in the laboratory, rates for a given chemical are likely to cover a two- to threefold range for a variety of surface agricultural soils with varying mineralogy, carbon content and pH.

The chemistry of the compound may give rise to a wider range of degradation rates under certain conditions. For example, the longer persistence of carbendazim at low pH is probably due to the strong adsorption of the weakly basic cation; the greater stability of sulphonyl ureas at high pH is due to the sulphonyl urea anion being much more hydrolytically stable than the unionized form.

Temperature affects microbial activity, resulting in an increase in degradation rate of about 2.5–3 for each 10 °C rise in temperature. Rates also increase with increased availability of moisture from wilting point to field capacity. In the field, temperature and moisture content are constantly changing. This results in fluxes in microbial and chemical reactivity of the soil. Simulation models based on laboratory dissipation rates at various temperatures and moisture contents (Walker, 1987) indicate that under Northern European conditions a chemical with a half-life of 30 days in the laboratory at 20 °C will have a half-life under outdoor conditions of 1–2 months in the summer and 4–6 months in the winter. In practice, less persistence is often observed in the field. Seasonal variability in other climates would depend on rainfall and temperature.

Fate

It is the combination of events whether climatic, soil-derived or the inherent properties of the chemical itself that determines what will happen to that compound. The complexities of the interactions are indicated in Figure 2. Thus, for example, a centimetre of rain may have the following effects: (1) contribute to leaching only if it falls on an already wet soil at low temperature, (2) lead to a pulse of vapour loss from an otherwise dry soil, (3) result in a surge of microbial activity followed by an enhanced rate of degradation caused by the provision of moisture in the rhizosphere in a situation of low water availability.

Similarly, the fate of a chemical will be substantially influenced by events: (1) a compound applied to dry soil with no rainfall will not leach, irrespective of its relative persistence, (2) a short-lived compound applied under cool, wet conditions may leach to lower soil horizons where microbial activity is reduced and thereby its persistence increased, (3) a relatively non-mobile parent compound may rapidly hydrolyze in wet conditions to a more mobile metabolite which, in turn, is rapidly degraded during its path down the soil profile.

It is, of course, not possible to simulate the complex interactions taking place in any one study or even in a series of studies; however, computer models are now being increasingly used to predict a measure of the likely fate of a compound under defined conditions. Predictions are generally based upon a combination of simple physical and chemical characteristics of the molecule such as vapour pressure, K_d, $t\frac{1}{2}$, and more complex inputs which are required to assess accurately soil wetting and drying and water flow. The physical and chemical properties of the molecule are therefore an essential first indication of the likely dissipation of the molecule in soil. When these components are combined with a preliminary half-life in soil they allow a better assessment of the likely fate of the compound and potential products arising from its transformation. Some examples of such predictions are given below.

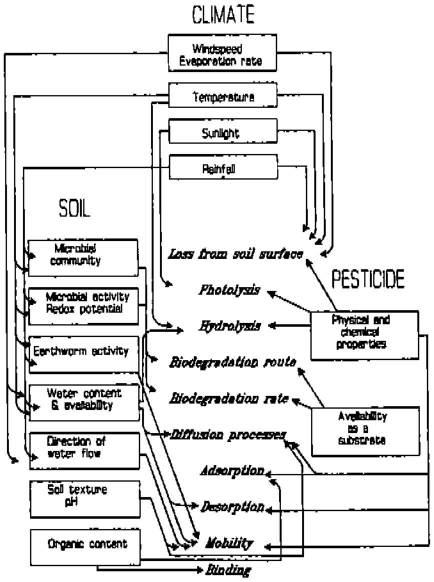


Figure 2 Interactions influencing the fate of the pesticide

In Figure 3 vapour pressure (or boiling point) is plotted againt log K_{ow}. Taking an air/wet soil distribution of 10^{-6} as an indicator of potential vapour loss, log $K_{ow} = 3$ as the upper limit for significant potential leaching and log $K_{ow} = 1$ as the upper limit for potentially easily leached compounds, a rapid assessment of potential behaviour is obtained. The application of this technique to a number of compounds and compound classes is shown in Figure 4. Figure 5 illustrates how log K_{ow} (or K_d for cations) and soil half-life under standard conditions of temperature (20–25 °C) and low moisture tension are related to current regulatory requirements.

For the present discussions we have taken four hypothetical structures

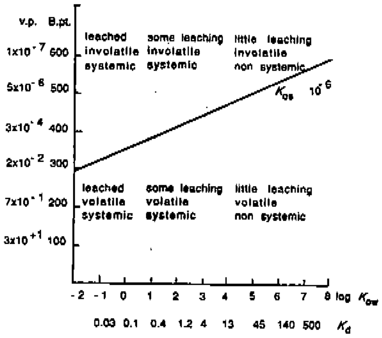


Figure 3 Physicochemical properties and behaviour in soil

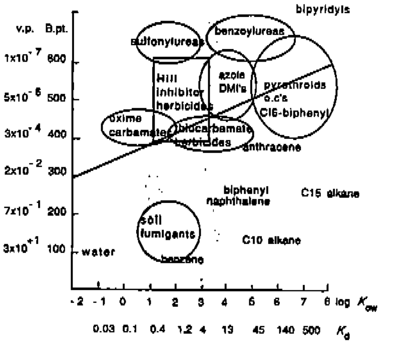


Figure 4 Physicochemical properties of major classes of chemicals

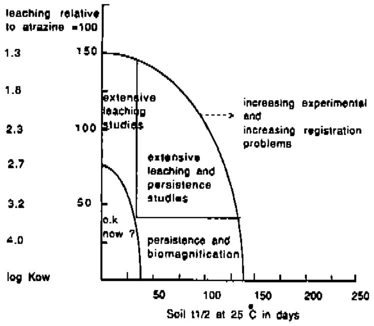


Figure 5 Registration criteria based on octanol–water partition coefficient and soil half-life

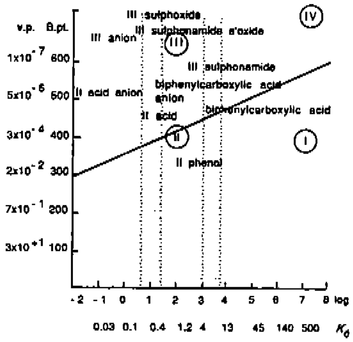
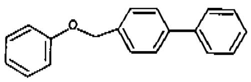


Figure 6 Physicochemical properties of hypothetical compounds and their metabolites

containing familiar structural fragments whose properties and metabolic pathways can be reasonably predicted as indicated in Figure 6. Areas of uncertainty or concern can be identified from the predictions and key experiments designed to elucidate the fate of the chemical. Such an approach is likely to provide more significant information than that obtained using the usual checklist of simple protocols which may have no relevance in certain areas of chemistry.

HYPOTHETICAL STRUCTURES AND BEHAVIOUR IN SOIL

Compound I



Physicochemical properties based on molecular structure:

Log K_{ow}	5.7
Vapour pressure	4×10^{-5} mmHg
Boiling point	450 °C
Water solubility	1 mg l^{-1}
K_{aw}	1×10^{-3}
K_{as}	2×10^{-5}
Soil K_d (2% organic matter)	100

Predicted behaviour in soil

Adsorption and mobility

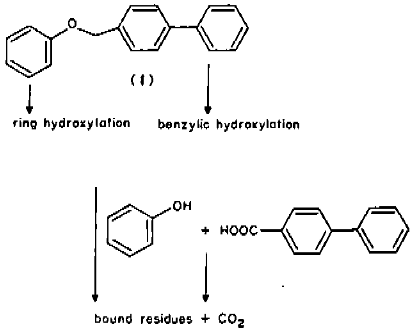
The compound is highly lipophilic and insoluble in water, leading to strong adsorption to soil as indicated by the high K_d value. The compound is therefore not expected to leach. The high lipophilicity of the compound indicates that although it may be taken up from soil by plant roots it will not be translocated to the leaves as the parent molecule. Mobility is, however, likely in the vapour phase due to the high predicted vapour pressure. Combined with low water solubility and high lipophilicity, vapour loss from the soil surface may be expected. Consequently, the compound may exhibit significant vapour transport to crop vegetation above ground if applied to the soil surface under warm conditions and moist surface soil. If incorporated below the surface, the high K_d indicates little redistribution towards the surface during water evaporation.

Persistence

The parent compound, acting as an substrate for oxidation, will be degraded under aerobic conditions. A 'predicted' half-life may be 30–60 days in warm, moist soil. Conversely, under anaerobic conditions, the compound will be more recalcitrant. No hydrolytic reactions in the normal soil pH range are possible and the usual hydrolysis studies would be of little value in this case. Most regulatory agencies, however, would require them.

Metabolic route

Ring hydroxylations to phenols would result in the formation of bound residues as well as further metabolism to CO_2. Benzylic hydroxylation would lead to phenol and biphenylcarboxylic acid, both of which could be readily further metabolized to bound residues and CO_2 (Scheme 1).



Fate in soil—proposed studies based on physicochemical indications

Synopsis

In terms of degradation in soil, recalcitrance may be of concern at low temperatures and under flooded soil conditions. Recalcitrance may give rise to vapour loss from the soil surface. Leaching is unlikely to occur to any degree.

Because the molecule will cleave at the ether bridge two radiolabelled samples would be required for experimental work: one ^{14}C-labelled in the phenoxy ring ring and the other in diphenyl moiety.

Proposed studies

Degradation. Degradation in two soils: (1) low organic matter sandy soil; (2) high organic matter loamy soil. Two conditions should be used:

(a) Conditions: Temp. 20 °C
 Moisture: 40% moisture-holding capacity (MHC)
 Aerobic incubation under enclosed conditions to trap volatile metabolites.
(b) Conditions: Temp. 20 °C
 Moisture: Flooded soil
 Incubation under enclosed conditions to trap volatile metabolites.

If rapid degradation takes place as predicted then a half-life of less than 90 days would be expected with substantial mineralization to $^{14}CO_2$. A further study at low temperature may be justified if the product were to be used for autumn applications in northern regions. Results from flooded soils giving reduced partial pressure of oxygen (flooding maintained from 1 day after treatment) will confirm stability of the molecule with probably little $^{14}CO_2$ evolution.

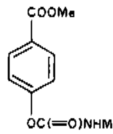
Leaching. Mobility should be studied in the same soils and at the same temperature as above using compound applied 'aged' and 'unaged' to soil columns. Using fresh soils, degradation will take place during the study. Low mobility of metabolites is expected if hydroxylation takes place leading to mineralization to $^{14}CO_2$; otherwise some mobility of the biphenyl acid may occur in the sandy soil. Collection of leachates will determine this and indicate the need for further outdoor investigations such as lysimeter studies.

Adsorption/desorption. K_d values can be predicted from log P and will not add anything that cannot be shown from leaching studies.

Volatility. Due to possible vapour losses from soil, volatilization of ^{14}C-labelled compound (one position only) should be carried out in one soil at high and low temperature.

Field studies. Inevitably, some field evaluation of pesticide dissipation is required. Problem areas such as cold, wet conditions should be included in the choice of sites if the normal use pattern and persistence studies indicate that the compound would be present under such conditions.

Compound II



Physicochemical properties based on molecular structure:

Log K_{ow}	1.5
Vapour pressure	5×10^{-4} mmHg
Boiling point	390°C
Water solubility	$3\,g\,l^{-1}$
K_{aw}	9×10^{-7}
K_{as}	1×10^{-6}
Soil K_d	1.0

Predicted behaviour in soil

Adsorption and mobility

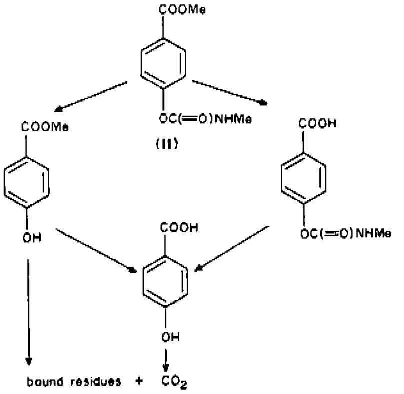
The compound is unlikely to be adsorbed to soil to any great extent. The K_d value and log K_{ow} indicate a potentially mobile compound, although leaching of this compound would be attenuated in warm soil conditions by rapid degradation via biological hydrolysis of the ester moiety. The resulting acid (pK_a 3.9), however, would also be mobile (log K_{ow} 1.2) at all soil pH values. Both the acid and the ester have the potential to be taken up by plant roots but further breakdown would limit this. In colder weather, ester hydrolysis would be reduced giving rise to possible movement of the parent or acid to lower soil horizons or groundwater. Non-biological hydrolysis of the carbamate group would be faster than the ester. The high water solubility will limit vapour loss from the soil despite the potentially high volatility of the parent.

Persistence

Persistence is governed by the rate of hydrolysis, particularly of the ester. Low persistence is likely in warm, moist soils with a predicted 'half-life' of 14 days. In cold conditions longer persistence is likely.

Metabolic route

Ester hydrolysis will probably be the major route in biologically active soils but in subsoils non-biological hydrolysis of the carbamate group would be faster at higher soil pH. The phenol would be readily degraded and form bound residues. Hydrolysis of both functional groups leads to 4-hydroxybenzoic acid, a readily degraded natural product (Scheme 2).



Fate in soil—proposed studies based on physicochemical indications

Synopsis

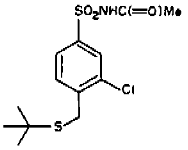
If applied in winter then mobility of the parent ester and more particularly the carboxylic acid would be of concern. A radiolabelled molecule (^{14}C-ring) label would be required.

Proposed studies

Degradation in one soil (loamy sand) at high and low temperature would enable determination of the metabolic route. 'Aged' leaching studies in a low organic matter sand and a heavy soil will give the relative mobility of the parent and carboxylic acid. Lysimeter studies using autumn-applied radiolabelled chemical in two soil types under outdoor conditions would provide the best indicator of the likely problems with groundwater contamination. Utilizing appropriate crops in replicate lysimeters may assist in determining the degree of plant uptake. Adsorption studies would not be feasible due to rapid ester hydrolysis.

For possible glasshouse use, a laboratory volatility study using a low soil moisture and high and low temperature would demonstrate the potential for vapour loss from soil of the parent compound under unfavourable biodegradation conditions. Soil dissipation studies in the field (winter and summer applications) will determine rates of compound loss under normal use conditions.

Compound III



Physicochemical properties based on molecular structure:

Log K_{ow}	2.6
Vapour pressure	$< 10^{-7}$ mmHg
Boiling point	650 °C
Water solubility	(20 mg l^{-1} pH 4, 2000 mgl^{-1} pH 7)
K_{aw}	10^{-8}
K_{as}	10^{-8}
Soil K_d	Range 1 (pH 7) – 3 (pH 5)
pK_a	4.5

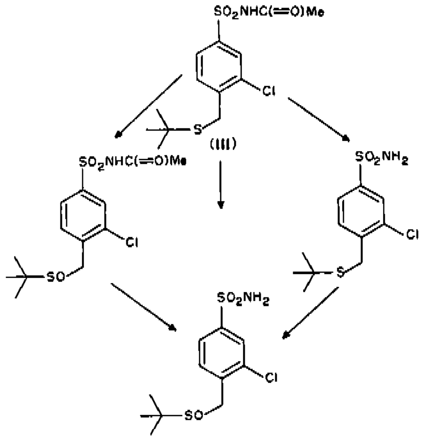
Predicted behaviour in soil

Adsorption and mobility

The compound is strongly influenced by pH, behaving as a weak acid. At low pH where the molecule is largely undissociated there is increased lipophilicity and decreased water solubility. Mobility is likely to be less than at higher pH where increased dissociation will lead to lowered lipophilicity and a lower soil adsorption coefficient (K_d). In the ionized form the molecule has the potential to move by mass flow to ground water.

Persistence and metabolic route

Hydrolysis of the acetyl sulphonamide to the slightly more lipophilic sulphonamide (log K_{ow} 2.9) would be much slower for the anion than for the undissociated molecule and therefore would be slower at high pH. Oxidation of the thio ether to form the sulphoxide should occur readily, although hindered sulphoxides would be only slowly further oxidized to the sulphones. Because log K_{ow} is now about 0.5 for the acetylsulphonamide sulphoxide and the sulphonamide sulphoxide, both will be highly mobile whatever the soil pH (Scheme 3).



Fate in soil—proposed studies based on physicochemical indications

Synopsis

The compound and its metabolites present a problem in terms of persistence and mobility and possible contamination of following crops. In summer conditions (warm climates) where the rate of soil/plant evapotranspiration balances the downward flow of water the chemical is likely to be more rapidly dissipated. Ground water contamination is clearly a risk in alkaline soils and at lower soil depths little degradation will occur.

Proposed studies

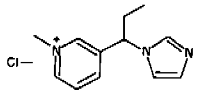
Degradation. Laboratory degradation studies should be targeted at soils with contrasting pH. Using ^{14}C-ring labelled compounds, metabolic profiles may be determined in one or two soils, light acid soil and heavy clay loam for example, while degradation rates may be examined in additional soil types. Rotational crop studies would be required in different soils to assess the potential for uptake of soil residues by plants.

Mobility. In view of the predicted mobility problems, lysimeter studies would provide the most appropriate mechanism for examining degradation and mobility in soils of contrasting pH. Using ^{14}C-material, the distribution of the compound and any degradation products can be examined at selected time intervals both in the soil and in the leachates. As the compound has a low vapour pressure no losses from the soil surface would be expected and mineralization to $^{14}CO_2$ would probably occur.

Adsorption. Laboratory studies would give results dependent upon pH. Low K_d values would be expected and the information gained would be of little value in comparison to measured soil mobility.

Field studies. It is likely that dissipation studies in a range of soils and climatic conditions would be needed in order to cover the patterns of major crop use.

Compound IV



Physicochemical properties based on molecular structure:

Log K_{ow}	-2
Water solubility	$50\,g\,l^{-1}$
Vapour pressure	Negligible
K_{aw}	10^{-10}
K_{as}	10^{-10}
Soil K_d	100–10000
	pH 9 pH 7
pK_a (imidazole ring)	6.0

Predicted behaviour in soil

The principal feature of the compound is strong adsorption to soil. In all soil types the compound is likely to be strongly bound, with K_d ranging from *ca.* 100 in highly alkaline soils to greater than 10 000 in neutral and acid soils. Negligible degradation is likely to occur and no leaching is predicted despite the high water solubility of the salt. Biological activity in soil would be undetectable.

Proposed studies

Laboratory studies should be designed to examine soils with low cation exchange capacity and to determine degradation of the radiolabelled compound in both aerobic and flooded soils. ^{14}C-Labelling the imidazole ring should allow the detection of any $^{14}CO_2$ as mineralized ^{14}C arising from ring opening. Soil adsorption studies should be carried out to determine relative K_d values in light–heavy soils. Results will confirm predicted binding and should obviate the need for laboratory leaching studies.

Behaviour of the chemical in the field will be of principal concern and ^{14}C-radiolabelled 'small plot' treatments may be an appropriate means of determining dissipation and availability of the 'bound' material to relevant crops *in situ.*

THE REGULATORY INFLUENCE

Highly standardized procedures are frequently required in studies for regulatory authorities where particular properties of a pesticide are to be evaluated as, for example, in the OECD guidelines (OECD, 1981). While such protocols are accepted for determining, for example, solubility in water, vapour pressure and so on, they are not applicable *in the same way* to the study of biological matrices such as soil or sediment/water. There is, however, an increasing tendency towards 'checklist' criteria even in the area of metabolism studies. This can be illustrated by the comment in EPA Fact Sheet Number 2, 30 March 1984, on simazine, which reads 'The available data are insufficient to fully assess the environmental fate of simazine', and indicates among other data requirements a need for aerobic soil metabolism and leaching and adsorption studies, subjects on which there are hundreds of papers in the scientific literature (EPA, 1988).

Requirements differ from one authority to another, and these differences can be

Table 1 US requirements for soil metabolism studies

Soils	Usually two contrasting soils typically of the area of use
Moisture	75% of field capacity at 0.33 bar
Temperature	One temperature between 18 and 30° C
Aeration	Aerobic and anaerobic (usually after 30 days aerobic incubation or one half-life)
Incubation	One year or until patterns of decline are established for the parent compound and its major metabolites
Analysis	Require identification of residues down to 0.01 $\mu g\,g^{-1}$
Additional state requirements	Arizona—pH range limited to 6.5–8.5—organic carbon ≤ 2.6%

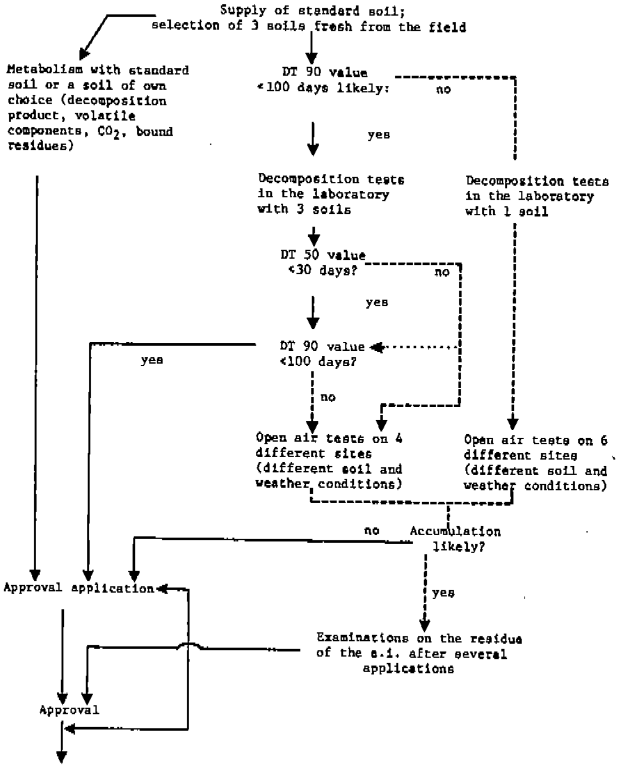


Figure 7 Scheme for determining the degradation of plant protection products in soil (adapted from BBA Guideline, Part IV, 4–1)

shown by examples. The 'fate in soil' requirements for the USA Environmental Protection Agency (EPA) and the West German Biologische Bundesanstalt (BBA) are shown in Table 1 and Figure 7, respectively (EPA, 1982; BBA, 1986). Both schemes are guided by 'half-life' or 'disappearance times', although BBA criteria are much more specific where the assumption is made that any compound with a DT_{50} of > 30 days and a DT_{90} of > 100 days is a persistent molecule triggering extensive field evaluation. Protocols for laboratory studies are also specific and vary from country to country; for example, with reference to incubation conditions such as soil moisture content and temperature. In laboratory degradation studies, the principal aim is to examine routes of metabolism. The justification for a lower temperature should be on the need to determine intermediates in a breakdown pathway which may otherwise be transient at higher temperatures. Pesticide behaviour influenced by climate can be evaluated in outdoor studies. The temperature range for EPA soil studies is 18°–30° C while BBA prefer 20 °C. However, lower temperature investigations are additionally required by West Germany (10 °C) while in Canada, by comparison, the recommendation is between 4° and 8 °C. It is academic as to whether a 2 °C shift in temperature will make a significant difference to the outcome of a soil-degradation study, but this is, nonetheless, an example of the disparity in approach.

Both EPA and BBA place strong emphasis on column leaching studies to demonstrate mobility in soil. Both guidelines require evidence of parent compound mobility and the study of the mobility of parent and degradation products following pre-incubation or 'ageing' in soil. The use of a low organic matter content sand is required to demonstrate movement in a low sorptive capacity soil. The BBA, however, require leaching comparisons in three standard soils Speyer 2.1, 2.2 and 2.3 (BBA, 1984). As these will have been supplied air dried, sieved and stored for any length of time, negligible microbial activity may be expected. Speyer soil 2.1 is additionally required for use in 'aged' leaching studies, where the principal aim is to examine the mobility of both parent compound and transformation products. The variability in these soils (up to threefold in organic matter content and a pH range from 5.5 to 7.5) must create large variations in the results of leaching tests particularly for weak acids. For example, weak acids with pK_a in the range 4–6, such as compound III, would not be leached at pH 5.5 but would be at pH 7.5. Hence the system can effectively manipulate the outcome of the study.

It is therefore debatable whether or not such studies are really suitable for the investigation of compound mobility. Wherever possible, the same soil types should be used in both laboratory and outdoor investigations in order to compare behaviour between experimental systems. Batch equilibrium studies are recommended for the determination of adsorption/desorption of compounds and the method is a commonly used technique, relying on the stability of the molecule during the equilibration period. The method is, however, unsuitable for readily hydrolysed compounds. Furthermore, aseptic techniques are required to limit degradation of compounds liable to rapid microbially mediated transformations.

Space does not permit discussion of other aspects of soil regulatory requirements, such as anaerobic soil studies and sediment/water systems. The recommendation of particular methodologies, however, requires further development and investigation within the scientific community.

SUMMARY AND CONCLUSIONS

There can be no absolute certainty of the way in which a particular pesticide will behave in soil but uncertainty is reduced by the execution of a sufficiently comprehensive series of investigations to determine patterns of dissipation, routes of metabolism and the magnitude of terminal residues. As we have attempted to demonstrate, many of the potential difficulties in assessing the behaviour of a compound in soil can be identified from the properties of the molecule itself. It is, however, not suggested that predicted behaviour based on physicochemical data should replace appropriate experiments but rather that they should enable research to be directed towards the highlighted problem areas. In theory, the physiochemical properties of a chemical should enable the selection of least problematic compounds well in advance of their development as marketable agrochemicals, but, as with many compounds, a high degree of efficacy may be accompanied by a particular 'negative' property such as persistence in soil.

Whatever the features of a particular compound, in order to achieve registration, regulatory guidelines for evaluating the pesticide in soil will generally be followed, although satisfaction of a regulatory guideline requirement may not address in the most effective way those issues which require investigation. The problem is one of the philosophy behind the regulations combined with the interpretation of data provided. It is here that differences of opinion guide the decision-making process and what may be deemed acceptable by one authority may be unacceptable to another.

If one of the four example compounds cited in this chapter were to be submitted for registration, how would it be viewed in the light of its fate in soil? Compound IV was predicted to be strongly adsorbed to soil, to be slowly degraded and not to leach. It would not, therefore, be a ground water contaminant. Even if studies showed that the compound had no biological activity in soil and was not translocated through uptake from plant roots, the fact that it was present as an inactive moiety would still be considered as highly undesirable by some registration authorities. Any amount of further investigation would not detract from the fact that the molecule persisted, albeit strongly bound to soil organo/clay complexes. Persistence, however, should only be an issue of major concern when accompanied by long-term biological effects. It is unlikely that, for example, organochlorine compounds would be registered for widespread use in the current light of our increased awareness of environmental safety.

There is also a distinct tendency for regulators to focus on specific trends. In the

1960s it was insecticide persistence; in the 1970s it was carry-over of plant growth regulators; in the 1980s it was ground water pollution by herbicides. We predict that volatilization will be the next major issue to confront the agrochemical industry—a subject that is not well understood and little researched (Travis and Hattemer-Frey, 1988). Whereas the potential for loss of the pesticide from soil and transport in the vapour phase may be recognized from the physicochemical properties of the molecule, current methods of determining the fate of agrochemicals in soil may not be adequate to allow extrapolation to particular use situations. Perhaps it is now time to develop appropriate and realistic methodologies to examine the phenomenon before inflexible protocols become part of the regulatory process.

REFERENCES

BBA (Biologische Bundesanstalt für Land und Forstwirtschaft) (1984). 'Examination of the seepage behaviour of agrochemicals', *Merkblatt No. 37*, 3rd edn.

BBA (Biologische Bundesanstalt für Land und Forstwirtschaft) (1986). *Guidelines for the Official Examination of Plant Protection Products*, Part IV, 4–1, Braunschweig, West Germany.

Briggs, G. G. (1981). 'Relationships between chemical structure and the behaviour and fate of pesticides', *Proc. British Crop Protection Conference–Pests and Diseases*, III, 701–10.

Duffy, M. J., Hanafey, M. K., Linn, D. M., Russell, M. H., and Peter, C. J. (1987). 'Predicting sulfonylurea herbicide behaviour under field conditions', *Proc. British Crop Protection Conference—Weeds*, II, 541–7.

EPA (1982). *Pesticide Assessment Guidelines*, subdivision N-Chemistry and Environmental Fate, US Environmental Protection Agency, Washington, DC.

EPA (1988). *Pesticide Fact Handbook*, pp. 703–7, Noyes Data Corporation, Park Ridge, New Jersey.

Hance, R. J. (1976). 'Adsorption of glyphosate by soils', *Pestic. Sci.*, 7, 363–6.

Jury, W. A., Winer, A. M., Spencer, W. F., and Focht, D. D. (1987a). 'Transport and transformations of organic chemicals in the soil–air–water ecosystem', *Rev. of Environ. Contam. and Toxicol.*, 99, 119–64.

Jury, W. A., Focht, D. D., and Farmer, W. J. (1987b). 'Evaluation of pesticide groundwater potential from standard indices of soil-chemical adsorption and biodegradation', *J. Environ. Qual.*, 16, 422–8.

Leonard, R. A., and Knisel, W. G. (1988). 'Evaluating groundwater contamination potential from herbicide use', *Weed Technol.*, 2, 207–16.

Nicholls, P. H., and Evans, A. A. (1985). 'Adsorption and movement in soils of chlorosulfuron and other weak acids', *Proc. British Crop Protection Conference—Weeds*, I, 333–9.

OECD (Organization for Economic Co-operation and Development) (1981). *Guidelines for Testing of Chemicals*, OECD, Paris.

Spencer, W. F., Cliath, M. M., Jury, W. A., and Lian-Zhong, Z. (1988). 'Volatilisation of organic chemicals from soil as related to their Henry's Law constants', *J. Environ. Qual.*, 17, 504–10.

Travis, C. C., and Hattemer-Frey, H. A. (1988). 'Uptake of organics by aerial plant parts: a call for research', *Chemosphere*, 17, 277–83.

Walker, A. (1987). 'Evaluation of a simulation model for prediction of herbicide movement and persistence in soil', *Weed Res.*, 27, 143–52.

CHAPTER 6

The fate of pesticides in aquatic ecosystems

J. Miyamoto, N. Mikami and Y. Takimoto

INTRODUCTION

Pesticides afford remarkable benefits to mankind not only by increasing crop yields and protecting forests but also by controlling arthropod vectors of serious human disease. It is well known, however, that residues of persistent pesticides, especially those of organochlorine insecticides, are found in terrestrial and aquatic environments, including their constitutive organisms (Edwards, 1976; Murty, 1986). Since these chemicals are highly lipid soluble, lengthy exposure to them results in their high accumulation in organisms, and hence they may produce adverse effects on ecosystems. These phenomena are clearly demonstrated in the hydrosphere rather than in the atmosphere and the lithosphere

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ENVIRONMENTAL FATE OF PESTICIDES

Edited by D. H. Hutson, *Shell Research Ltd, Sittingbourne, UK and*
T. R. Roberts, *Hazelton UK, Harrogate, UK*

This seventh volume in the series brings together reviews and updates which address one of the most important aspects of environmental toxicology—that of the fate of pesticides in the environment.

Chapter 1 highlights some of the important issues which arise when scientists try to predict problems and encourage the development of, for example, screening methods and modelling procedures to identify compounds worthy of more detailed investigation. The issue of pesticides in ground water is covered in Chapter 2 and this is followed in Chapter 3 by a description of current methodology for the conduct of field studies of the phenomenon. Chapter 4 discusses the application of hydrogeological principles applied to pesticide movement in ground water. A rational approach to the studies of the fate of pesticides in soil is dealt with in Chapter 5. The theoretical aspects and value of laboratory studies for the study of the aquatic environment and the misuse of agrochemicals is covered in Chapter 6 and is followed by a consideration of studies in the 'field' in Chapter 7. A treatise on the fate of pesticides in fish, an important factor in the aquatic food chain, is detailed in Chapter 8. Finally, the importance of sunlight in pesticide degradation including vapour phase and aquatic photolysis is considered in Chapter 9.

[illegible]ut the Editors—

[illegible]id H. Hutson obtained his BSc at the University of Birmingham, and his PhD at the University of London where he did his research in carbohydrate chemistry and biochemistry. He also did research at Ohio State University and the University of Edinburgh, and spent a period in 1977 at the University of California at Berkeley. He joined Shell Research Limited in 1965 and is currently studying the fate of pesticides in plants and soils and the metabolism and toxicology of pesticides and other xenobiotic chemicals in mammals. David Hutson is the author of research papers and reviews in metabolism of pesticides including Chemical Society Specialist Periodical Reports and has edited proceedings of ACS symposia. He is a Fellow of the Royal Society of Chemistry.

Terry R. Roberts obtained his BSc in chemistry and his PhD at the University College of North Wales, Bangor. He then went to Case Western Reserve University in Cleveland, Ohio to do research in organic chemistry and this was followed by a Research Associateship at the University of St Andrews. He joined Shell Research at Sittingbourne in 1969 to work on metabolism of pesticides in plants and soils. Subsequently, he was responsible for residue and environmental chemistry and environmental toxicology activities and until recently was head of the Environmental and Biochemical Toxicology Division. In March 1990 he joined Hazelton UK, a contract research laboratory as Head of the Agrochemicals Department. Terry Roberts is the author of research papers and reviews on pesticide metabolism and environmental chemistry, and of a book entitled *Radiochromatography*. He is a Fellow of the Royal Society of Chemistry and a member of the IUPAC Agrochemicals Commission.

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