

3. Characterisation and Consequences of Persistence

Session Organiser and Chairman: MR JIM ORSON

THE CHARACTERIZATION OF HERBICIDE PERSISTENCE

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ABSTRACT

Herbicide persistence, i.e. the continuation of herbicidal activity beyond the time of planting a sensitive following crop, is determined by the interaction of 3 factors: application rate, crop sensitivity and rate of dissipation. The treatment dose, together with the sensitivity of the rotational crop, define how much of the applied herbicide must be removed from the root zone before recropping can be safely performed. The rate of herbicide dissipation in soil determines how long it will take for the necessary loss to occur. Soil properties and climate greatly influence the processes of herbicide dissipation and the bioavailability of the herbicide to the following crop. Consequently, the observation of persistence is usually sporadic. The potential for persistence can be assessed by direct measurement of the herbicide residue in a field or by means of computer simulation models.

INTRODUCTION

Season-long weed control from a soil-active herbicide is often considered to be a desirable attribute. In order to manage the use of potentially persistent herbicides in a way that acceptably limits the risk of damage to following crops, an understanding of herbicide properties and behavior in soil is required. The duration of herbicidal activity is dependant upon the attributes of the herbicide and on the soil and climate with which it interacts (Beyer *et al.*, 1988; Hance, 1988; Nash, 1988; Leistra, 1990). If the herbicide remains in the soil at concentrations above the injury threshold of a sensitive crop during the following season, then injury symptoms and, in extreme situations, reduced yields, can be expected. Experience has shown that some persistent herbicides may affect a particular following crop in one year but not the next, at one location and not another and/or at some application rates but not others (Barnes *et al.*, 1989; Basham *et al.*, 1987; Duffy *et al.*, 1988; Lloyd *et al.*, 1986; Nicholls *et al.*, 1987). Clearly, the occurrence of persistence can be variable.

Whether or not a herbicide will exhibit persistence in a specific situation depends on three factors:

- the amount of herbicide applied,
- the extent to which the herbicide dissipates from the root zone of the following crop prior to recropping, and
- the sensitivity of the following crop to the herbicide in a given soil.

These factors are illustrated in figure 1. Following application, the herbicide concentration in the plow layer of the soil [C_0] is at a maximum. The processes of dissipation (i.e. loss of herbicide from the root zone by degradation, leaching, sorption, volatilization, etc.) begin to occur immediately, and the concentration of the herbicide gradually declines over time. Efficacy continues as long as the herbicide concentration remains above the threshold for acceptable weed control [C_w]. Beyond this time [T_w], efficacy is gradually lost as herbicide concentration decreases.

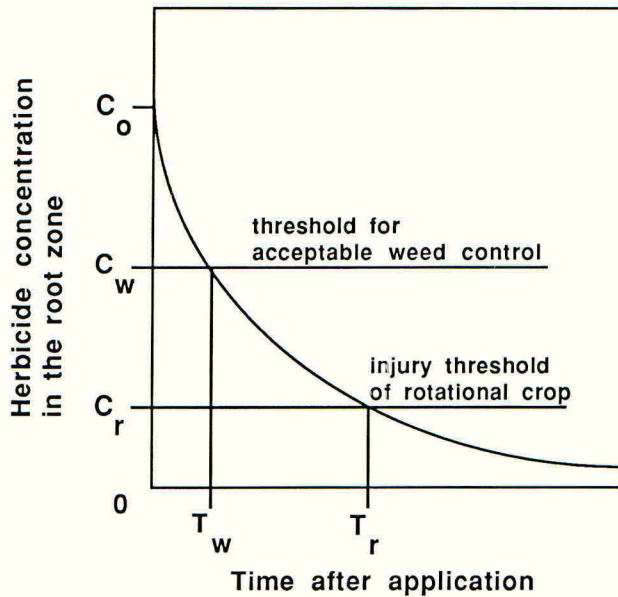


Fig. 1. Herbicide performance vs. time.

At some time $[T_r]$ the residual concentration of the herbicide falls below the threshold level for injury to a following crop $[C_r]$ meaning it is then safe to plant that crop. If the time interval to reach the safety threshold for a particular following crop extends beyond the time when that crop would normally be planted, evidence of persistence will likely be observed.

THE VARIABLE NATURE OF PERSISTENCE

Figure 1 illustrates in a generic way how herbicide dose and the rate of herbicide dissipation from soil, together with the sensitivity of the rotational crop, determine if persistence will occur. One can readily see in figures 2a-c how changing any one of these parameters will effect the potential for carryover relative to that defined in figure 1.

The influence of application rate can be seen in figure 2a. As expected, when the dose is increased (upper dashed curve) the time required for the herbicide concentration to fall below the injury threshold of the following crop is increased, even though no other parameter is changed. If the following crop were planted in the additional time interval required to reach the injury threshold as a result of the increased dose, carryover symptoms would be expected, even though none would be seen at the lower application rate. A decreased application rate (lower dashed curve) would result in a shorter time interval before the following crop could be safely planted.

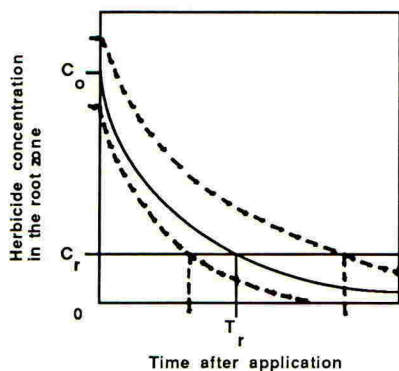


Fig. 2a. Effect of application rate on herbicide performance vs. time.

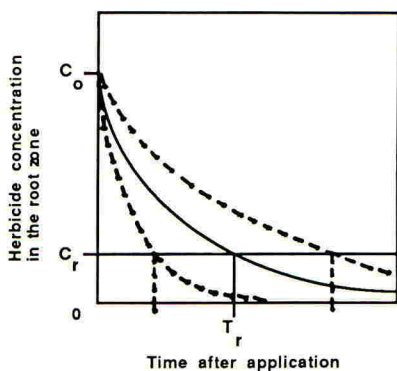


Fig. 2b. Effect of dissipation rate on herbicide performance vs. time.

Figure 2b illustrates the effect of changing the rate of herbicide dissipation. If conditions for herbicide dissipation are less favorable (upper dashed curve), then the rate of herbicide loss from soil will be slower and it will take longer to reach a concentration that can be tolerated by the rotational crop, even though no other factor is changed. Again, if the following crop were planted during the additional time interval resulting from the decreased dissipation rate, carryover symptoms would be expected, even though none would be seen at the higher dissipation rate. A increased dissipation rate (lower dashed curve) would result in a shorter time interval before the rotational crop could be safely planted.

The role of rotational crop tolerance, which may be due to the inherent sensitivity of the crop and/or to the fraction of herbicide that is bioavailable, is shown in figure 2c. A more tolerant following crop can be planted sooner (upper dashed curve) because less time is needed to reach its safety threshold. Conversely, a more sensitive rotational crop (lower dashed curve) requires a longer time interval before it can be safely planted. The same situation exists when one considers the fraction of herbicide residue that is available to a following crop. Higher total residues are tolerated in soils in which the herbicide is more strongly bound (e.g. heavier textured, higher organic matter soils) compared to soils in which the herbicide is more weakly bound (e.g. lighter textured, lower organic matter soils) because with increased sorption a smaller fraction of the herbicide residue is available for uptake by the following crop. If recropping took place during the additional time interval required by the increased sensitivity or bioavailability of the rotational crop, carryover symptoms would be expected, even though none would be seen for a less sensitive species or in soils where the herbicide was less bioavailable .

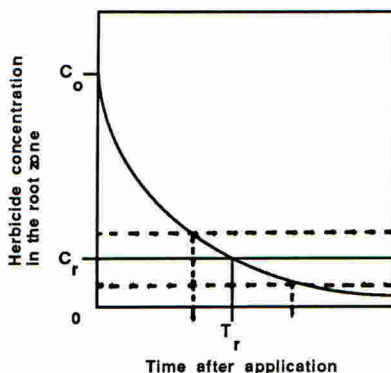


Fig. 2c. Effect of following crop sensitivity on herbicide performance vs. time.

KEY FACTORS INFLUENCING PERSISTENCE

Even when the location, date and rate of herbicide application are known, and the following crop is selected and about to be planted, one can not be

certain if symptoms of persistence will be observed. This reflects the wide variation in herbicide bioavailability and rate of dissipation which are determined, in large part, by the local soil properties and weather. The effect of variation in these factors on persistence was shown above.

Soil properties (pH, organic carbon, CEC, texture, etc.) and soil structure (spatial distribution of properties in the profile) influence thermal conductivity (heat flow) and hydrology (water movement) as well as pesticide speciation (of a weak acid or base), degradation and sorption. The extent to which the pesticide is sorbed to the soil determines both its mobility and bioavailability to soil microorganisms and following crops (Bollag & Liu, 1990; Hance, 1988; Khan & Dupont, 1987; Nash, 1988).

In warmer climates (or in years with above normal temperatures) degradation by chemical reactions will typically be faster than that observed in cooler climates (or in years where temperatures are below normal). This is also true for metabolism by soil microorganisms, at least until temperature extremes reach the point where microbial dormancy or death occurs.

In drier climates (or in years having below normal rainfall) the probability that a herbicide will remain in the root zone is typically higher than in wetter climates (or in years having above normal rainfall). This is due to the lower net precipitation of the drier climate or year and/or the greater upward movement of soilwater which would move at least a fraction of any pesticide that had been leached deeper into the profile back into the root zone.

ASSESSING THE PROBABILITY OF PERSISTENCE

A farmer who previously used a potentially persistent herbicide may be concerned about planting a highly sensitive following crop. Although every effort may have been made to use the product according to label precautions, above label doses can nonetheless result either from overlap during application (e.g. in the end rows, near obstacles in the field, due to swath displacement, etc.) or from poorly calibrated application equipment. Locally slower herbicide dissipation rates, which can lead to following crop injury in one part of a field and not another, can be caused by weather extremes (e.g. drought, below normal temperatures, etc.), unfavorable soil characteristics (e.g. "hot spots" where soil properties are off label in an otherwise acceptable field, subsoils having impeded flow, etc.), and certain surface features (e.g. compaction in wheelings, low areas where water accumulates, etc.). Reliable assessments of the potential for herbicide persistence can put a farmer's carryover concerns into perspective, or guide in the selection of a rotational crop if he has planting options.

Direct measurement of the residual herbicide concentration in the root zone at recropping, is a common method of defining the risk of carryover. A bioassay of soil samples taken from a herbicide treated field along with an untreated

check can give quite accurate projections of the potential for following crop injury, providing the bioassay has been calibrated with extensive field recrop results and no other soil-active herbicides are present (Lavy & Santelmann, 1986). For example, in the cereal growing regions of the northern United States and neighboring Canadian Provinces where chlorsulfuron has been used to control broadleaf weeds for nearly a decade, a bioassay employing lentils as the indicator was developed and used to expand recrop options available to farmers (Peter *et al.*, 1988; Strek *et al.*, 1989). Although bioassays have the distinct advantage of measuring only plant available herbicide residues, they have the disadvantages of responding to any soil-active herbicide residues in the soil and often requiring up to several weeks to produce results.

An alternative is to use a traditional analytical determination to measure the herbicide residual in an extract of a soil sample. The detection method used for this analysis (e.g., GC, HPLC, ELISA, etc.) will likely have much greater specificity for the herbicide and require considerably less time to produce results (Peter *et al.*, 1989). However, the analytical results will be more difficult to interpret since not all of the herbicide remaining at the time of recropping is available to the following crop. In fact, for many herbicides only that which is in the soilwater is available for plant uptake and this is precisely what is measured with the bioassay. For example, while greenhouse GR₅₀ values for sunflower and corn to chlorimuron ethyl showed a 30-fold difference across 13 diverse soils, the calculated herbicide concentration in the soilwater at the GR₅₀ treatment rate was found to be constant for both species regardless of soil type (Duffy *et al.*, 1988).

More recently, using direct analysis of soilwater which has been separated from the soil by centrifugation, these calculated results have been confirmed experimentally (Carski, 1990). Figure 3a shows the response of lentils to the total applied chlorsulfuron in 3 diverse soils. Three distinct curves, one for each soil, are apparent. However, when lentil response is plotted against the chlorsulfuron concentration in soilwater (Fig. 3b), a single response curve emerges independent of soil. This approach combines the speed and

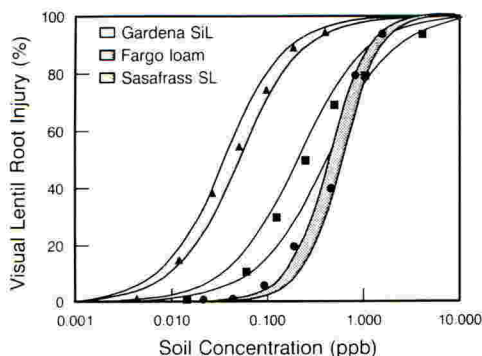


Fig. 3a. Lentil response to total chlorsulfuron concentration in 3 soils

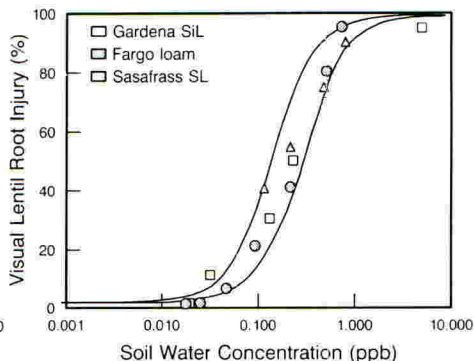


Fig. 3b. Lentil response to chlorsulfuron concentration in soilwater of 3 soils

specificity of traditional analytical techniques while removing the confounding effects of herbicide sorption that typically make it difficult to assess potential for carryover compared to bioassay methods.

Computer simulation models have been used to explain observed dissipation under field conditions as well as to predict the likelihood of herbicide persistence under many soil and weather scenarios. Use of these predictive mathematical models requires information about soil properties and weather patterns at the location for which the simulation is being made, as well as data describing the physico-chemical properties of the herbicide and its interaction with the soil as the environment changes from time of application to recropping. Additionally, if the goal of the simulation is to assess the probability of persistence, one must be able to translate the nonuniform distribution of herbicide residue to an estimate of following crop response. Despite the inherent complexity and difficulty in developing such models, Walker and Welch (1989), Duffy *et al.* (1987), Walker (1987), and Nicholls *et al.* (1982, 1983, 1987), among others, have either successfully modeled herbicide dissipation compared to actual measured residual concentrations, and/or accurately projected carryover potential.

The recrop intervals that appear on product labels are based on extensive field testing during development of a herbicide and on commercial experience after introduction into the marketplace. However it is impractical to evaluate persistence under all (or even most) combinations of soil, weather and recropping practices because such tests are expensive to conduct and typically take longer than a year to complete. This situation presents a significant opportunity to the modeler who is able to reliably simulate herbicide persistence over diverse geography, for decades of weather data and, an extensive cross section of soil characteristics. Such global sensitivity analyses can identify the most unfavorable scenarios for a herbicide and guide the establishment of further field tests as necessary. Use of the herbicide can thus be maximized while simultaneously minimizing the risk of persistence.

ACKNOWLEDGEMENTS

I am indebted to my colleagues Ted Carski, Dan Linn and Monica Ball for their helpful discussions and assistance in the preparation of this paper.

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SOIL PROPERTIES AFFECTING THE CARRY-OVER OF A HERBICIDE

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ABSTRACT

Soil physical properties at five trials sites were investigated to try to explain differences in the persistence of an experimental herbicide, as indicated by field bio-assay experiments. The degree of damage suffered by subsequent crops varied with the aggregate stability and pore-size distribution of the topsoil. However, there is unlikely to be a simple causal relationship. Soil structure and soil biological activity are interdependent, and the rate of degradation of a herbicide is influenced by both factors.

INTRODUCTION

Field bio-assay experiments indicated that the residual properties of an experimental herbicide (not a sulphonyl urea) should be investigated to evaluate the risk of damage to subsequent crops. The amount of damage varied with the application rate and timing, and also in other ways thought to be related to soil differences.

The herbicide is strongly adsorbed with a K_{oc} (adsorption per unit of organic carbon) minimum value of 2072 ml/g. It has a very low water solubility of 1.0 mg/l at pH 7.4 and 5.0 mg/l at pH 5.1.

A programme of measurements and field investigations of soil physical properties which might influence the fate and behaviour of the herbicide was designed, in an attempt to differentiate five experimental sites in Belgium, England, France and Germany. The half-life of the compound was thought to be independent of pH, and the problem confined to the immediate topsoil where germinating or young seedlings were affected. This programme did not evaluate the parent or daughter compounds in underlying soil horizons.

Factors controlling absorption and bio-availability of a herbicide are influenced by the particle-size distribution of the soil, its organic matter (nature and content) and calcium carbonate content (Nicholls, 1988; Arnold & Briggs, 1990). The stability of soil aggregates to rain drop impact may be important in controlling herbicide release and availability, and the size and distribution of fissures and pores control the way in which water (and herbicide) is held within the soil and how it is released to the crop. The pore-size distribution also influences aeration and biological activity within the soil.

SITE INVESTIGATIONS

The soils of the experimental sites were examined to 1.2 m depth and samples taken from the top 15 cm for analyses (Tables 1 & 3). Clods were taken for aggregate stability tests and undisturbed samples for water release measurements. At sites C1, C2 and H cultivation had been the same across the site and four points were chosen and sampled to represent the whole site. However, at sites F and LT some plots had been rotavated and others ploughed, and therefore two sample points were selected from each cultivation treatment.

METHODS

Particle-size analyses, pH measurements, organic carbon and calcium carbonate content determinations were carried out using the standard methods of the Soil Survey and Land Research Centre (Avery & Bascomb, 1982).

Water release characteristics were determined from undisturbed topsoil samples collected using a falling hammer corer and then equilibrated on a sand bath and pressure cells at increasing suctions (0, 0.01, 0.05, 0.33 and 2 bar) (Hall et al., 1977). 0 bar is, for this purpose, saturation by capillary rise, representing 'field', rather than complete, saturation; the larger pores, fissures and isolated voids remain air-filled. Water release results and density measurements give a measure of the air capacity of the soil.

To assess the stability of the soil aggregates a method involving water dropping onto the soil was chosen, since the primary interest here was their stability to raindrop impact. The method described by Grieve (1979) was used. A small (4-5 mm diameter) aggregate was wetted on a sand bath to a suction of 0.005 bar and then held in a mesh cone over a 3 mm hole at the base of the cone. The number of drops of water needed to wash the aggregate through the hole was counted for 20 aggregates. The count was ceased at 100 drops. Logarithmic transformation (to the base 10) of the data enables distribution classes of stability to be characterised. The stability index for each site is expressed as the mean number of raindrops required to disperse the soil aggregates.

RESULTS

Soils of the five sites

The properties and classification of the soils are summarized in Tables 1, 2 and 3. The soils at site F in Belgium and site H in south west Germany are very similar and uniform. They are both developed in silty loessial (windblown) material. Such soils are extensive in north-west Europe. Site C2 near Orleans in France has by far the heaviest soils and these calcareous clayey upper layers overlie soft rubbly limestone, sometimes with much clayey interstitial material. Site C1 is near Auxerre in France and the soils are developed in loess-covered clay-with-flints.

TABLE 1. Soil analyses

	C1	C2	Site			
			F	H	LT	
Sand %	(600 μ m - 2mm)	4	9	0	0	3
	(200 μ m - 600 μ m)	9	9	0	0	17
	(100 μ m - 200 μ m)	8	2	0	0	13
	(60 μ m - 100 μ m)	5	1	1	1	4
Silt %	2 μ m - 60 μ m	56	17	82	79	33
Clay %	<2 μ m	18	62	17	20	31
CaCO ₃ equivalent %		nd	1.75	0.12	0.06	0.21
Organic Carbon % C		1.05	1.64	1.10	1.36	3.44
pH (1:2.5) in water		6.1	8.3	8.1	7.5	7.6

nd - not determined

TABLE 2. Soil classification

	C1	C2	Site		
			F	H	LT
Avery (1980)	Stagnoqlevic paleoargillic brown earths	Typical calcareous pelosols	Typical argillic brown earths		Stagnoqlevic argillic brown earths
CEC (1985)	Chromic luvisols	Calcario-gleyic cambisols	Orthic luvisols		Stagnogleyic luvisols
Topsoil particle-size class	clay loam/ sandy silt loam	clay	silt loam	silty clay loam	clay loam

Similar soils are extensive on chalk plateaux in southern England and northern France. Upper horizons have a large silt content. Site LT in eastern England has soils developed in clay loam drift material over Jurassic and Pleistocene clay.

Particle-size analyses

There is little variation within each site and only the means have been tabulated in Table 1. At sites F and H topsoils have almost identical particle-size distributions. Even the size distribution within the silt size grade (2 to 60 μ m) shown in Table 3 is remarkably similar.

TABLE 3. A comparison of the silt fraction at sites H and F

	Site H	Site F
(48 μ m - 63 μ m)	1	4
(32 μ m - 48 μ m)	17	21
(24 μ m - 32 μ m)	14	14
Silt % (16 μ m - 24 μ m)	18	16
(8 μ m - 16 μ m)	15	15
(4 μ m - 8 μ m)	8	6
(2 μ m - 4 μ m)	3	3

Aggregate stability

The most striking thing about these results (Fig. 1) is the difference between site F and site H, since the particle-size distribution is almost identical. Silty soils are generally structurally weak and would have a low stability index, but this appears not to be the case at site F. The index here is 86 compared to 21 at site H.

Aggregates are also relatively stable at site LT (stability index 64), and here those from ploughed land (stability index 83) are more stable than those from rotavated soil (stability index 46). However, this difference in management history is not evident at site F and so for both sites F and LT the results from the two treatments were averaged.

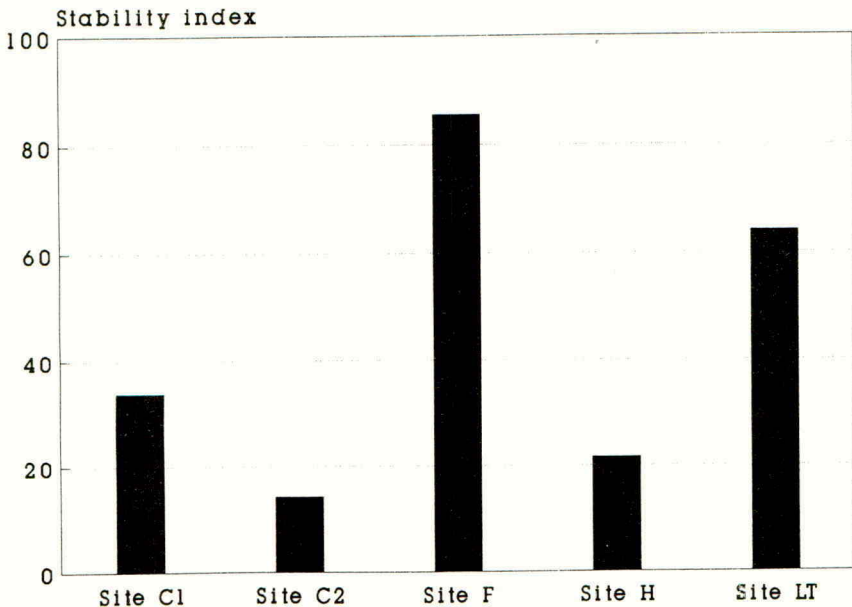


Fig. 1. Topsoil aggregate stability

Water release characteristics

Figure 2 shows the water retention characteristics for each of the five sites. For this purpose easily available water (EA_v) is defined as that held between 'field' saturation and 2 bar suction, and very easily available water (VEA_v) as that held below 0.33 bar suction. 'Field' saturation as defined above was used since it is a more realistic model of what will happen after heavy rain than is total saturation, and this water is then available to growing seedlings. The quantity of very easily available water may be critical for the survival of a young plant.

Because of the almost identical particle-size distribution, the most obvious comparisons are again between sites H and F. Figure 2 shows that site H loses most water at very low suctions (<0.01 bar) indicating a large number of very coarse pores compared with site F. This would be expected from the differences in bulk densities shown below.

Site	C1	C2	F	H	LT
Bulk density ($g\ cm^{-3}$)	1.31	0.81	1.28	1.08	0.97

Figure 2 also highlights the differences in easily available water between site F and site H, although between 0.01 and 2 bar suction the water loss is similar at both sites. The difference in water release characteristics between these two sites is emphasized by the time taken for soil cores from each site to reach an equilibrium water content at 0.01 and 0.05 bar suctions. A more gradual release of water held at low suctions, as occurred at site H, suggests that the water soluble pesticide may be more bioavailable for uptake by the original crop or to microbes, and so less will persist to damage the following crop.

Air capacity

This represents the volume of pores and fissures that will drain under gravity and is usually measured by the difference in water holding capacity between total saturation (all pores and voids filled) and 0.05 bar suction (total air capacity).

However, of interest here is the air capacity of the aggregates as well as that of the whole soil. To estimate this the difference between 'field' saturation by capillary rise on a water bath and 0.05 bar suction is used.

Figure 3 shows both the total air capacity and the air capacity of the aggregates. The total air capacity has been estimated from particle density and bulk density. It can be seen that there is no clear relationship between these two figures but that the aggregate air capacity at site H is double that at site F. This has implications for the breakdown of pesticide residues held within the aggregates since better aeration gives faster degradation.

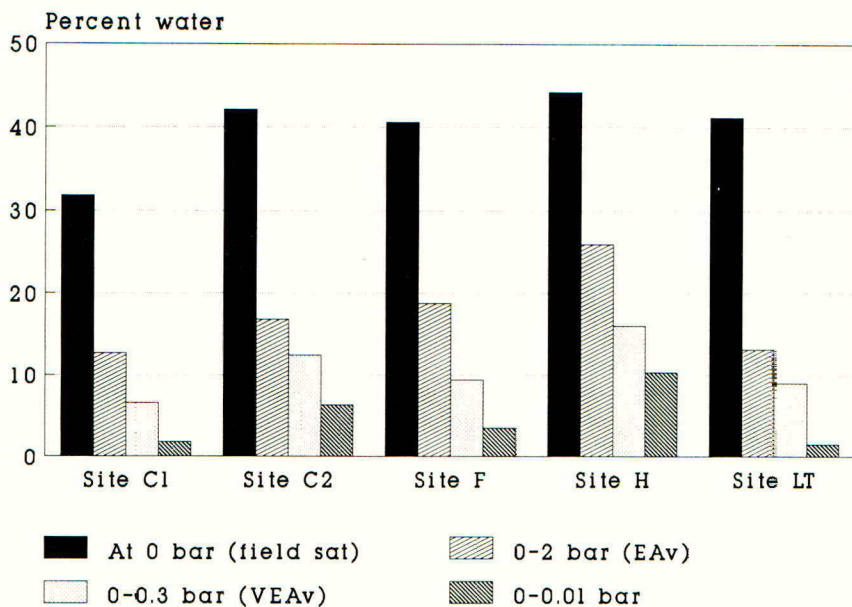


Fig. 2. Topsoil water retention

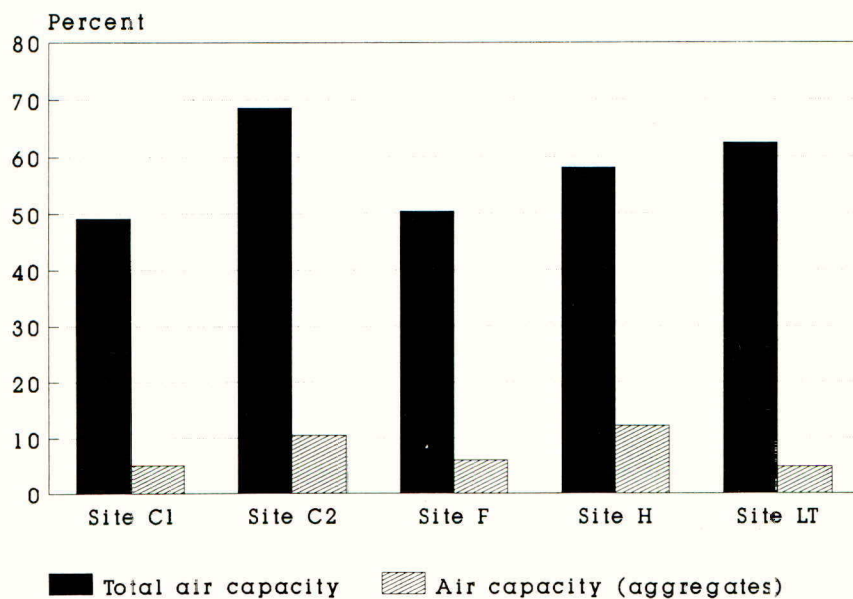


Fig. 3. Topsoil air capacity

DISCUSSION

Although five sites were visited and examined, in some ways the most interesting comparisons can be made between just two of them. Sites F and H have almost identical soils in terms of their particle-size distribution, organic carbon and calcium carbonate contents, and yet carry-over of biological activity of the herbicide was a problem at site F and not at site H.

The soil at site F was more dense than at site H and its aggregates were very much more stable to raindrops. At site H the soil had more easily and very easily available water (Fig. 2) because of a greater number of coarse pores, and so the seedlings have easier access to more of the soil water than at site F.

There are two interacting elements working on the chemical here - the soil physical properties and the biological activity. Considering the former alone, although adequate aeration for plants and microbial activity depends on the stability of soil aggregates, the compound may be held within the more stable aggregates at site F at such tensions or locations that it is unavailable to the plant. This residue is then released in the following autumn as the soil wets and aggregates break down. Carry-over problems were also encountered at site LT which has relatively stable aggregates. At site H the aggregates are less stable and so less of the chemical is held over in the soil until the following autumn to damage the subsequent crop. The soil aggregates at site F have a smaller air capacity than those at site H (Fig. 3) and this difference in aeration will affect the rate of degradation of the compound. Also at site H, with more easily available water (Fig. 2), the herbicide is mainly taken up by plants (crop and weeds) in the first crop.

Biological activity affects the soil structure, which in turn affects the biological activity; they are interdependent. Changes in the physical and chemical properties of the soil cause large and rapid changes in microbial populations (Somerville 1987) and also influence the fungal population. The breakdown of the compound is thus influenced directly and indirectly by soil physical properties. Plant and microbial exudates and secretions bind soil particles, thus, generally, the greater the biomass the more stable the aggregation.

The age and type of organic matter, which reflects land use history, will also affect the biological activity and soil aggregate stability (Baldock & Kay 1987). For example, maize and potato residues support greater activity than cereal residues since C/N ratio and lignin content are significantly different. The crops preceding use of the herbicide were cereals at site F and cabbages at site H. Haynes & Swift (1990) link greater stability to grass leys in a rotation, under which the hot water extractable carbohydrate in the soil is increased. Cultivation history and land management technique will also physically affect the soil, its pores, structure and biological activity and so will have a direct effect on the fate of the compound.

Short term fluctuations of topsoil temperature and moisture content may be critical to the degradation of the compound and so partly responsible for the different carry-over behaviour. Monitoring of these two parameters was outside the scope of this study.

CONCLUSIONS

The persistence of this compound varies with the physical structure of the soil as defined by the stability of aggregates and the number and size of pores and fissures indicated by water release measurements. There may be a direct causal relationship between physical properties and persistence, but it is more likely linked to the biological activity and type of organic matter as well.

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1991 BCPC MONO. No. 47 PESTICIDES IN SOILS AND WATER

THE INVESTIGATION OF DEGRADATION AND METABOLISM OF CLOPYRALID IN TWO STANDARD AND THREE AGRICULTURAL SOILS

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ABSTRACT

To more fully understand the fate of the herbicide clopyralid in soil, its degradation and metabolism was investigated in a laboratory study using five soils. Clopyralid is metabolised in all the soils studied to give CO₂ as the sole observed metabolite. The rate of degradation of the herbicide could be roughly correlated to the microbial biomass of the soils. Soils with higher biomass degraded clopyralid faster than those with lower microbial biomass. Temperature, soil moisture and initial clopyralid concentration all influenced the rate of degradation of the herbicide. Overall, higher temperatures and higher soil moistures led to more rapid degradation of clopyralid. Lower DT50 and DT90 values (disappearance time for 50% and 90% of the initial concentration) were obtained at lower initial clopyralid concentrations indicating that residues disappear from the soil sooner at lower concentrations.

INTRODUCTION

3,6-dichloropyridine-2-carboxylic acid, common name clopyralid, is the active ingredient of the herbicide LONTREL 100*. Clopyralid is a systemic herbicide with exceptional activity against the creeping thistle (Cirsium arvense) and is very selective in a number of broad leaved crops (Worthing & Hance, 1991).

In order to understand the fate of clopyralid in soil its degradation and metabolism was investigated in a laboratory study using five soils. Two standard German soils, as designated by the German regulatory authority, The Biologische Bundesanstalt (BBA), (2.1, sand and 2.2, loamy sand) and three agricultural soils (German Parabraunerde, silt loam; UK Marcham soil, sandy clay loam and UK Castle Rising soil, organic sandy loam) were used in the experiment. For the major part of the experiment clopyralid was incubated with the different soils at a concentration of 0.3 mg/kg soil (field rate) with the moisture content of the soils set at 40% maximum moisture holding capacity (MHC) and the temperature at 20°C.

In addition, the effect of a number of environmental factors on the rate of clopyralid degradation and metabolism was investigated in the 3 agricultural soils. Incubations were carried out at two

* LONTREL 100 Trademark of DowElanco Ltd.

different temperatures 10°C and 20°C and 3 different soil moisture contents, 10%, 40% and 60% MHC. The effect of different initial clopyralid concentrations on the rate of degradation was also studied by incubating soil with 3 different concentrations of the herbicide 0.05mg/kg, 0.3mg/kg and 1.0mg/kg.

MATERIALS AND METHODS

50g oven dry equivalent of soil was weighed out into one side of a biometer flask. The moisture content of the soils was adjusted to that required (40, 10 or 60% MHC) with the addition of distilled water. [^{14}C pyridine] clopyralid, formulated as the monoethanolamine salt, was added to the soil to give the appropriate concentration (0.05, 0.3 or 1mg/kg) and well mixed. In the other side of the biometer flask was added 100 mlitres 0.1M NaOH solution which served as a CO_2 trap. The biometer flasks were then incubated at either 10°C or 20°C. The CO_2 traps were changed at regular intervals and monitored using scintillation counting. Biometer flasks were removed from the incubators 0, 7, 14 and 28 days and 3 and 6 months after application. For the incubations at 20°C, 40% MHC and 0.3 mg/kg clopyralid concentration, additional sampling times of 1 and 3 days, and 9 and 12 months after application were also included.

The soil samples were extracted sequentially with 0.01M CaCl_2 , followed by acidified acetone and finally with 0.5M NaOH. The radioactivity extracted was determined by scintillation counting and those extracts with greater than 10% of the applied radioactivity were analysed by thin layer chromatography (TLC).

RESULTS AND DISCUSSION

The monitoring of the CO_2 traps throughout the experiment showed that ^{14}C -clopyralid was readily degraded and extensively mineralised to $^{14}\text{CO}_2$ in all 5 soils studied. Analysis of all the extractable radioactivity by TLC showed only clopyralid to be present. No other metabolite apart from CO_2 was observed. In this case it can be assumed that the rate of mineralisation can give an indication of the rate of clopyralid degradation. Figure 1 shows that rate of mineralisation is dramatically reduced after about 92 days. This decrease in the rate of degradation is possibly due to depletion of nutrients in the soil and/or an increased binding of clopyralid to soil particles and soil organic matter (Frehse & Anderson, 1983).

By day 92 the majority of the radioactivity was mineralised to CO_2 and only a small amount was readily extractable into CaCl_2 in all of the soils studied. In Parabraunerde soil about 11% of the applied radioactivity remained bound to the soil particles and organic matter. This fraction is unlikely to be available for movement in the soil or for biological activity.

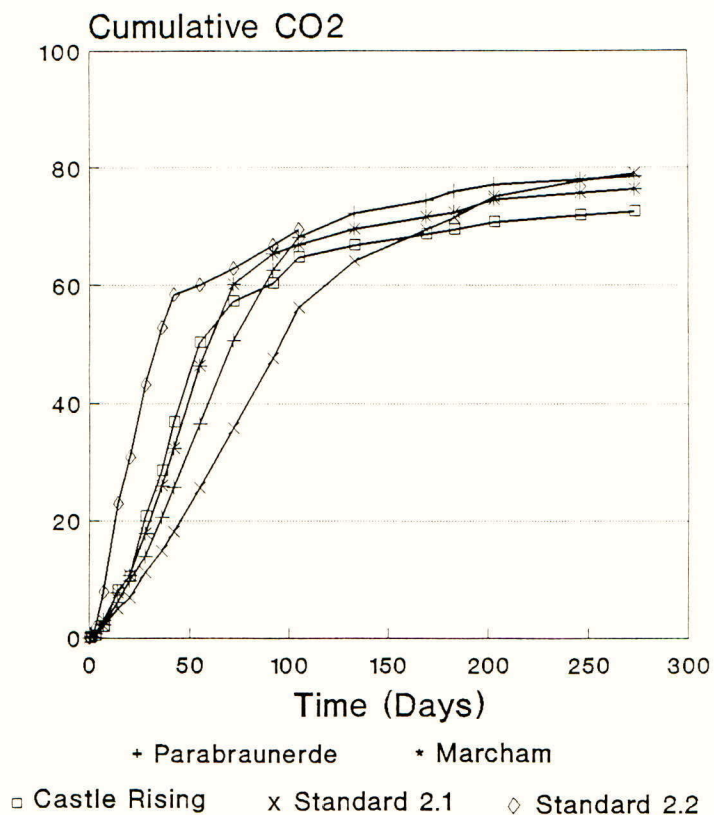


Figure 1. Mineralisation of clopyralid in all five soils studied

TABLE 1. DT50 AND DT90 values for 5 soils using data from 3 months with 20°C, 40%, CaCl₂ extractable samples

Soil	DT50 (Days)	DT90 (days)
Parabraunerde	25	82
Marcham	14	46
Castle Rising	16	54
2.1 Standard	39	90
2.2 Standard	13	66

The rate of clopyralid degradation in all the soils was calculated as DT50 and DT90 values (disappearance time for 50% and 90% of the initial concentration) using the Timme-Frehse programme (Timme & Frehse, 1980; Timme *et al.*, 1986). The results obtained using the readily extractable data for the first 3 months showed that in all soils clopyralid has DT50 and DT90 values of less than 100 days (Table 1).

It is interesting to note that the rate at which clopyralid degrades in soil can be roughly correlated to the microbial biomass of the soil. Marcham soil had a relatively high biomass value at the start of the study (17.0mgC/100g) reflecting the rapid rate of clopyralid degradation while 2.1 standard soil had a biomass of <1mgC/100g soil corresponding to a slow degradation rate. Castle rising soil had the highest microbial biomass of 31.3mgC/100g soil but the rate of clopyralid degradation was not the fastest under these conditions. This would indicate that although microbial biomass is important for microbial degradation it is not the only factor affecting the rate of clopyralid degradation.

Effect of temperature on clopyralid degradation rate

To study the effect of temperature on the rate of clopyralid degradation the three agricultural soils were incubated at 10°C and 20°C for 6 months. Table 2 shows the DT50 and DT90 values at the two temperatures studied.

TABLE 2. DT50 AND DT90 values in days showing the effect of temperature on clopyralid degradation

Soil	20°C		10°C	
	DT50	DT90	DT50	DT90
Parabraunerde	25	82	177	>200
Marcham	14	46	69	>200
Castle Rising	16	54	66	>200

In all 3 soils the rate of degradation of the herbicide was found to be significantly slower at 10°C than at 20°C. As clopyralid degradation is microbial in nature (Swann & Unger, 1980) then increases in temperature would be expected to increase the rate of degradation until an optimum is reached dependent on the temperature optimum of the soil micro-organisms involved in the degradation process (Lynch, 1983).

Effect of soil moisture on clopyralid degradation rate

As well as the incubations set up at 40% MHC, additional incubations were set up where the soil moisture was set at 10% and 60% MHC. Table 3 compares the DT50 and DT90 values obtained with the 3 different moisture contents. At 10% MHC degradation and metabolism of clopyralid was not observed at all in any of the soils. There was no mineralisation and even the bound fraction was small. Close to 100% of the applied radioactivity could be readily extracted and on analysis was found to be clopyralid. This result suggests that at 10% MHC the soil is too dry to sustain the activity of the micro-organisms involved in clopyralid degradation (Paul & Clark, 1989).

TABLE 3. DT50 AND DT90 value in days showing effect of soil moisture on clopyralid degradation

Soil	40% MHC		10% MHC		60% MHC	
	DT50	DT90	DT50	DT90	DT50	DT90
Parabraunerde	25	82	>200	>200	24	79
Marcham	14	46	>200	>200	14	46
Castle Rising	16	54	>200	>200	1	15

For Parabraunerde and Marcham soils the DT50 and DT90 values obtained at 60% MHC were almost the same as at 40% MHC. However, with Castle Rising soil the DT50 value was dramatically reduced from 16 days (40% MHC) to 1 day (60% MHC). It would appear that at around 40% MHC and above, the moisture content of the Parabraunerde and Marcham soils is sufficient to ensure that clopyralid is available to the micro-organisms for degradation and that microbial activity is not limited by lack of water. It is likely that moisture could be increased in these two soils and rate of degradation will stay the same until the soil becomes flooded and oxygen becomes limiting (Paul & Clark, 1989).

In the case of Castle Rising soil it is likely that at 40% MHC the moisture content of the soil is too low to allow sufficient clopyralid to be available in solution for optimal microbial activity. Castle Rising soil has a high organic matter content, 27.6% compared to Marcham and Parabraunerde soils of 3.19% and 1.74% respectively. As such a much larger quantity of clopyralid is likely to be associated with the soil organic matter and more water is

required to bring it into solution so that it becomes available for microbial activity (Bartha *et al.*, 1983). This serves to illustrate that it is not just the microbial biomass of the soil which is important for optimum rate of degradation but also the availability of the compound. It would seem that at 40% MHC soil moisture was the limiting factor in Castle Rising soil and could explain why despite having the highest microbial biomass value the fastest rate of degradation was not observed in this soil at 40% MHC.

Effect of initial clopyralid concentration on clopyralid degradation rate

In addition to the field rate concentration (0.3mg/kg) incubations, two other concentrations, 0.05mg/kg and 1.0mg/kg were incubated with the 3 agricultural soils. The DT50 and DT90 values are shown in Table 4. In general the results show that the lower the initial clopyralid concentrations the lower the DT50 and DT90 values obtained. Thus suggesting that, clopyralid residues disappear from the soil sooner at lower concentrations.

TABLE 4. DT50 AND DT90 values in days showing the effect of different initial clopyralid concentration on disappearance time from soil

Soil	0.3mg/kg		1mg/kg		0.05mg/kg	
	DT50	DT90	DT50	DT90	DT50	DT90
Parabraunerde	25	82	177	>200	13	42
Marcham	14	46	83	>200	9*	26*
Castle Rising	16	54	46	>200	17	57

* Data does not correlate to 95% significance

If the rate of mineralisation is considered in terms of dpm/day and this is plotted against time (Figure 2), it is observed that the amount of radioactivity released as ¹⁴C₂O increases for the first few days at the about same rate for all three concentrations. After this, for the two lower concentrations of clopyralid, 0.05mg/kg and 0.3mg/kg, the expected decline curve is obtained. One possible explanation for this shape of curve is to consider that the first part of the curve is due to a "lag" phase during which time the microbial population responsible for clopyralid degradation is being established. This population is established at the time a normal decline curve is observed which is then just concentration dependent.

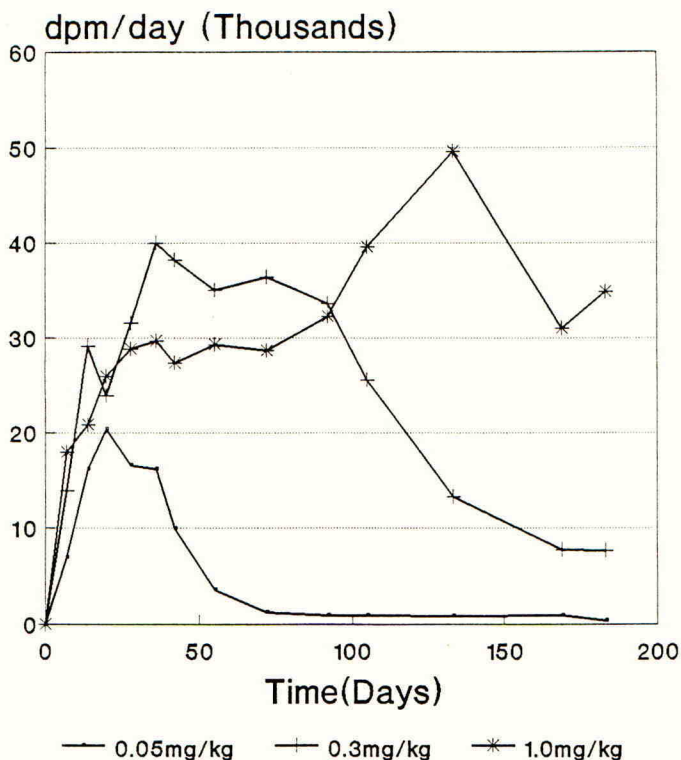


Figure 2. Effect of initial clopyralid concentration on the rate of degradation in parabraunerde soil

With 1mg/kg however it was observed that after the initial phase, which appears to be the same for all three concentrations, instead of the normal decline curve, a plateau is observed; after about 90 days the amount of $^{14}\text{CO}_2$ again starts to increase. This observation can possibly be explained by considering the presence of a second population. It can be envisaged that two different populations of micro-organisms are involved in degrading clopyralid. The first population establishes quickly (15-20 days) and is able to metabolise clopyralid to a certain concentration. The second population requires more time to establish and it is the combined effect of the two populations, the first which is declining in activity and the second which is establishing which causes the plateau effect with the 1mg/kg initial concentration curve.

CONCLUSION

Clopyralid is metabolised in soil to give only CO_2 as a metabolite. The rate of degradation of the herbicide in different

soils appears to be roughly correlated to the microbial biomass of the soils. In general, the results show that soils with higher microbial biomass degraded clopyralid faster than those with lower microbial biomass.

Temperature and soil moisture both influenced rate of clopyralid degradation, Overall, higher temperature and higher moisture led to a more rapid degradation of clopyralid.

The lower the initial clopyralid concentration the lower the DT50 and DT90 values obtained. This suggests that residues disappear from the soil sooner at lower concentrations.

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COLLABORATIVE BIOASSAYS TO MONITOR THE BEHAVIOUR OF METSULFURON-METHYL AND METRIBUZIN IN THE SOIL

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ABSTRACT

A collaborative study was initiated by the European Weed Research Society (EWRS) to assess a simple bioassay as a tool to study the residual activity of herbicides in the soil at different locations.

In field experiments the herbicides metsulfuron-methyl or metribuzin were applied. Soil samples were collected and used for bioassays in the greenhouse for up to 90 days after application. At most locations a decrease in herbicidal activity and consequently extensive dissipation was evident in the upper soil layer. Movement of small amounts of both herbicides down to 30 cm occurred in some cases. Fresh weight measurements and visual assessments revealed similar trends. The latter therefore seems to be the more appropriate method, if a large number of samples has to be processed and a statistical analysis is not intended. Parallel to the laboratory experiments field bioassays were carried out. There was a relatively good correlation between indoor and outdoor results. With the help of a parallel-line assay residual activities can be related to herbicide concentrations and dissipation curves can be described, if the data meet the statistical requirements.

INTRODUCTION

In recent years the behaviour of herbicides in soils has become more and more important and is the topic of intensive discussions. Information about the soil behaviour of herbicides is not only needed from an ecotoxicological point of view, but also for practical aspects: for example sufficient residual activity as well as possible damage to succeeding crops.

For many years bioassays have been used to investigate the behaviour of herbicides in soil (Gerber *et al.*, 1975; Hurle, 1977). Especially if expensive instrumentation is not available, bioassays have proven valuable. For very new compounds, sensitive analytical methods may not yet have been developed or may be too laborious. In these cases, bioassays are suitable methods. Furthermore for sulfonylureas with recommended rates of only a few g AI/ha bioassays may be equally sensitive to analytical methods (Iwanzik & Egli, 1989).

The following collaborative bioassays were initiated by the main subject area "Herbicides" of the EWRS. The intention was to investigate methodological aspects: if, for example, a standardized test, which is not optimized for a certain group of compounds, might be suitable to monitor the behaviour of different herbicides in soils under different field conditions. Comparisons were therefore made between indoor and outdoor bioassays or between fresh weight measurements and visual assessments. In a first step, only residual herbicidal activity expressed as percent growth inhibition was measured. In a second step we tried to correlate some of these results with amounts of active ingredients per ha by comparing them with dose-response curves.

The tests were carried out by 21 participants/institutions in Australia, Europe, New Zealand and South Africa. Metsulfuron-methyl and metribuzin were chosen as test compounds.

MATERIALS AND METHODS

For the field trials, plots of 24m x 4m, which had not received any herbicide treatment for at least 1 year, were selected. Light soils, i.e. sandy loams or loamy sands with about 1 % organic carbon or soils with similar characteristics were chosen. Spray applications of Gropper® 20 DF (metsulfuron-methyl, 8 g AI/ha) or Sencor® 70 WG (metribuzin, 750 g AI/ha) on bare soil was in April 1989 except Australia (Sept. 89). Soil samples were taken to a depth of 30 cm from treated and untreated control plots at day 0, 30, 60 and 90 after application. At each sampling date, indoor and outdoor bioassays were carried out. For the indoor bioassays the soil samples were divided into 0 - 10, 10 - 20 and 20 - 30 cm sections and filled into pots (10cmx10cmx10cm, 3 replicates). Additional replicates were diluted 1 + 1 and 1 + 3 with untreated soil. 15 seeds of Brassica rapa sp. rapa (cv. Salusia) were sown at a depth of 0.5 cm and thinned to 8 plants/pot after emergence. The pots were watered as required. After a period of 2 weeks (metribuzin) or 3 weeks (metsulfuron-methyl) visual assessments of the herbicidal activity (in % to untreated) as well as fresh weight evaluations were carried out. If necessary, the fresh weight data were adjusted to equal numbers of plants to have a uniform basis. The data were compared with dose-response curves, run parallel to the bioassays.

At each sampling date for the outdoor bioassays, three rows of *B. rapa* were sown into the untreated and treated plots. Visual and fresh weight evaluations (10 plants per row) were carried out like in the greenhouse. Before the later sampling dates weeds were removed either by hand or with a non-residual herbicide.

RESULTS AND DISCUSSION

Figures 1a and 1b show the results of the indoor bioassays (soil layer 0 - 10 cm; visual assessments) for metsulfuron-methyl and metribuzin. Every test location is shown by a letter symbol (A-V), which was assigned arbitrarily.

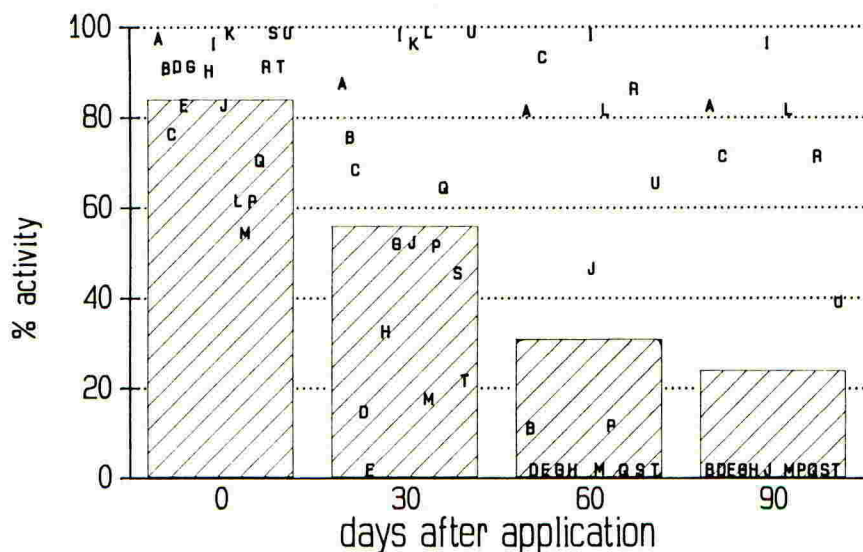


Figure 1a. Residual activity of metsulfuron-methyl
Indoor bioassay - visual assessment (%)

In order to visualize the trends within the mass of data, the mean values for each sampling date were included, although different locations were compared. The mean herbicidal activity of metsulfuron-methyl decreased from 84 % at day 0 to 24 % at day 90, and of metribuzin from 95 % at day 0 to 20 % at day 90 as shown in Figures 1a and 1b. For both herbicides a decrease in residual activity was evident, although at some locations, activity remained high, even at day 90. Most of the differences can be explained by specific soil or climatic conditions. For example, extremely light soils were used, rainfall was pretty low like in Europe or application was during the cold season like in New Zealand and South Africa. The course of residual activity may not be mixed up with dissipation. For both herbicides, the applied amounts were far above the concentrations, which resulted in complete growth inhibition. From the dose-response curves it can be concluded, that for the majority of locations approximately 90 % dissipation are necessary for both herbicides to reach dose ranges, which result in about 50 % growth inhibition.

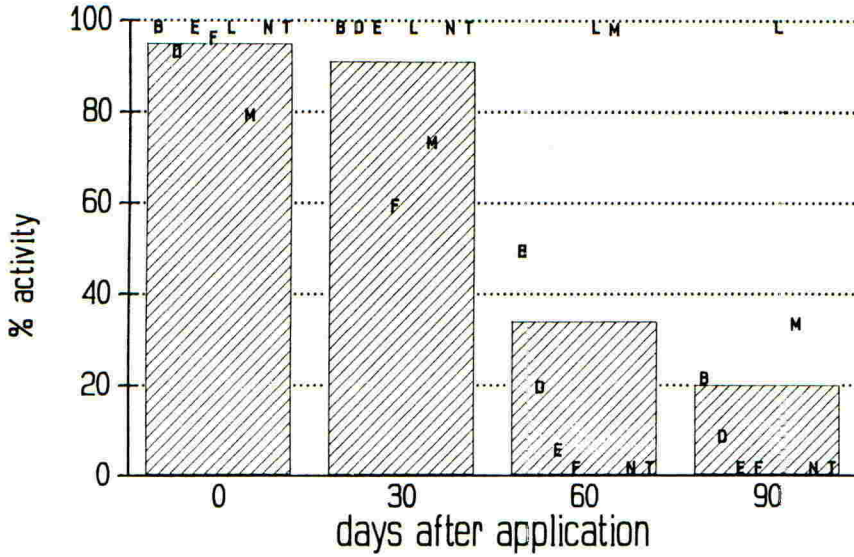


Figure 1b. Residual activity of metribuzin
Indoor bioassay - visual assessment (%)

Obviously in some cases small amounts of both herbicides moved into the 10-20 cm and 20-30 cm soil layers (Table 1), but the activities, which could be detected, were relatively low compared to the 0-10 cm soil layer.

TABLE 1. Mean residual activity +/- standard deviation (indoor bioassay; visual assessment; % herbicidal activity) of metsulfuron-methyl and metribuzin at different locations (number of locations)

soil layer	metsulfuron-methyl				metribuzin			
	days after application				days after application			
	0	30	60	90	0	30	60	90
0 - 10	84±14 (18)	56±33 (17)	31±40 (18)	24±37 (18)	95±7 (8)	91±17 (8)	33±43 (8)	20±34 (8)
10 - 20	-	27±34 (14)	7±20 (15)	9±24 (16)	-	43±42 (8)	17±34 (8)	15±34 (8)
20 - 30	-	11±21 (14)	4±7 (15)	3±7 (15)	-	2±3 (8)	10±8 (8)	2±6 (8)

Figures 2a and 2b show the outdoor results for metsulfuron-methyl and metribuzin. They should be compared with Figures 1a and 1b. In the case of metsulfuron-methyl the mean herbicidal activity decreased from 86 % at day 0 to 27 % at day 90. The mean activity of metribuzin decreased from

93 % to 39 %. The relatively good correlation between indoor and outdoor results is surprising, and is obvious for both herbicides, without regard to the sampling date, the soil layer or the method of evaluation. The main reason might be the fact that the indoor and outdoor tests were usually run simultaneously. Consequently there were no drastic differences between climatic conditions in the greenhouse and in the field.

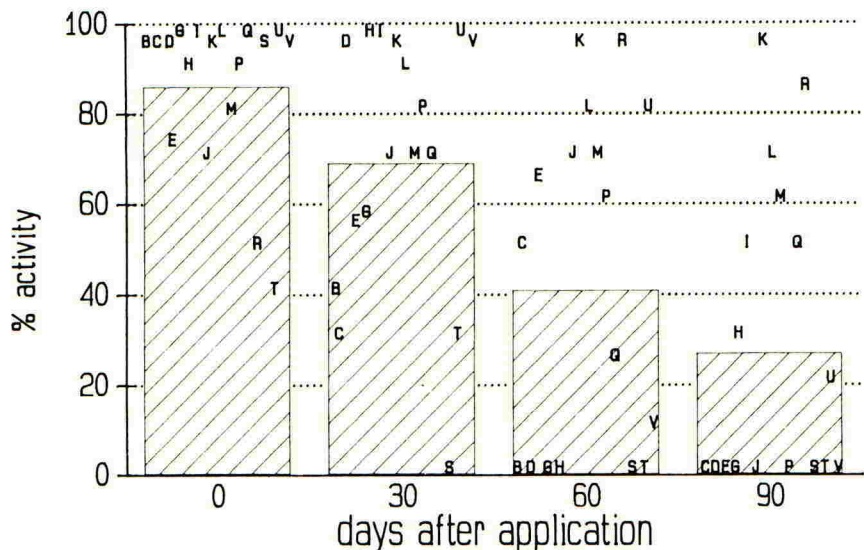


Figure 2a. Residual activity of metsulfuron-methyl
Outdoor bioassay - visual assessment (%)

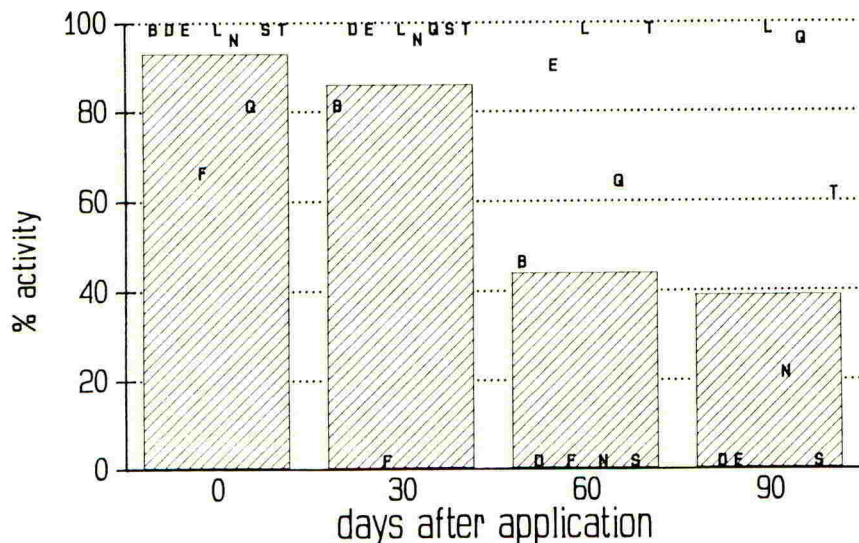


Figure 2b. Residual activity of metribuzin
Outdoor bioassay - visual assessment (%)

A comparison of fresh weight data and visual assessments can be made by Figures 3 and 1b. Generally both methods of evaluation showed similar trends. The mean residual activity of metribuzin decreased from 96 % to 20 % in the case of indoor bioassays, and from 95 % to 20 % in the outdoor bioassays. For the purpose of describing residual activity and showing tendencies in dissipation processes, visual assessments seem to be a less time consuming and more efficient tool. This is especially true, if a large number of samples has to be processed and a thorough statistical analysis is not intended. Furthermore visual assessments might describe slight effects like chlorosis which freshweight data may not reflect.

In some cases negative values for the inhibition of fresh weight were measured, especially in deeper soil layers or at the late sampling dates. This means that growth of test plants in the treated plots was better than in control plots. The reasons for this phenomenon are not clear, but might be explained by factors like the dry conditions during the experimental period in Europe, the permanent growth of weeds in the untreated plots, their water and nutrient consumption, changes in soil structure and different activity of the soil microflora. As a consequence, "control" plots should be treated with a non-residual herbicide and in greenhouse experiments pots should receive nutrient solution instead of pure water. An additional reason might be the stimulating effect of small amounts of active ingredients, which is often observed in dose-response curves.

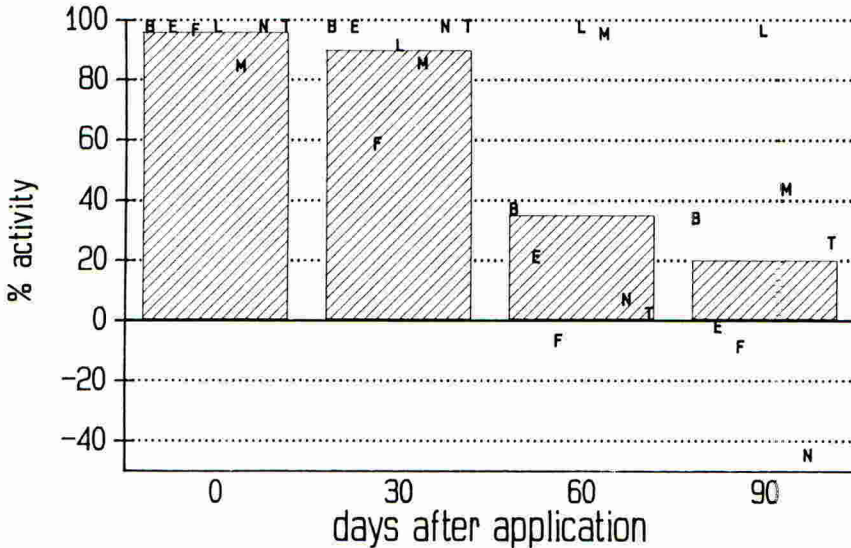


Figure 3. Residual activity of metribuzin
Indoor bioassay - fresh weight reduction (%)

To transform the measured residual activities into herbicide concentrations, these activities have to be compared with dose-response curves, which were run in parallel. This statistical treatment was done

according to Streibig (1988). As a first step a non-linear regression analysis of the data from the dose-response curves was carried out, to give a sigmoid dose-response curve. Besides the bioassays with the treated soil samples tests were also carried out with 1+1 and 1+3 dilutions of treated and untreated soil, which resulted in concentrations of 100%, 50% and 25% of treated soil. This "dilution series" also represents some kind of dose-response curve. Based on the assumptions of the parallel-line assay (Streibig, 1984) this curve should be identical to the dose-response curve, the only difference being a horizontal displacement, which is denoted as "relative potency".

To compare both curves, the highest concentration of the logarithmic dose-response curve was arbitrarily set to 100% or 1. In the same way it was arbitrarily assumed, that the undiluted soil samples also contained the highest concentration, i.e. 100%. If this assumption is right, both curves should be identical. If this assumption is wrong, the "dilution series" shows a horizontal displacement or a relative potency not equal to 1. A relative potency in the dilution series of 0.5 means, that the concentrations in the undiluted soil sample is half the amount of the highest concentration of the dose-response curve.

Figure 4 gives the results for metsulfuron-methyl in the upper soil layer of location P, which met the statistical requirements of the parallel-line assay. On the right scale, the relative potencies are given. As the highest concentration in the dose-response curve was 8 g AI/ha (relative potency = 1), a relative potency of 1.24 at day 0 corresponded to 9.9 g AI/ha. Running this procedure for all sampling dates, resulted in the shown dissipation pattern. No residual activity could be detected at day 90 (Fig. 4).

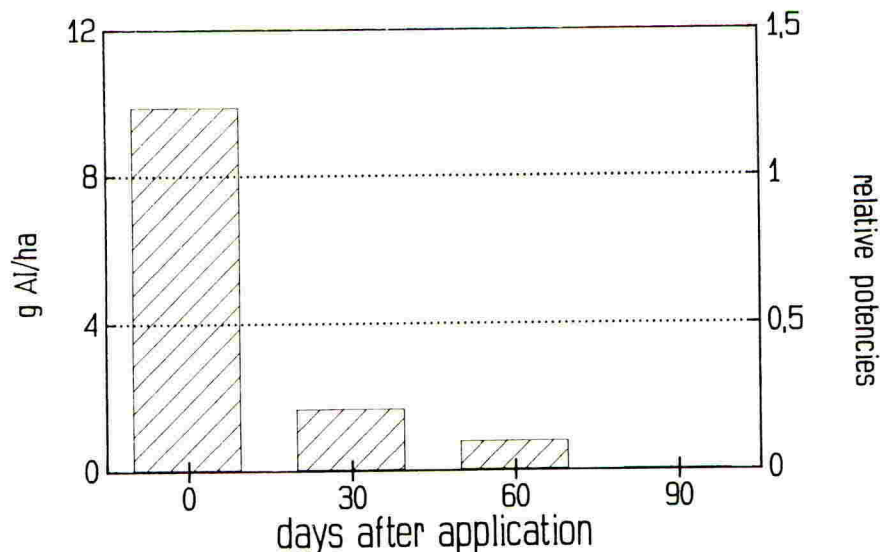


Figure 4. Calculated dissipation of metsulfuron-methyl (0-10 cm, Location P)

This example demonstrates the feasibility of bioassays to calculate dissipation curves using the parallel-line assays. However it is time consuming to run the dilution curves for all samples. Furthermore many data (e.g. the results with metribuzin) did not meet the statistical requirements, e.g. parallelism of curves, which was checked by a F-test.

CONCLUSIONS

The objectives of the collaborative bioassays were to investigate, if a simple test procedure can be used on a broad basis under different climatic conditions to monitor the residual behaviour of herbicides.

The results show that especially if it is only intended to describe residual activities without a thorough statistical analysis, a simple time-saving procedure is sufficient. The observed deviations between different locations can be explained partly by specific soil or climatic conditions. But there are still several cases which remain uncertain. In these cases further tests would be necessary.

Describing residual activities might be valuable for practical purposes like estimating a possible damage to succeeding crops, but the results do not reflect the dissipation behaviour. Depending on the shape of the dose-response curve and on the amount of herbicide which was applied, extensive dissipation might have occurred, even if very high growth inhibitions are still measured.

Gaining information about the amounts of active ingredients at different sampling dates or soil layers proved to be much more difficult and laborious than only describing residual effects. Usually the deviations were very high and do not allow to draw conclusions about the dissipation behaviour. For this purpose analytical methods should be used or the tests must be optimized and have to be much more time consuming.

ACKNOWLEDGEMENTS

We are very grateful to Prof. Dr. J.C. Streibig for doing the statistical analysis of dose-response curves and parallel-line assays.

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QUANTIFICATION AND LOCATION OF TRIASULFURON IN THE SOIL AFTER THREE OR FOUR ANNUAL APPLICATIONS IN THE WINTER OR SPRING

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ABSTRACT

Triasulfuron is a sulphonylurea herbicide under development by Ciba-Geigy Agrochemicals for the control of broadleaved weeds in cereals. The studies described in this paper were designed to determine the extent and position in the soil profile of triasulfuron residues after three or four yearly repeated applications in the winter or spring or after application to soil types thought to be conducive to persistence. Application at four sites with analysis of soil samples taken to a 75 cm depth revealed very low or non-detectable quantities of triasulfuron, demonstrating that bioaccumulation and significant leaching of triasulfuron did not occur. There were some differences in the quantities of triasulfuron detected following winter and spring applications, their significance is discussed in the context of potential phytotoxicity to following crops.

INTRODUCTION

The known sulphonylurea herbicides vary in their soil behaviour, crop tolerance and potential for causing carry-over damage. The sulphonylurea herbicide chlorsulfuron, was withdrawn from sale in 1988 due to the occurrence of phytotoxicity in following crops. This phytotoxicity was associated with autumn use of the herbicide and linked with, although not confined to, use on high pH soils with impeded drainage or waterlogged sub-strata. Investigation revealed the phytotoxicity was due to the extreme sensitivity of certain broadleaved crops to chlorsulfuron combined with the persistence of the herbicide in certain soil conditions. This persistence being largely due to the low dissociation constant (pKa) value, causing high leaching in alkaline soil conditions to areas of the soil profile with low biological activity. Chlorsulfuron degrading only slowly under alkaline conditions, with rapid degradation being favoured by low pH and high biological activity soils.

Field trials were initiated in 1985 to investigate the soil behaviour of triasulfuron (a sulphonylurea herbicide) under UK soil and climatic conditions. The residue and leaching behaviour would be most extreme following repeated annual applications to the same trial areas. This type of study will also yield information regarding the potential for bioaccumulation at the depths tested. The soil distribution of triasulfuron is a function of leaching, in turn largely dependent on the relationship of precipitation to evapotranspiration. As precipitation significantly exceeds evapotranspiration in the winter (Smith & Trafford, 1975), if a propensity to leach is a major factor in enhancing persistence, winter applications should result in higher quantities of triasulfuron remaining in the soil than result from spring applications.

As the major use of triasulfuron will be for the control of broadleaved weeds in the spring, trials were also undertaken to determine soil behaviour (following spring application)

in areas with waterlogged subsoils, or imperfect and intermittent drainage, such soil factors having been identified with phytotoxicity to sugar beet crops of other sulphonylurea herbicides (Nichols *et al.*, 1987). The activity, fate and mode of action of sulphonylurea herbicides have been extensively reviewed by Blair & Martin (1988).

MATERIALS AND METHODS

Four sites were treated with a 20% water dispersible granule formulation of triasulfuron at a rate of 15 g ai/ha. Applications were made using a precision plot sprayer calibrated to deliver 200 litres/ha at 1 m per second. The booms incorporated 6 Lurmark 02.F110 nozzles which operate at 207 kPa. Sites 1 and 2 were unreplicated with a plot size of 50 m x 24 m. These sites were cropped with winter cereals and ploughed annually to 20 cm. Sites 3 and 4 were replicated three times with plots of 12 m x 6 m. Dates of application are presented in Tables 2 and 3. These sites were cropped with cereals when the applications were made and were ploughed to 25 cm before planting winter oilseed rape and sugar beet respectively. All sites were sampled to a depth of 75 cm in 25 cm increments utilising a Humax earth borer. The Humax earth borer consists of a heavy duty electric drill to which a hollow auger is attached into which 25 cm PVC sleeves are fitted. Three samples from the same hole were taken reaching a total depth of 75 cm. Samples were labelled (A) 0-25 cm, (B) 26-50 cm and (C) 51-75 cm. Sampling dates are presented in Tables 2 and 3. Each sample was packed in double wrapped polythene bags and stores at -18°C until analysis. Analysis for triasulfuron was undertaken using the quantitative chemical method described by Iwanzik & Egli (1989), with a limit of detection of 0.02-0.06 parts per billion (ppb). All samples were also subjected to mechanical analysis to determine total sand, silt and clay. Percentage organic matter and pH were also determined, details are given in Table 1. The textural class was determined using the MAFF Soil Texture (85) System.

TABLE 1. Mechanical analysis of soil samples

Textural class	pH	Site No.	Horizon	% Total Sand	% Total Silt	% Total Clay	% Total organic matter
sandy clay	8.2	1	A	50.1	13.3	36.6	3.1
sandy clay loam	8.6		B	49.0	21.4	29.6	1.0
clay	8.6		C	22.0	24.2	53.8	0.6
sandy clay	7.6	2	A	43.9	10.5	45.6	3.1
sandy clay loam	8.2		B	37.9	15.5	46.6	1.1
sandy clay loam	8.3		C	36.0	20.4	43.6	0.9
organic sandy clay	7.8	3	A	51.6	15.8	32.6	10.7
sandy clay	7.9		B	44.0	19.4	36.6	3.9
clay	7.7		C	30.2	23.2	46.6	2.1
sandy clay loam	7.2	4	A	65.8	11.6	22.6	3.1
sandy loam	7.8		B	64.2	17.2	18.6	1.9
sandy loam	8.0		C	64.2	21.2	14.6	1.0

RESULTS

Annual repeated application studies (Table 2)

Site 1

Winter applications were made in the December of each year from 1985 to 1987, the spring applications occurring in March or April of 1985 to 1988. The analysed soil samples were collected 351 days after the last winter application and 259 days after the last spring application, in both cases some three to four months prior to a normal sugar beet drilling date. On this site which was not ploughed prior to sampling, both application timings resulted in similar triasulfuron residues in the 0-25 cm segment. However, the 0.15 ppb residue from the winter applications was a result of a total use over three years of 45 g AI/ha with a last application to sampling period of 351 days. In contrast the 0.13 ppb residue from the spring applications resulted from a use over four years of 60 g AI/ha with a last application to sampling interval of 259 days. The residues found in the 0-25 cm segment could be further dissipated by ploughing. Residues in the 26-75 cm samples were very low, less than 0.04 to 0.06 ppb.

TABLE 2: Quantity and location of triasulfuron (ppb) following yearly repeated applications

Site	Application Rate (g AI/ha)	Date applied	Date sampled	Days after last Application	Depth of sample(cm)		
					0-25	26-50	51-75
1	15	1/12/85 9/12/86 2/12/87	17/11/88	351	.15	<.04	<.04
		1/3/85 1/3/86 22/4/87 3/3/88					
2	15	1/12/85 9/12/86 2/12/87	17/11/88	351	.7	.04	<.04
		1/3/85 1/3/86 22/4/87 3/3/88					

N/A = not analysed

Site 2

Applications were as for site 1, however, at this site, ploughing was employed prior to sampling. Triasulfuron was absent or present in very low concentrations from soil segments 26-50 cm and 51-75 cm, ranging from less than 0.04 ppb to 0.04 ppb, posing no hazard to sugar beet. Trials have demonstrated that the field no effect level for sugar beet is greater than 0.1 g AI/ha triasulfuron (Ciba-Geigy unpublished data). In the 0-25 cm soil segment there was a significant difference between the two application timings in the quantity of residue determined. The winter application resulting in 0.7 ppb and the spring applications in 0.05 ppb. Thus although leaching from either time of application was negligible, the winter applications resulted in a greater residue than the spring applications even though the total quantity of triasulfuron applied was less and the time to sampling greater.

Application at impeded drainage sites (Table 3)

These sites were situated in areas where phytotoxicity to sugar beet had reportedly occurred from chlorsulfuron usage in the previous crop.

Site 3

This site was located near Deeping, Lincolnshire, on an organic sandy clay which increased in clay and declined in organic matter content with depth, the pH varied from 7.9 to 7.7. The soil at this site, (Hodge, *et al.*, 1984) Downholland 1 Association is a clayey humic alluvial gley often with acidic subsoils. Most of the soils in this area are in Wetness Class I or II where the water levels are controlled by ditches and pumps, the degree of waterlogging is dependent on the efficiency of the drainage systems. Applications of triasulfuron was made at this site on 8th April with sampling 293 days later on 26th January. No residues were detected in any soil segment down to 75 cm with a limit of detection (LOD) of 0.05 to 0.06 ppb.

Site 4

This site was located near Sutterton on a sandy clay loam which declined in clay content with depth, the pH ranging from 7.2 to 7.9. The soil at this site (Hodge *et al.*, 1984) is a typical alluvial gley, Tanvats Association. Drainage is usually by ditch and pipe and occasional waterlogging occurs (Wetness Class II), in addition agricultural machinery use can result in soil compaction and temporary surface ponding. Application of triasulfuron was made on 8th April with sampling 293 days later on 26th January. No residues were detected (LOD 0.05 - 0.06 ppb), in any part of the sampled soil profile.

The results from both sites indicate considerable degradation, no significant leaching and a significant safety margin for sensitive broadleaved crops.

TABLE 3. Quantity and location of triasulfuron (ppb) following application at impeded drainage sites

Site	Application Rate(g AI/ha)	Date applied	Date sampled	Days after Application	Depth of sample(cm)		
					0-25	26-50	51-75
3	15	8/4/88	26/1/89	293	<.06	<.05	<.05
4	15	8/4/88	26/1/89	293	<.05	<.05	<.05

DISCUSSION

In the yearly repeated application studies reported here, leaching of detectable quantities of triasulfuron was very low following repeated winter or spring applications. The total active ingredient applied in the spring was greater than that applied in the winter, and as the time to sampling following the spring applications was less, it does appear that winter applications result in an overall slower rate of degradation of triasulfuron as the total residue detected following spring application was similar to or less than that following early winter application. The increased residue from the winter application being retained in the upper soil profile rather than being leached to depth. The lack of leaching may be due to the relationship of precipitation to evapotranspiration in the six months period following a December application. It is reasonable to assume that the majority of the triasulfuron degradation takes place during this six months, the 30 year mean figures for precipitation and evapotranspiration reveal an excess of precipitation of 72 mm, probably not sufficient to cause significant leaching. In contrast, for an application made in October precipitation is in excess by 210 mm which may well cause significant leaching.

It appears that the very long half-lives reported for chlorsulfuron, a function of leaching to depths in the soil where degradation is very slow, are not applicable to triasulfuron applied no earlier than December where the majority of the herbicide is retained in the top 25 cm and available for further degradation a result supported by the work of Iwanzik & Amrein (1988) and Iwanzik & Egli (1989) on spring applications of triasulfuron in Switzerland. This has further implications for possible effects on following crops as the retention of triasulfuron in the top 25 cm enables dilution and further dissipation by cultivation methods such as ploughing.

The behaviour of triasulfuron in soil was also investigated at two sites where the soil type and structure would be conducive to slow degradation - alluvial gley soils with low microbiological activity and impeded drainage. These sites were located in an area where chlorsulfuron usage had resulted in incidences of phytotoxicity to sugar beet. At both sites triasulfuron did not behave as might have been predicted for earlier developed sulphonylureas, displaying an apparent rapid rate of degradation and no detectable leaching. At both sites, however, applications were made in the spring where evapotranspiration would exceed precipitation. The use of an autumn/early winter application at such sites was not investigated.

The fate of triasulfuron in the soil is a result of the interaction of adsorption (to the soil), leaching, degradation and plant uptake, possible effects on following crops are further modulated by the cultivation method employed prior to drilling and the inherent sensitivity of the crop. The adsorption of the sulphonylurea herbicides in general and triasulfuron in particular have been studied and described (Nicholls & Evans, 1985; Beyer *et al.*, 1987; Walker *et al.*, 1989; Walker & Welch, 1989) and are generally characterised as being relatively mobile compounds, although the degree of mobility varies, triasulfuron having been found to be less mobile than metsulfuron-methyl and chlorsulfuron (Walker & Welch, 1989). The rate of degradation of the sulphonylureas is significantly affected by pH decreasing with increasing pH, degradation rates are also reduced where microbial activity is impaired. These features have led to the generally accepted belief that it is the leaching of sulphonylureas to subsoils with low microbial and hydrolysis potential which has resulted in increased persistence and phytotoxic effects on sensitive following crops. Thus the use of certain sulphonylureas in situations where precipitation significantly exceeds evapotranspiration in the months following application (autumn/early winter) or use on sites with

waterlogged or impermeable substrate could lead to phytotoxic effects on following crops. It is likely that the coincidence of these two factors is required combined with a sensitive following crop and a cultivation method which does not dilute residues, to induce a phytotoxic response.

It would appear that triasulfuron applied in the early winter to a freely draining soil, or applied to any soil in the late winter/spring behaves as a 'traditional' herbicide with respect to degradation. From such applications the degradation rate would be described by typical first order kinetics or possibly by the two-stage (two compartment) model postulated by Duffy *et al.*, (1987).

Slow degradation of triasulfuron may only occur from autumn/early winter applications into soil types such as alluvial gley, however, given the reduced mobility of triasulfuron relative to other sulphonylureas, even this possibility remains to be proven.

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EFFECTS OF METSULFURON-METHYL ON FOLLOWING CROPS OF SUGAR BEET AND POTATOES

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ABSTRACT

Metsulfuron-methyl was applied at 1, 2, and 3 times the label recommended rate of 6 g AI/ha to wheat crops in spring 1988 on three different soil types. In spring 1989, these treatments were planted with sugar beet and potatoes grown in normal rotation and as normal commercial practice. No treatment on any soil type resulted in any yield or quality effect on potatoes. The recommended rate of metsulfuron-methyl resulted in no effect on sugar beet in any of the three soil types. In two out of three soil types, no effect on sugar beet was observed at double and triple the recommended rate. Yield loss did not occur in the absence of crop symptoms.

INTRODUCTION

Metsulfuron-methyl has been marketed in the U.K., as 'Ally' (20% water dispersible granule), since 1984 and is used extensively for spring broad-leaved weed control in winter and spring cereals. The product exhibits many of the characteristics of the sulfonylurea group of herbicides: low dose, low mammalian toxicity, rapid metabolism in cereal plants and herbicidal activity via foliage and root uptake (Doig *et al.*, 1983). The recommended use rate of 6 g AI/ha in spring enables the product to dissipate in soil and allows planting of sensitive rotational crops such as sugar beet the following year (Duffy *et al.*, 1987). This predicted behaviour has been confirmed by detailed visual assessments on a large number of field trials done by Du Pont and on commercial crops growing throughout the UK since 1982. The field trials comprised non-replicated treated areas on 169 sites replanted to sugar beet or oilseed rape. Application rates of up to 32 g AI/ha applied to a wide range of soil types and growing conditions indicated no damage and a large margin of safety for rotational crops. However, yield data were not available in these trials and the present work was done to determine if yield effects occurred in the absence of visual symptoms.

This paper describes trials determining the yield and quality of sugar beet and potatoes grown in rotation with cereals treated with metsulfuron-methyl.

MATERIALS AND METHODS

Trials were done on soil types representative of major sugar beet and potato growing areas, details are given in Table 1. Cereal

crops, grown as normal commercial practice were treated post-emergence in spring 1988 with metsulfuron-methyl at 6, 12 and 18 g AI/ha. Other herbicides were applied as necessary but do not confound the test. Sugar beet and potatoes, grown as normal commercial practice, were grown in 1989 as following crops to the treated cereals.

TABLE 1. Location and soil details of trial sites

Location	Crop	Soil Type	pH	% o.m.
Cambridge-shire	potato	organic sandy loam (oSL)	7.8	11.3
	sugar beet	organic sandy loam (oSL)	7.3	15.7
Nottingham-shire	potato	loamy sand (LS)	6.9	1.4
	sugar beet	loamy sand (LS)	7.2	0.9
Norfolk	potato	silty clay loam (ZCL)	8.0	2.4
	sugar beet	sandy silt loam (SZL)	7.8	1.9

Each trial comprised a randomised block design with nine replicates; the number of replicates was calculated from analysis of the levels of background variation recorded in previous sugar beet and potato trials on the three farms, so that the present trials could detect real yield differences of approximately 5 per cent. Assessments were made of plant growth and vigour during the growing season and of yield and quality of the crops at harvest. Soil samples (to a depth of 15 cm) were taken in early May 1989 (approximately 12 months after treatment) and analysed for the presence of metsulfuron-methyl residues using a lentil bioassay (Strek *et al.*, 1989) and an enzyme-linked immunosorbent assay (Peter *et al.*, 1989).

RESULTS

Growth and yield of potatoes

The June-July assessment of crop ground cover and saleable yield of tubers from each of the three sites are shown in Table 2. The metsulfuron-methyl treatments applied to the previous wheat crop had no significant effect on the growth or yield of potatoes at each site. After harvest the crops were graded for size and quality and at none of the sites did the metsulfuron-methyl treatments have any consistent effects on yield of small tubers or on any category of reject tubers.

Growth and yield of sugar beet

The June-July assessment of crop ground cover and yield of clean beet from each of the three sites are shown in Table 3. The metsulfuron-methyl treatments applied to the previous winter wheat crops had no significant effect on the growth or yield of sugar beet

TABLE 2. Growth and yield of potatoes following treatment of cereals with metsulfuron-methyl at 3 sites

Previous cereal treatment	% crop ground cover (June-July)			Saleable yield (t/ha)		
	oSL	LS	ZCL	oSL	LS	ZCL
metsulfuron-methyl 6 g AI/ha	60.4	49.3	64.9	24.9	51.7	34.8
metsulfuron-methyl 12 g AI/ha	57.6	49.0	62.2	23.2	53.6	34.4
metsulfuron-methyl 18 g AI/ha	65.2	48.1	63.6	24.1	52.0	33.5
Untreated	61.4	48.4	64.4	24.7	53.7	34.4
LSD (5%)	8.12	4.63	3.62	2.27	2.79	2.15

TABLE 3. Growth and yield of sugar beet following treatment of cereals with metsulfuron-methyl at 3 sites

Previous cereal treatment	% Crop ground cover (June-July)			Clean beet yield (t/ha)		
	oSL	LS	SZL	oSL	LS	SZL
metsulfuron-methyl 6 g AI/ha	52.5	64.4*	89.3	63.1	70.4	63.6
metsulfuron-methyl 12 g AI/ha	60.7	56.1*	86.9	64.6	67.5*	61.9
metsulfuron-methyl 18 g AI/ha	58.3	42.2*	86.8	62.2	63.9*	64.0
Untreated	59.4	73.9	86.7	63.6	71.0	62.9
LSD (5%)	8.40	6.95	3.25	2.64	3.37	6.09

* Significantly different from untreated.

at the organic sandy loam and sandy silt loam sites. At these two sites, the treatments had no significant effect on sugar content, sugar yield, amino-nitrogen content or degree of root fanging at harvest.

At the loamy sand site, metsulfuron-methyl at 6 g AI/ha applied to the previous spring wheat crop had no significant effect on clean beet yield, sugar content, sugar yield, amino-nitrogen content or

degree of root fanging despite the occurrence of transient crop effects in June. Treatment of cereals at 12 and 18 g AI/ha resulted in reduced growth and vigour of sugar beet assessed in mid and late June but no visible differences in the crop canopy were present by 19 July, when full crop cover had been reached on all treatments. The early effects on plant vigour were reflected in final yields of clean beet with a slight reduction ($P < 0.05$) following 12 g AI/ha and a greater reduction ($P < 0.001$) with the 18 g AI/ha treatment. The same two treatments increased root fanging at harvest but only the higher rate treatment significantly reduced sugar content; 17.3% compared with untreated 17.8%.

Assessment of soil residues

Soil samples taken in early May 1989, immediately after the sugar beet and potatoes were planted, were assayed using lentils as a test plant and the percentage root injury detected is shown in Table 4. Symptoms on all test plants were characteristic of sulfonylurea residues and no other symptoms were noted indicating that the lentil response was associated with the presence of metsulfonyl-methyl residues. Du Pont laboratory work and experience with the Laboratory Recrop Bioassay (IRB) (see Peter *et al.*, 1989) indicates that sugar beet grown in the field in U.K. shows visual symptoms of crop damage when metsulfuron-methyl or chlorsulfuron residues are present in soil at the level which causes 50% lentil root injury or above in the bioassay. Potatoes are more resistant than sugar beet to these sulfonylurea herbicides. Hence the bioassay predicted some visual symptoms of sugar beet damage on the loamy sand site following 12 g AI/ha and more severe symptoms following 18 g AI/ha. Part of the soil samples was analysed for the presence of metsulfuron-methyl using an enzyme-linked immunosorbent assay technique and mean results, in parts per trillion (ppt) are shown in Table 5. The untreated plots contained less than the minimum level of quantification; less than 50 ppt.

TABLE 4. Percentage lentil root injury in soil from 3 sites sampled May 1989 (mean of three samples)

Previous Cereal treatment	Potatoes			Sugar beet		
	oSL	LS	ZCL	oSL	LS	SZC
metsulfuron-methyl 6 g AI/ha	13	2	0	0	22	0
metsulfuron-methyl 12 g AI/ha	25	1	0	5	50	0
metsulfuron-methyl 18g AI/ha	39	53	0	7	70	0
Untreated	22	0	0	0	2	0

TABLE 5. Comparison of lentil root injury and immunoassay analysis of soil from sugar beet plots at the loamy sand site sampled May 1989 (mean of 3 samples)

Previous cereal treatment	% lentil root injury	metsulfuron-methyl (ppt)
metsulfuron-methyl 6 g AI/ha	22.0	59
metsulfuron-methyl 12 g AI/ha	50.3	78
metsulfuron-methyl 18 g AI/ha	69.7	159
Untreated	1.7	N.D.

N.D. = Below minimum level of quantification; less than 50 ppt

DISCUSSION

The results indicate that metsulfuron-methyl applied to cereals as recommended, at 6 g AI/ha, is safe to sugar beet and potatoes grown in normal rotation across the range of soil types. On medium and heavy soils, there is a large margin of safety with three times the label rate having no effect on following crops. This has been confirmed by the very extensive commercial use of the product in arable rotations in UK, Ireland, France and Germany over five seasons.

The results from the loamy sand site indicate that 6 g AI/ha had no effect on yield or quality of sugar beet or potatoes but double the recommended rate resulted in visible reduction of sugar beet, growth and an associated loss of almost 5% in clean beet yield. At this site, the residues of metsulfuron-methyl, as measured by the bioassay, were markedly higher in the sugar beet field compared to the nearby potato field. This may be explained by the crop preceding sugar beet being spring wheat which was poorly established at the time of application (only 50% ground cover) and hence intercepting less spray, together with the lack of irrigation of the spring wheat during the very dry summer of 1988 (the winter wheat prior to potatoes received two doses of irrigation totalling 50 mm during the same period) which would reduce chemical and microbial breakdown in soil. Both these factors could increase the likelihood of herbicide residues remaining in the soil. In addition, the sugar beet was growing in soil with less than 1.0% organic matter and this very unusual situation increases the phytotoxic activity of metsulfuron-methyl in soil (Beyer *et al.*, 1987). In view of these factors, it is considered that the result obtained at this site represents a "worst-case" scenario, and again this is confirmed by commercial experience on light soils.

These trials confirm that where residues of metsulfuron-methyl are at damaging levels in soil, then any yield loss is associated with easily visible and characteristic crop symptoms. In the absence of visible crop symptoms, reduction in yield, or loss of quality did not occur and these experiments allay the fears of some agronomists (J. Orson ADAS Cambridge pers. comm.) that "sub clinical yield effects" may be associated with low levels of residues in soil.

The work also confirmed the correlation between results obtained in the lentil bioassay and the occurrence of crop damage in the field. The bioassay has proved valuable in investigating field problems associated with residues of sulfonylurea herbicides in soil where the extremely sensitive immunoassay technique (detection limit 50 ppt) cannot be used routinely due to sampling difficulties and possible contamination during collection and transport with extremely small amounts of chemical.

ACKNOWLEDGEMENTS

The author thanks the Agricultural Development and Advisory Service for doing the field work and Oxford Plant Sciences for the lentil bioassay work.

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CONCEPT, STRUCTURE AND VALIDATION OF THE EXPERT SYSTEM HERBASYS
(HERBICIDE ADVISORY SYSTEM) FOR SELECTION OF HERBICIDES,
PROGNOSIS OF PERSISTENCE AND EFFECTS ON SUCCEEDING CROPS

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ABSTRACT

The concept and structure of an expert system for herbicide advice (HERBASYS) is described, and results of field experiments for its validation are presented. HERBASYS is designed for the agricultural extension services and includes 3 different modules for the selection of herbicides (HERBASEL), the site-specific estimation of potential ground-water contamination (CHEMPROG) and the prognoses of herbicide persistence and effects of residues on succeeding crops (ANPROG). Field experiments for the validation of the predictions by the sub-models of ANPROG generally show good agreement between observed and predicted residues and prognoses of crop response and actual loss of yield although there exists a tendency for overestimating the residue level and crop damage.

INTRODUCTION

Herbicides are an essential part of modern techniques in plant and food production by agricultural and horticultural systems. Every cropping system has a temporary impact on the agro-ecosystem.

Several computerized decision systems have been developed to support the selection of appropriate herbicides (e.g. Edwards-Jones *et al.*, 1989). Additionally, it is necessary to develop decision support systems in plant protection that do not account primarily only for economical aspects but also enable agricultural extension services and farmers to use evaluated simulation models and estimation procedures for prognoses of possible side effects. Some applications of the use of simulation models for the prediction of herbicide persistence have been described by Walker & Eagle (1983) and Ferris *et al.* (1990).

CONCEPT OF HERBASYS

Solving problems in agriculture require, interdisciplinary knowledge which is sometimes empirical and heuristical and may depend on the evaluation of a great number of data. Biological processes can be described by simulation models which are developed in many places and represent procedural knowledge. In order to make all different kinds of knowledge available in a herbicide advisory system, techniques of computer programming used in the development of 'artificial intelligence'- systems have been combined with elements of data base technologies, rule-based systems and simulation models in the presented system HERBASYS (= herbicide advisory system).

HERBASYS is designed as a knowledge-based computer system to support the agricultural extension services. It contains expert knowledge and strategies for the solution of problems concerning some economic and ecological aspects of herbicide use in agricultural practice, i.e. the selection of herbicides, the site-specific assessment of potential ground-water contamination and prognoses of herbicide dissipation and effects of residues on succeeding crops.

For the adaptation of the advisory system to the decision processes of the individual farmer, HERBASYS considers site and user-specific conditions. The lack of information available in actual field situations, limits the use of complex simulation models for advisory purposes and requires a more simple procedure which may be less precise but could be used more widespread. Routines for the actualization of the knowledge bases according to the registration of pesticides in Germany and simple hardware requirements, that allow to run the system on low-cost DOS computers with 640 Kbytes base memory and a hard disk, are implemented in order to guarantee the acceptance of HERBASYS in agricultural practice. In addition, computer/user interfaces that minimize typing and control the logic of input data provide for a comfortable access to the program and the use of expert knowledge. According to the concept of knowledge-based systems, HERBASYS is designed only to support decision processes but not to decide by itself.

STRUCTURE OF HERBASYS

The expert system includes different modules (HERBASEL, CHEMPROG and ANPROG) which are described in detail by Gottesbüren *et al.* (1990a), (1990b) and Pestemer *et al.* (1990). Figure 1 shows the modular structure of HERBASYS, connections between the different modules and the general data base.

HERBASEL (Herbicide selection), which is mainly a data-base program, was designed for an appropriate selection of registered herbicides for site-specific weed problems taking into account economic thresholds and herbicide activity.

CHEMPROG enables a site-specific assessment of the potential danger of ground-water contamination by pesticides accor-

ding to the concept of Blume & Brümmer (1987) for the use of field methods for predicting pesticide behaviour in soil.

It combines parameters of the pesticide behaviour in question and site-specific data about soil (texture, pH-value, organic carbon content), climate (mean temperature, precipitation, climatic water balance), depth of the ground-water table and agricultural practice in order to describe the relative sorption and elimination in soil.

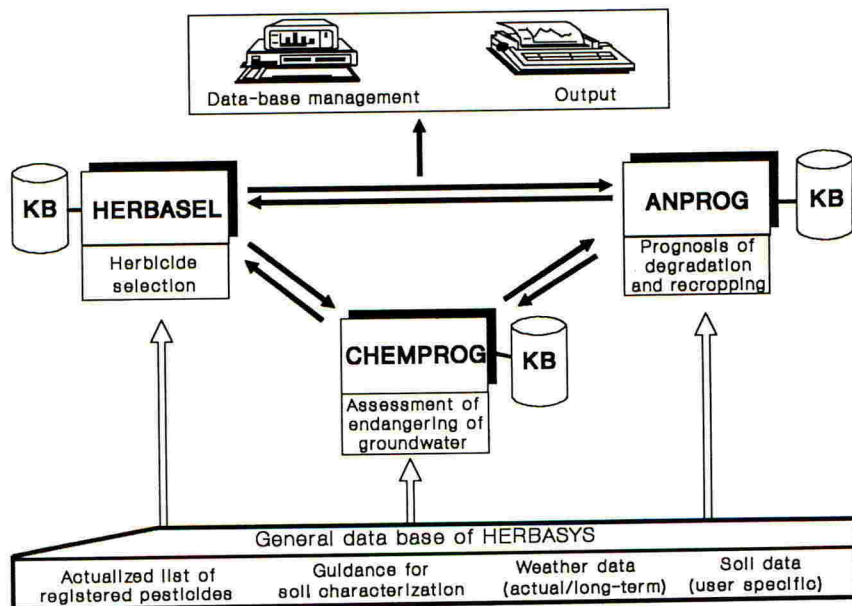


Figure 1. Modular structure of HERBASYS (KB = Knowledge base)

By using this module of HERBASYS, no quantitative results, but estimations of a relative endangering of ground-water are given. This procedure was chosen for a widespread application, because of continuous uncertainties in knowledge and predictability of the processes of pesticide leaching to ground-water for a great number of sites, limiting the use of existing leaching models, where detailed informations are lacking.

ANPROG combines prognoses models in order to simulate the degradation of several herbicides in soils (Walker & Barnes, 1981) and to predict the potential effects of their available residues on succeeding crops (Pestemer *et al.*, 1980), considering site-specific soil and weather data (Figure 2). Due to user-specific informations about the site, date and dosage of applied herbicide and following crop the expert system selects appropriate degradation parameters for the corresponding herbi-

side from the knowledge base, quantifying the dependence of degradation on soil temperature and moisture content.

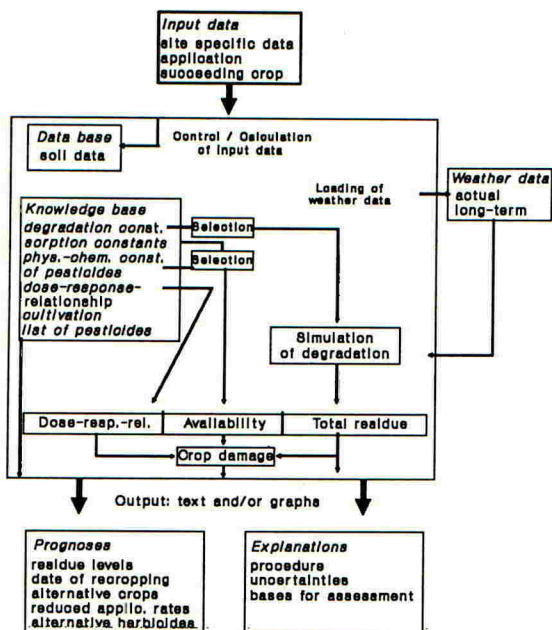


Figure 2. Schematic diagram of ANPROG for the prognoses of herbicide degradation and effects on succeeding crops

The amounts of total residues are simulated, and their potential availability to plants is calculated by using the distribution coefficients (K_d -values). These data are used for the prediction of potential effects on succeeding crops by comparing the residues available to plants with the dose-response relationship for the corresponding herbicide and the crop in question. In addition to the predictions of crop safety, safe re cropping dates, less sensitive crops, reduced amounts of applied herbicide that allow re cropping at the fixed date as well as appropriate alternative herbicides can be recommended. The procedures and uncertainties of the prognosis are explained to the user by the expert system.

VALIDATION EXPERIMENTS

Field experiments have been carried out at different field sites to validate the predictions of the sub-models of ANPROG.

Prognosis of persistence

The dissipation rates of chlortoluron under field conditions were measured from August to November 1989 at two sites

near Braunschweig (Ahlum and BBA) with a loamy silt soil (pH 7.0, organic carbon 1.02%) and a sandy loam soil (pH 6.3, organic carbon 1.0%) respectively. Considering site specific soil and weather data, the degradation of chlortoluron was simulated with ANPROG. Using a matching function in order to consider relevant soil characteristics, degradation parameters of the simulation model were chosen from the knowledge base of ANPROG which have been estimated from previous laboratory incubation experiments with chlortoluron in BBA soil in 1983. The activation energy (E_a) according to the Arrhenius equation was 42 kilo Joules/mol, and the parameters for the description of moisture dependency according to the equation used in the model by Walker & Barnes (1981) ($\text{Half-life} = A * \text{moisture}^{-B}$) were 366 (A) and 0.791 (B). The dissipation rates of chlortoluron were higher in Ahlum soil than in BBA soil (Figure 3).

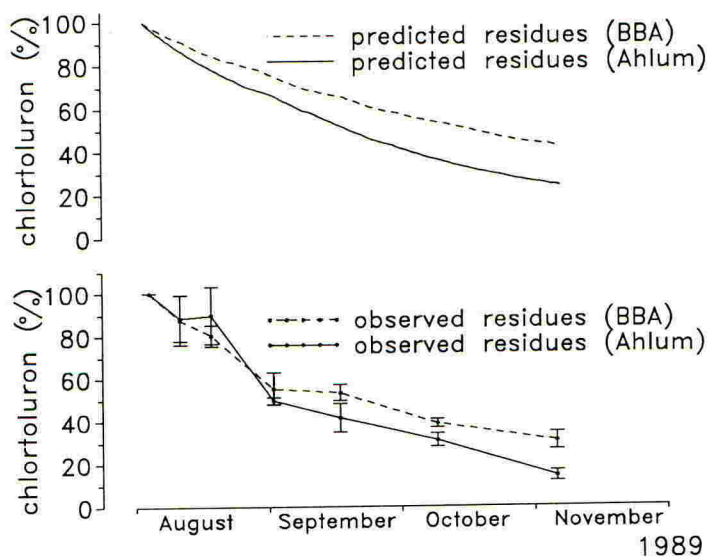


Figure 3. Observed and predicted residues of chlortoluron in different soils

The actual differences in the speed of degradation of chlortoluron in the soils could be estimated by the simulation model although the measured residue levels were overestimated. Therefore, it appears that appropriate degradation parameters for the simulation model can be estimated from laboratory incubation experiments and transferred to similar soils under different climatic conditions.

Prognosis of crop response

In order to validate the prognosis model by Pestemer *et al.* (1980) for safe recropping, field experiments were conducted at the Ahlum site with different succeeding crops and herbicides. At practice oriented sowing dates, different concentrations of

the herbicide were applied and residues incorporated into the topsoil (0-10 cm) to simulate residue levels at post-harvest or after crop failure. The potential available amounts are compared with the ED-values (ED = effective dose) of herbicide/crop-combinations from hydroponic experiments. The prognosis is made according to the activity categories of Pestemer *et al.* (1980). Results gained with pendimethalin, methabenzthiazuron and different crops are given in Table 1, which generally show good agreement between the observed and the predicted crop response. A tendency for overestimating the crop damage level was marked.

TABLE 1. Prognoses of recropping and results of field trials

Herbicide µg AI/l soil (0-10 cm)	total residue	potential available	Succeeding crops	Activity category	
				Prognosis	Result
pendimethalin	200	14	spinach	x	+/-
	300	21	flax	+/-	+/-
	600	43	flax	+/-	+/-
	800	57	spinach	xxx	xxx *
	1200	85	flax	+/-	+/-
	1650	117	spinach	xxx	xxx *
methabenz- thiazuron	400	70	flax	+/-	+/-
	700	123	corn salad	xxx	xx *
	800	140	flax	xxx	+/-
	1400	245	corn salad	xxx	xxx *
	2000	350	flax	xxx	+/- to x
	2000	350	corn salad	xxx	xxx *

+/- = no response = safe, x = slight damage = slight risk,

xx = moderate damage = significant crop damage,

xxx = severe damage = crop failure likely

* = crop damage significant [Dunnett (P = 0.05)]

Validation under practical conditions

Crop-rotation experiments had been carried out with winter wheat as a following crop after maize in 1985, 1986 and 1987 on a silty soil in Bernburg/Saale (pH 7.5, organic carbon 1.33%) by Kreuz & Hamann (1989) and Kreuz *et al.* (1990). After the application of atrazine (1.25 kg AI/ha) to maize in May, residue levels in the range of 0.14, 0.21 and 0.28 mg AI/l soil in the 0-10 cm layer (assuming bulk density of 1.4 g/ml) could be detected after harvest 1985, 1986 and 1987, and an average loss of 10% of the yield of the rotational crop winter wheat was recorded.

Using this data for recalculation of the experiment with the module ANPROG of HERBASYS (weather data of Braunschweig 1987-1989) and the degradation parameters of atrazine (Activation energy (Ea) = 70 kilo Joule/mol, A= 60.8, B= 0.167)

by Walker (1978), residue levels from 0.14 to 0.21 mg/l soil were calculated by the simulation model for October. This fairly well agrees with the original field data (Figure 4).

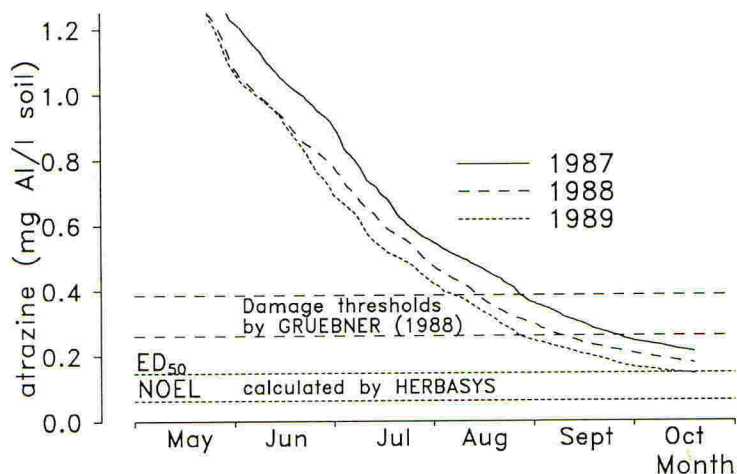


Figure 4. Simulated degradation curves of atrazine (1987-89) and ranges of damage thresholds in the Bernburg-soil according to Grübner (1988) and calculated by HERBASYS

NOEL = No Observable Effect Level; ED₅₀ = Effective Dose for severe crop damage (50% loss of yield)

Comparing the potentially available amounts of simulated residue levels with the ED-values of the dose-response relationship for atrazine with winter wheat calculated for the particular soil, ANPROG gives the advice that recropping winter wheat will probably lead to severe crop damage, and crop failure will be likely. In contrast to the damage thresholds by Grübner (1988) for the phytotoxic levels of chlortriazines for winter cereals of 0.28-0.42 mg AI/l soil (assuming a bulk density of 1.4 g/ml), which predicted no loss of yield, the recropping prognosis of ANPROG indicated the measured crop damage but overestimated the amount of loss of yield.

Investigations of atrazine residues in soils after being applied to maize and their effects on the rotational winter cereals on large scale fields of farmers's cooperatives with practical production systems in the region of Dresden were conducted in 1988 and 1989 by the local plant protection authorities. Using specific soil and weather data and the history of application, recalculations of the residue behaviour of atrazine were made with ANPROG. A comparison between measured and simulated residue levels of atrazine after single or double application in the top 10 cm layer of 17 different fields at post-harvest is given in Figure 5 and Table 2.

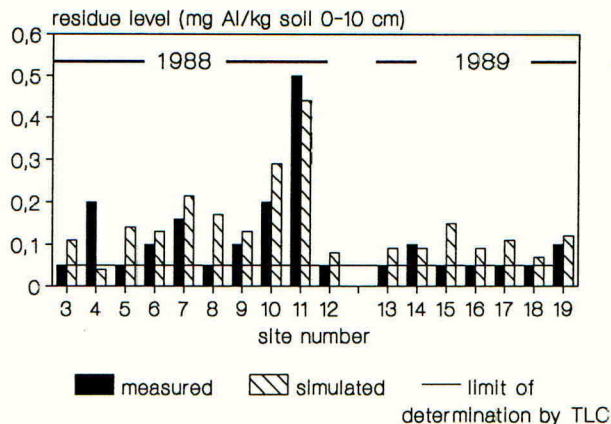


Figure 5. Observed and simulated atrazine residues in top soil (0-10 cm) at 17 different sites near Dresden (1988/89) (TLC = Thin-Layer Chromatography)

TABLE 2. Prognoses of crop safety by HERBASYS and crop response of winter wheat at different sites near Dresden 1988/1989 (n.d. = not detectable)

site no.	atrazine residues (mg AI/ kg soil 0-10 cm)		Crop damage prognosis (activity category)	
	predicted	observed	prognosis	observed
3	0.11	n.d.	x	+/-
4	0.04	0.2	+/-	+/-
5	0.14	n.d.	xxx	+/-
6	0.13	0.1	--	--
7	0.24	0.16	--	--
8	0.17	0.05	xxx	+/-
9	0.13	0.1	--	--
10	0.29	0.2	xxx	x - xx
11	0.44	0.5	xxx	xxx
12	0.08	0.05	x	+/-
13	0.09	n.d.	x	x
14	0.09	0.1	x	+/-
15	0.15	n.d.	xx	+/-
16	0.09	n.d.	x	+/-
17	0.11	n.d.	x	+/-
18	0.07	n.d.	x	+/-
19	0.12	0.1	xx	+/-

+/- = no response, x = slight damage, xx = moderate damage, xxx = severe damage

With the exception of site no. 4, observed and predicted residues agree well. The prognosis of the crop-damage level of winter wheat by ANPROG and actual crop responses are compared in Table 2. In 3 out of 14 cases, the predicted and observed crop response were of the same category; in 6, 3 and 2 cases, crop-damage level (reduction in the number of plants/m²) was overestimated by ANPROG by 1, 2 and 3 activity categories, respectively. There was no underestimation.

CONCLUSIONS

The tendency for overestimation of existing residue levels by the simulation model and the prediction of crop damage by the HERBASYS includes a safety factor for the prognosis of the effects of available herbicide residues in soil to succeeding crops.

ACKNOWLEDGEMENTS

The authors thank Dr. Grübner, Pflanzenschutzamt Dresden, for providing field and residue data.

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Movement in Soils: Methodology

Session Organiser and Chairman:

DR RICHARD ALLEN

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1991 BCPC MONO. No. 47 PESTICIDES IN SOILS AND WATER

EXPERIMENTAL METHODS FOR MEASURING MOVEMENT OF PESTICIDES IN SOIL

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(NO WRITTEN SUBMISSION)

1991 BCPC MONO. No. 47 PESTICIDES IN SOILS AND WATER

METHODS OF MONITORING SOIL WATER REGIMES AND THE INTERPRETATION OF DATA RELEVANT TO PESTICIDE FATE AND BEHAVIOUR

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ABSTRACT

Characterization of soil water regimes is an essential component of field studies investigating the fate and behaviour of pesticides. The measurement of soil water content, potential and movement is described and appropriate field monitoring procedures suggested. Interpretation of analytical data must be carried out with reference to the prevailing water regimes.

INTRODUCTION

Knowledge of water content, energy status and fluxes within the soil is fundamental to the understanding of the environmental fate and behaviour of a pesticide. Pesticide adsorption, degradation, hydrolysis, retention and leaching are just a few of the important processes concerned. Laboratory tests are carried out to simulate some of the different water regimes encountered in a field situation but, in reality, soil water status and fluxes are dynamic and are influenced by a variety of factors including soil type, topography, drainage, climate and land use. The interaction of these factors are known to contribute to forms of pesticide behaviour not predicted by the closely controlled, albeit variable, conditions of laboratory testing.

The mass or volume fraction of water in the soil is termed the soil water content. Water is held within and around soil particles, aggregates, organic complexes or pore spaces by pressure forces or potentials. As soil dries from saturation the potential decreases as large pores empty of water. Progressive decreases in potential continue to empty narrower pores and the films of water held around soil particles are reduced in thickness and consequently soil water content decreases.

The relation between water content and water potential controls the amount of water retained in the soil and thus the volume and rate at which water percolates through the soil. The two phases are sometimes termed immobile and mobile soil water fractions and the relative proportion varies for different soil types (Carter, 1989). When the soil is saturated there is no potential and fluxes can be very rapid, e.g. a hydraulic conductivity of 6 m day^{-1} in a sandy soil. It is unusual for saturated conditions to persist in many agricultural soils and water movement, termed unsaturated flow, continues through the smaller soil pores at a much slower rate, e.g. 0.01 m day^{-1} at -5 kPa in a sandy soil.

Established field techniques are available to characterize the dynamic nature of soil water regimes (Smith and Mullins, 1990). Some are currently the subject of International Standardization on aspects of Soil Quality within the Physical Methods working group.

MONITORING METHODS

Water content

Soil water content is most simply measured by sampling a small amount of soil, oven drying it and then calculating the gravimetric water content. The method is site destructive and requires repetition and replication to express vertical and lateral soil variability. Soil bulk density data is required to express mass data on a volumetric basis - this being essential for flux and mass balance calculations.

A neutron probe contains a radioactive source which emits fast neutrons into the surrounding soil. On collision with hydrogen atoms in soil water they slow and their extent is sampled by a slow neutron detector. Electrical pulses from the detector are converted into mean count rate, which is translated into a volumetric soil water content using an appropriate calibration curve. The neutron source and detector can be lowered into permanent access tubes or holes and readings taken at predetermined depth intervals (Bell, 1976). Neutron probes are ideal for non-destructive measurement of water content change in the same soil profile over time and resulting data can be used to calculate evapotranspiration and drainage. Radiation safety procedures must be followed when this equipment is in use.

Time domain reflectometry (TDR) (Topp et al., 1980) and the capacitance probe (Dean et al., 1987) are relatively new methods and are not extensively used in the U.K. to determine soil water contents. Both methods are particularly promising since they have the advantage of the neutron probe but have no radiation source.

Soil water potential

Tensiometers consist of a water-filled instrument with a porous, usually ceramic, tip. Several tensiometers are normally installed at different depths to characterize a soil profile. As a soil layer dries, the potential decreases, water is drawn from the tensiometer and a negative pressure is created equating to that of the soil. Various methods including mercury manometers, pressure transducers and vacuum gauges are used to provide a direct measure of soil water potential. Tensiometers can also measure positive pressures in soil which indicate the presence of a water-table and/or the flow of water.

Hydraulic conductivity

The auger hole method is a common technique used to determine the saturated hydraulic conductivity of a soil layer. A water-table can be drawn down within a borehole and the rate of recovery plotted (Boast and Kirkham, 1971). A lateral saturated hydraulic conductivity is derived by calculation. The inverse auger hole method provides a vertical/lateral measurement of hydraulic conductivity where a water-table is not present. A head of water is maintained in an auger hole and the rate at which that water is replaced used to determine saturated hydraulic conductivity. Replication is simple and relatively rapid, for example six soil profiles per day can be characterized with the latter method.

Soil water can move rapidly through certain soils (Hollis and Carter, 1990) but it is difficult to quantify the relative volumes involved. Dye tracing is a common technique used to follow the pathways of water movement. Preferential flow can be observed in sandy soils whilst evidence of fissure and macropore flow are well documented (Van Genuchten et al., 1990). Methylene blue powder can be applied (1-2 grams per square metre) before the soil profile begins to wet up in autumn. As water infiltrates, test squares can be dug out periodically and a semi-quantitative estimate of flow made. In a soil at Rosemaund EHF macropore/fissure flow may only account for 2% of total water fluxes in the late autumn-winter period. However, during and immediately after heavy rainfall events 60% of flow may occur in the larger voids.

Auger holes or wells are used to monitor water-table levels. In freely draining soils an auger hole is placed to the maximum depth required whilst in soils with slowly permeable horizons the holes are nested to characterize perched water-table levels. A perforated lining tube is used to prevent soil slump and a lid placed to prevent infill.

Piezometers are used to monitor water-table levels and pressure potentials in soil profiles, but at specific depths. Only one end of a piezometer is porous - e.g. sand, ceramic or metal - and groundwater only enters the device at the tip. Water from auger holes and piezometers can be sampled to determine the presence of pesticides.

Surface and lateral flow

Surface runoff occurs when the infiltration capacity of the soil surface is exceeded by rainfall intensity and surplus water ponds or moves downslope. Intercepting devices placed across slope with continuous recording gauges provide an estimate of runoff losses. The lateral movement of water through the soils (throughflow) usually occurs above a less permeable horizon. Pits can be dug in the soil profile and lateral flow intercepted at the base of each relevant soil horizon. A metal or plastic sheet is inserted in the base of the relevant soil horizon and is connected to a bottle by a collection trough or pipe. Only saturated fluxes can be intercepted but the method is disruptive to normal field activities. Total volumes of water fluxes can be estimated by defining the contributing area to the throughflow pit. Tensiometers are often used to help characterize flow pathways but such data is difficult to obtain and interpret and only semi-quantitative calculations can be made. Soil water in the unsaturated zone can be intercepted (Clark et al., 1990), but the sampling zone and type of soil water obtained is difficult to characterize.

MONITORING PROCEDURES

Soil is a heterogenous medium and water status and hydraulic conductivity can vary considerably for even a closely defined soil type. Replication of measurements and sampling is therefore necessary. A typical experimental plot for pesticide fate investigations of 0.1 ha situated on a freely draining soil overlying a water-table within 2 m depth would contain three neutron probe access tubes to 1.6 m depth, three sets of triplicated soil water suction samplers at 1.5 m depth and six piezometers at 2.0 m depth. The site should be monitored and water

samples taken before a pesticide application and then visited on a routine basis, e.g. fortnightly and then after significant rainfall events (approximately 10 mm). Where lateral or surface flow are dominant processes drain outflows and adjacent surface waters should also be sampled. The development of Standard Operating Procedures for monitoring to Good Laboratory Practice compliance is relatively straightforward for certain methods and could be based on the International Standard methodologies. Other techniques like characterization of macropores, the decision as to when to monitor and the interpretation of field results can only be made by an experienced scientist.

Interpretation of data

The seasonal variation in the water content of a soil profile (determined by the neutron probe) is shown in Figure 1. During late autumn-winter months evaporation and evapotranspiration are low and rainfall is retained in the soil profile until a field capacity state is reached. In freely draining soils subsequent rainfall events initiate drainage from the soil profile. Water contents steadily decrease in spring and summer months in response to a net upward flux caused by evapotranspiration. Figure 2 shows the temporal decrease in soil water contents and illustrates how drainage volumes can be estimated. The rate and direction in which water moves is related to the soil water potential. A water-table or saturated zone is identified when the potential due to gravity equals the total soil water potential. Figure 2 also illustrates evapotranspiration and drainage zones. The two zones are separated by a zero flux plane which is identified by an inflexion of the potential line. This can be interpreted as the maximum depth of water abstraction by plants and the point at which drainage commences.

The water collected from suction samplers and surface and lateral flow samples can be analysed, and pesticide concentrations related to the prevailing water regime, to obtain an estimate of leaching or runoff losses.

CONCLUSION

Field data on soil properties and water regime are essential input parameters to predictive models. Data from an experimental site representative of the typical usage area will provide essential validation data and extrapolation of data to a wider area than the test plot itself, provided consideration is given to all the relevant inter-related factors.

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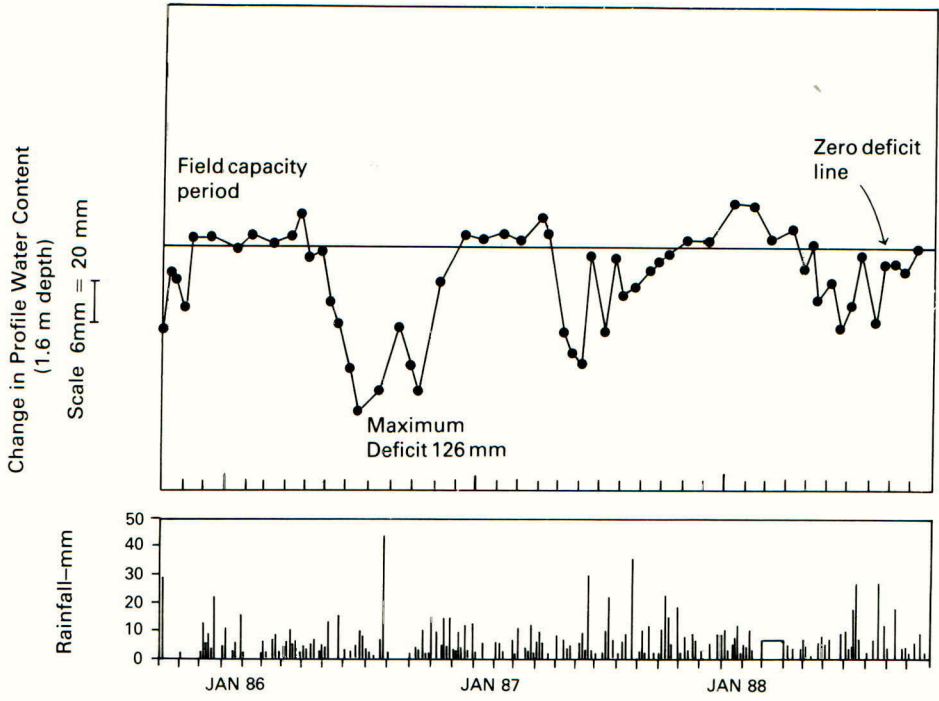


Fig. 1 Soil water changes of a coarse loamy soil profile

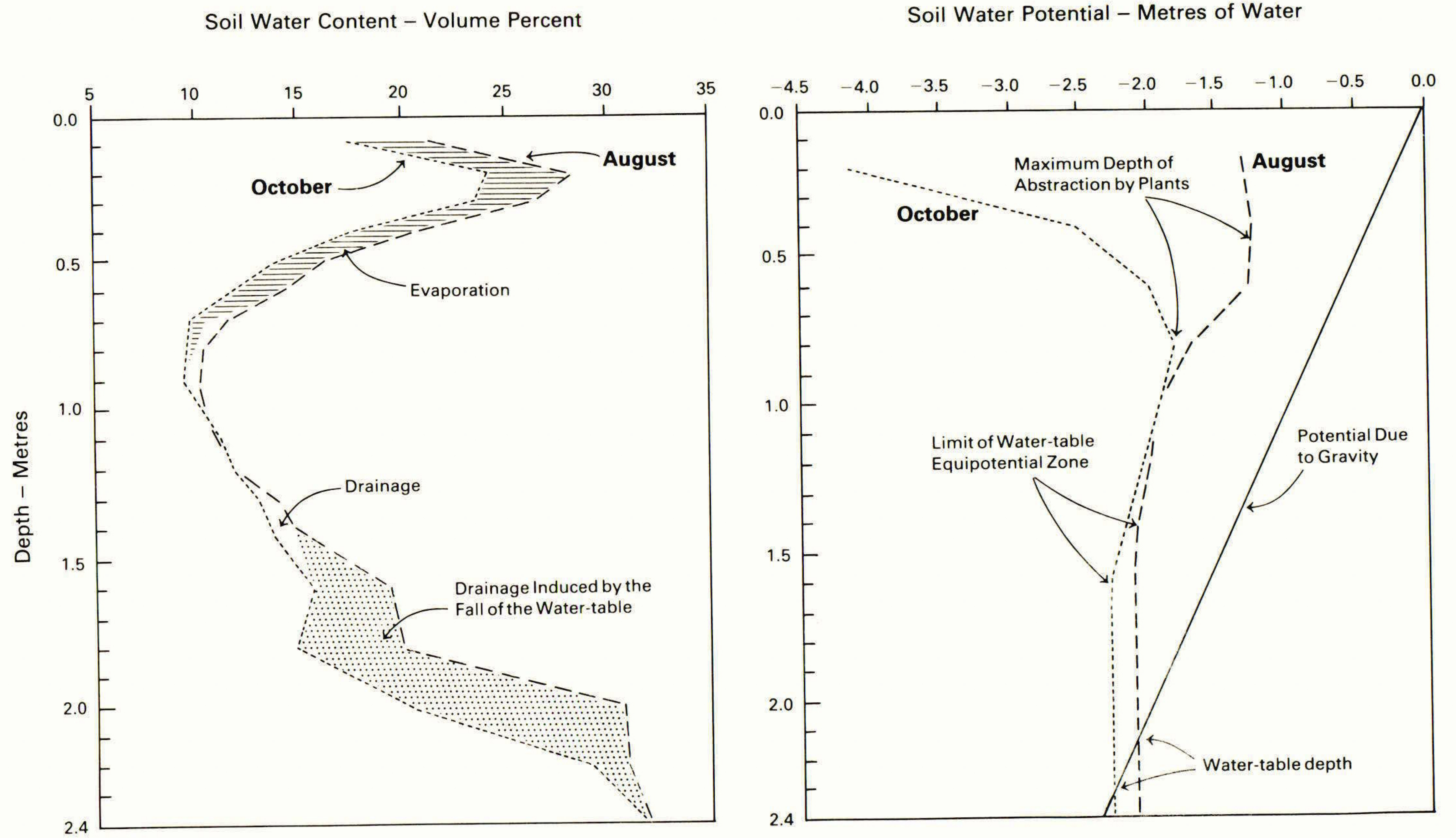


Fig. 2 Water content and potential profiles for a sandy soil

1991 BCPC MONO. No. 47 PESTICIDES IN SOILS AND WATER

THE USE OF LYSIMETERS TO STUDY THE BEHAVIOUR OF PESTICIDES IN THE ENVIRONMENT: SOME PRACTICAL CONSIDERATIONS

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ABSTRACT

Lysimeters have been used for the last 40 years as a means of studying the environmental fate of the use of such diverse species as radionuclides (nuclear industry), nitrates (agriculture), water (hydro-geological studies) and pesticides (groundwater vulnerability assessment). They provide valuable information, obtained under realistic field conditions, on metabolism in plants and soil, mobility through the soil profile and leaching below the depth of the soil profile which cannot be obtained from any single laboratory experiment.

INTRODUCTION

Lysimeters are soil monoliths which can either be made by filling suitable containers with soil and then allowing them to settle so that a soil structure can develop or more realistically are undisturbed soil monoliths which are removed intact from a suitable agricultural location. Sizes and shapes may vary considerably but generally they should be large enough to support a good crop stand.

The lysimeters are generally brought to a central location so that only one set of climatic conditions apply and are kept outdoors. They may also be kept in either a cropped or uncropped condition according to the design of the experiment. A comprehensive review of lysimetry has recently been published (Bergstrom, 1990) and reviews lysimeter size, shape, method of filling and general maintenance.

The comments and observations listed below are from the experiences gained during the renovation of the Letcombe lysimeter complex at the DowElanco R&D laboratories.

MATERIALS AND METHODS

Soil Selection

At present only the BBA guideline (Führ et al., 1990) on lysimeter studies stipulates a soil type. This is a sandy soil with >75% sand and <1.5% organic carbon. This soil is regarded as a notional worst-case and water movement is essentially by pore flow.

At DowElanco two other soils have been selected for inclusion in lysimeter tests. These are a medium loam over clay (with ca. 70 cm of loam) and a loamy soil which is uniform to a depth of 1 m.

In principle any soil types could be studied in lysimeters but obviously, heavy clays, chalky soils and flinty/stoney soils will be very difficult to collect.

Collection and Installation of Lysimeters

The lysimeters at Letcombe were collected by piling glass-fibre cylinders (0.8 m diam. x 1.0 m depth) into the ground, excavating out the surrounding soil and then lifting out the monolith. This is now fairly standard practice and minimises disturbance at the edge of the monolith. The cylinders are sealed into metal base plates and are installed into the lysimeter complex in bays, which when filled with soil allow guard crops to be grown around the lysimeters.

Maintenance of Lysimeters

Lysimeter experiments conducted at Letcombe are all carried out with suitable crops growing in the lysimeters. This is an important consideration as it allows realistic upward movement of water in the form of evapotranspiration. This is particularly important in spring.

The lysimeters are cultivated, fertilised and treated with pest control agents in accordance with agricultural practice in order to mimic farming practice. This includes the use of proprietary seeds and fertilisers at recommended rates and the use of insecticides and herbicides and fungicides for the control of weed and insect infestations which occur during the experiments. Guard crops were also grown around the lysimeters in order to provide a small micro-climate around each resembling those found in the middle of a field.

Test Chemical and Application

The use of radiolabelled test chemicals is strongly recommended for these experiments as it maximises the metabolism information that can be gained. It also allows an accurate picture of the distribution of the test chemical and its metabolites between the crop, the various soil layers and soil solution although a complete mass balance is not possible because there are no traps for volatile components.

The test chemical should be formulated and dispersed as a spray solution in water at a realistic spray rate. Applications should be made at the proposed use rate although for extremely low use rate chemicals it may be necessary to use higher rates.

The application should also be made as realistic as possible in order to achieve a realistic wetting of the crop. Special consideration should be being given to spray droplet size and velocity. Application timing should be dictated by the proposed use pattern for the test chemical and where applicable multiple applications should be used.

Rainfall and Irrigation

Lysimeter studies should be conducted outdoors ensuring that they receive natural precipitation. This will be sporadic and seasonal, allowing periods for wetting and drying of the soil. Combined with a natural temperature regime, this will allow natural fluctuations in the soil biota populations which are responsible for the metabolism of pesticides.

The German guideline on lysimeter studies require that lysimeters receive 750-850 mm of precipitation. In the UK this may not be possible and will require the addition of extra water during the summer months. This is best added during or immediately after a rainstorm or early in the morning or late in the evening.

DISCUSSION

Experiences during the last year have highlighted several important practical considerations.

So far applications of the test chemical have been made using commercially available hand operated garden sprayers. These deliver a great range of droplet sizes from a fine mist to large drops which form at the end of the application and fall straight down. The application will be improved by modifying commercially available spray nozzles. This is no simple achievement as a tractor sprayer moving at 8 km/h covers 1 m in less than 1 s and in order to mimic this, each lysimeter has to be evenly sprayed with 10-20 ml of spray solution in less than 1 s.

Because of the size of the guard crop used to date soil temperatures in the lysimeters have been higher than those observed in lysimeters with larger guard crops and are therefore probably higher than those in the middle of a field. To correct this moves are currently being made to increase the size of the guard crop at Letcombe to at least 1 m in all directions.

The addition of extra water to the lysimeters to come up to the 750-850 mm specified in the German guideline has caused a few problems. Although the addition of water during the summer did not produce any leaching events the water was not always added at the optimum time. Because of the warm dry summer of 1990, the water was frequently added when air temperatures were $>20^{\circ}\text{C}$ and relative humidity was low, conditions when it would not naturally rain, consequently, the addition of water under these conditions was unrealistic. There are also additional considerations to the extra watering: (a) The crops are probably weakened by watering under these conditions, (b) the soil micro-flora are subjected to conditions of high soil moisture and temperature, conditions under which metabolism is favoured producing degradation rates which may be artificially high and (c) when rainfall resumes in autumn, lysimeters which have received additional water start producing leaching water long before those which do not.

The final point to be considered is that of taking soil cores from the lysimeters during the experiments. It is always a temptation to do this in order to find out how far the test chemical or its metabolites have moved down the soil profile. However, the removal of a 1 m deep soil core creates a hole right through the soil profile which, even after backfilling with a suitable soil, could provide a route for the preferential flow of water through the soil profile, especially through heavier soils and this could greatly change the water movement characteristics of the profile for the rest of the experiment. To get around this in future a series of small lysimeters are also prepared and treated and these will be removed for analysis at intervals during the experiment, probably at harvest and perhaps prior to the sowing of follow-on crops.

CONCLUSIONS

Lysimeter studies provide a wealth of valuable information on the metabolism of pesticides in plants and soil, the uptake of soil residues into rotational crops and the mobility of the parent compound and its breakdown products. All of the data is obtained under realistic field conditions and is generated over several growing seasons allowing for seasonal variation.

Lysimeter experiments also give a good indication of the proportion of the applied test chemical that leaches below the depth of the soil profile. It is important, however, to realise that concentrations measured in leaching water samples from lysimeters are not the same as concentrations in groundwater. This is because additional dilution occurs before the chemicals reach groundwater in the form of diluting water from non-treated areas and also limited market shares for individual chemicals.

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FACTORS INFLUENCING RATES OF DEGRADATION OF AN ARYLAMIDE IN SUBSOILS

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ABSTRACT

As an initial approach, *N*-(4-nitrophenyl)propanamide was used to investigate the change in degradation rate with depth in soil of a compound which degrades by simple hydrolytic processes. Measurements on three soils showed that this compound is sorbed only to a moderate extent, and that sorption decreases with depth. Rates of chemical hydrolysis were measured in acidic and basic buffers in the absence of soil to estimate the rate of hydrolysis at neutral pH, and this proved to be extremely slow. Rates of degradation were measured in three soils of differing pH, with samples taken from depths down to 2 m. Degradation in all soil samples was very much faster than the estimated hydrolysis rate at the same pH; the reaction in soil was indeed hydrolysis, as indicated by the production of 4-nitroaniline, but was a microbial rather than a chemical process. Partial sterilisation of the soil with azide slowed this reaction down to a hundredth of that in unsterilised soil. Degradation rates in subsoils, where microbial populations can be much less, were down to a thirtieth of those in topsoil. Degradation in some subsoils showed a marked lag-phase of between 3-6 days, and this indicates that indigenous microbial populations can rapidly adapt to degrade an intruding xenobiotic compound.

INTRODUCTION

Although there is a broad understanding of how organic compounds behave in topsoils and also information from surveys of chemicals in groundwater, there is little understanding of such behaviour in subsoils. The objective of the present project is to investigate some of the fundamental reactions (hydrolytic, oxidative and reductive) undergone by organic compounds in subsoils and the factors which influence the rates of such reactions.

One of the most important soil factors influencing leaching and degradation of chemicals in topsoils is organic matter content. There are two reasons why this is so. Firstly, leaching is governed by sorption which is, in turn, strongly correlated with soil organic matter content for non-ionised compounds. Secondly, rates of degradation of compounds are usually considerably enhanced by soil microbial activity, which is low in soils lacking much organic matter. In subsoils, little organic material is present and so the factors which dominate in topsoils are virtually absent in subsoils. The important

factors determining breakdown and leaching of chemicals in subsoils need to be established before models can be developed to predict risks of pollution of drainage and groundwater.

The compound used in these studies, *N*-(4-nitrophenyl)propanamide, was chosen because it can be hydrolysed or reduced. Hydrolysis reactions are of particular interest because they are considered to be an important degradation process in subsoils and aquifers. Rates and pathways of degradation of *N*-(4-nitrophenyl)propanamide were measured in topsoils and subsoils of different pH and the breakdown rates compared with aqueous hydrolysis rates.

The role of microbial breakdown was investigated further using partial sterilization of soil with azide.

MATERIALS AND METHODS

Chemical

N-(4-Nitrophenyl)propanamide was synthesised by a standard method from 4-nitroaniline and propionyl chloride.

Soils

Samples of light sandy soils were taken from depths down to 2.2 m at Woburn (about neutral pH) and Shuttleworth College of Agriculture (acidic), both in Bedfordshire.

Samples of light calcareous soil (alkaline) were taken from the Ciba-Geigy farm at Whittlesford, Cambridge. Soils were sampled using either a Jarrett augur or a Humax electric corer. The latter machine packages soil samples into PVC cylinders (each of length 25 cm) by means of an inner stainless steel sleeve. This minimises the risk of contamination of soils taken from a deeper layer by soil from upper layers. Soil was stored at 10°C and at field water content, and was used within seven weeks of collection. Analyses of organic carbon content, using a wet oxidation method, were made by the Soil Survey and Land Resource Centre at Silsoe.

Soil/water distribution coefficients (K_d)

Soil/water distribution coefficients were measured for each depth at room temperature by gently shaking the air dried soil (10 g) for ten minutes with a solution of *N*-(4-nitrophenyl)propanamide (20 ml; 25 mg/l) in 0.01M calcium chloride in Pyrex centrifuge tubes (30 ml). After centrifugation at 1000 rpm for 10 minutes, the concentration of the compound remaining in solution was determined by hplc. Aliquots (20 μ l) were injected into a high performance liquid chromatograph and eluted with methanol + water (70 + 30 by volume). A stainless steel column (25 cm long x 5 mm i.d.) packed with Lichrosorb ODS (10 μ m) was used, preceded by a guard column of Lichrosorb ODS RP18 (4 mm x 4 mm) i.d. Detection was spectrophotometric at 326 nm.

Peaks for *N*-(4-nitrophenyl)propanamide and 4-nitroaniline were well separated and no interference was noted from soil coextractives. The compound was quantified by comparing peak heights with standards, and a precision of 1.4% r.s.d. was obtained.

The distribution coefficient for soil at each depth was calculated using equation 1

$$K_d = \frac{S}{C} \quad (1)$$

Where S is the amount of chemical (g) adsorbed per gram of soil and C is the concentration of chemical in aqueous phase (g/ml).

Chemical hydrolysis in buffer solution

Solutions of different pH were prepared in distilled water using the following buffers:- pH 0.34 (0.5M HCl), pH 1.5 (KCl:HCl), pH 5.05 (CH₃COONa:CH₃COOH), pH 6.93 (Na₂HPO₄:NaH₂PO₄), pH 8.74 (Na₂B₄O₇:KOH), pH 11.2 (KCl:KOH) and pH 13.04 (KOH). A stock solution of *N*-(4-nitrophenyl)propanamide (0.5 ml; 2 mg/ml) in methanol was added to each buffer (100 ml) in conical flasks and stoppered and stored at 10°C. Duplicate samples taken at intervals from the flasks were analysed by hplc as described above. Buffer solutions of pH 11.2 and 13.04 were protected from atmospheric CO₂ with a trap of KOH pellets. The pH of the solutions was measured at monthly intervals.

Degradation rates in unsterilised soils

Soil (c. 1.5 kg) was passed through a 2-mm sieve and divided into three samples each of 500 g wet weight. *N*-(4-Nitrophenyl)propanamide was incorporated into two of the soil samples by spraying an aqueous solution (10 ml) onto the soil surface and mixing by sieving through a 2-mm sieve; this gave a concentration of 8-9 mg/kg soil (oven-dry basis). The third sample was sprayed with distilled water alone (10 ml). The soil samples were placed in amber glass jars (1 litre) with loose-fitting screw caps. The water content was adjusted, using distilled water, to the value that it had when collected. Replicate sub-samples (20 g) were taken immediately after preparation and then at set time intervals, and were extracted with methanol (20 ml) and analysed by hplc as described above. After sampling, the jars were incubated at 10°C in a controlled environment room.

Degradation in sterilised soil

Soil (1.0 kg) was sieved (2-mm) and sub-divided into two samples (500 g). One sample was treated with *N*-(4-nitrophenyl)propanamide as described above. After mixing by sieving, a solution of sodium azide in water (10 ml; 24 g/l) was added to the sample by pipette and mixed in by passing twice through a 2-mm sieve. The treated and blank soil samples were incubated and soil samples taken for analysis as described above.

RESULTS & DISCUSSION

Sorption

Sorption of *N*-(4-nitrophenyl)propanamide (Table 1) decreased with decreasing organic carbon content which itself decreased with depth. In the deepest samples, sorption was very weak. Values for K_{oc} were greater in subsoils (>30 cm depth) than in topsoil. Unless the sorptive strength of organic matter in subsoils is much greater than in topsoil (which is unlikely), an appreciable amount of sorption in subsoils is probably by the soil minerals.

TABLE 1. Soil properties and sorption coefficients for *N*-(4-nitrophenyl)propanamide

Soil	Depth (cm)	Organic carbon (%)	pH		Sorption	
			0.01M CaCl ₂		(K _d)	(K _{oc})
Woburn loamy sand	0-30	0.52	6.57	0.87	167	
	60-100	0.08	6.87	0.27	338	
	190-220	0.11	7.00	0.23	209	
Whittlesford calcareous sandy loam	0-25	1.26	7.54	1.10	89	
	100-125	0.45	7.73	0.25	55	
	160-200	0.09	8.00	0.18	201	
Shuttleworth sandy loam	0-30	0.99	4.95	0.66	67	
	60-100	0.05	4.95	0.14	280	
	190-210	0.03	5.64	0.07	233	

Rates of hydrolysis in buffer solutions

Rates of chemical hydrolysis of *N*-(4-nitrophenyl)propanamide were too slow to measure at pH values close to neutral. However the hydrolysis was both acid and base catalysed (Table 2). The rate at pH 7 could be obtained by extrapolating from rates measured at higher and lower pH values. The extrapolated half-life at pH 7 was 790 years, indicating that chemical hydrolysis is very slow and so contributes insignificantly to the degradation in soil which was five orders of magnitude faster. No measurable degradation was observed in buffer at pH 7 after 3.5 months at 10°C.

Degradation in field soils

The only product of degradation detected by HPLC was 4-nitroaniline, which in turn was degraded quite slowly so that a mass balance could be made. The only reaction occurring in aerobic subsoils was hydrolysis and no reduction of the nitro group was observed.

TABLE 2. Rate of hydrolysis of *N*-(4-nitrophenyl)propanamide in buffer solution at 10°C

pH	First order rate constant k_1 (h ⁻¹)	Half-life $t_{1/2}$ (day)
0.34	9.4×10^{-3}	3.1
1.5	6.5×10^{-4}	44.2
7.0	1.0×10^{-7} *	2.9×10^5 *
11.2	3.1×10^{-4}	94.4
13.04	8.2×10^{-2}	0.35

* Value obtained by extrapolation

The fastest rate of degradation in topsoil was in the alkaline Whittlesford soil which also contained most organic carbon (Table 3). Rates of degradation in soils taken from 2 m depth were similar for all three soil types. Rates of degradation decreased with depth to about 1/30th of the topsoil values for the Whittlesford soil of and to about 1/10th of the topsoil value for the Shuttleworth and Woburn soils.

TABLE 3. Rates of degradation of *N*-(4-nitrophenyl)propanamide in soil at 10°C

Soil	Depth (cm)	Unsterilised		Sterilised	
		k_1 (h ⁻¹)	$t_{1/2}$ (h)	k_1 (h ⁻¹)	$t_{1/2}$ (h)
Woburn	0-30	0.066	11	0.017	42
	60-100	-	46*	0.0046	150
	190-220	-	105*	0.0002	3620
Whittlesford	0-25	0.15	4.4	0.072	8
	100-125	0.15	4.4	0.051	13
	160-200	-	136*	0.00005	13100
Shuttleworth	0-30	0.060	12	0.005	147
	60-100	0.012	57	0.005	150
	180-210	-	120*	0.0002	3600

* A lag phase was observed in these experiments and so here the values quoted are the time at which only 50% of the parent compound remained

Lag phases of about 3 days were observed in the degradation kinetics in some deeper soils before a phase of quite rapid degradation (Figure 1). Lag phases were more pronounced as depth increased. Dual phase kinetics were observed consistently in replicate measurements and on soil sampled at different dates from the same site.

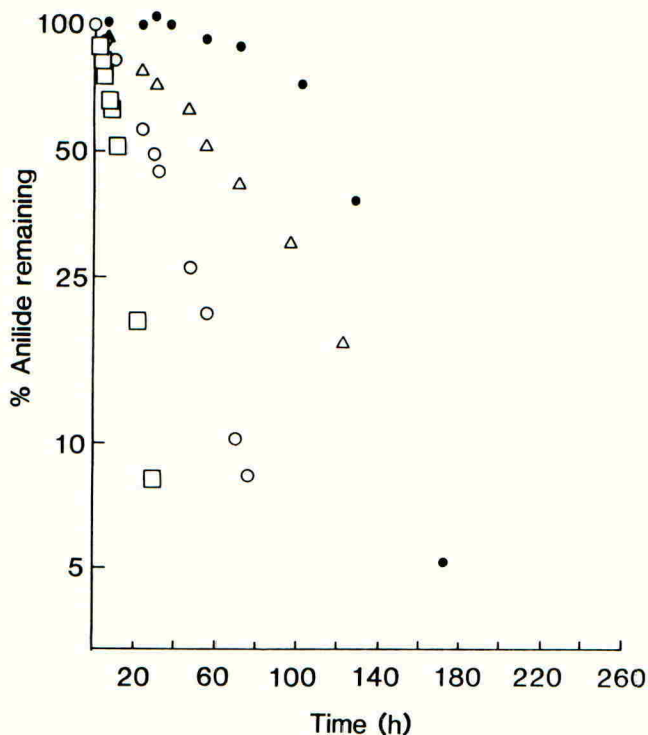


FIGURE 1. Degradation of *N*-(4-nitrophenyl)propanamide in Shuttleworth soil at 10°C, □ 0-30 cm, ○ 30-60 cm, △ 60-100 cm, ● 180-210 cm depth

Degradation in sterilised soils

Treatment of soil with sodium azide increased its pH by up to about 0.5 pH units, an effect which might influence the interpretation of the results from sterilised soils (Table 3, Figure 2). Sterilization decreased rates of degradation to between 1/2 and 1/100th of those in unsterilised soil. The greatest effect in topsoil was for the Shuttleworth soil (acidic) and the least effect was for the Whittlesford soil (alkaline). In contrast, for soils taken from 2 m depth, the greatest effect was for the Whittlesford and the least effect for the Shuttleworth soil. The Shuttleworth and Woburn (neutral) soils gave similar results for both sterilised and non-sterilised treatments, which implies that microorganisms which catalyse the hydrolytic reaction can have similar effects in soils of different pH. The slowest rate of degradation occurred in the sterilised Whittlesford subsoil which is predominantly calcium carbonate.

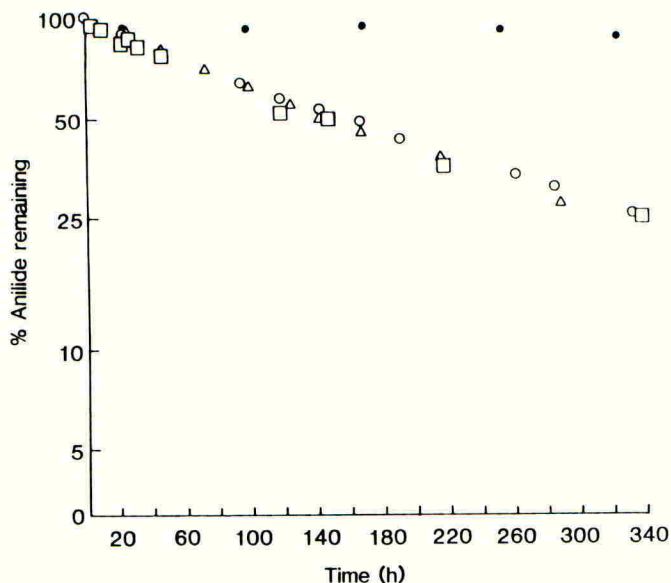


FIGURE 2. Degradation of *N*-(4-nitrophenyl)propanamide in Shuttleworth soil treated with sodium azide, at 10°C, □ 0-30 cm, ○ 30-60 cm, △ 60-100 cm, ● 180-210 cm depth

CONCLUSIONS

Even in sterilised subsoils, rates of degradation of *N*-(4-nitrophenyl)propanamide were considerably faster than the estimated hydrolysis rate at the same pH which emphasises the importance of microbial degradation. Rates of degradation were slowest and sorption least in soil samples from the greatest depth, consistent with their being least microbial activity and organic matter in these subsoils. Partial sterilisation greatly slowed rates of degradation in all soil samples taken from the greatest depth indicating the importance of microorganisms even in these microbially depleted soils. Lag phases were most pronounced in the kinetics of degradation of the deepest soils from Shuttleworth (acid) and Woburn (neutral). This demonstrates that populations of microorganisms in subsoils are able to adapt to degrade more rapidly intruding xenobiotic compounds.

ACKNOWLEDGEMENTS

We are grateful to Shell Internationale, The Hague, Netherlands for funding the project and to Dr I J Graham-Bryce, Dr T R Roberts and Dr V T Edwards for their encouragement. We thank Ciba-Geigy, Whittlesford and Shuttleworth Agricultural College for providing sites for soil sampling.