We measured large differences in the case of the decomposition of EPTC which depended on the microbial activity of soil. This microbial decomposition of EPTC was affected by the number of herbicide exposures, the inoculation with herbicide degrading bacterial strains, microbicide handlings and the type of soil.

ACKNOWLEDGEMENTS

We are grateful to Dr B. Kadlicsko for supplying soil samples with 16 years previous exposure to EPTC from the plot of Res. Group of Putnok of the Res. Inst. of the Univ. of Agric. Sci., Godollo.

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SULFONYLUREA HERBICIDE SOIL RELATIONS

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ABSTRACT

Sulfonylureas degrade under field conditions at rates similar to, and often faster than conventional herbicides. Chemical hydrolysis and microbial breakdown are the principal modes of degradation. In acidic soils, chemical hydrolysis is the main degradation pathway while in alkaline soils, where rates of chemical hydrolysis are minimal, microbial breakdown predominates. Breakdown is generally the fastest in warm, moist, light-textured, low pH soils and slowest in cold, dry, heavy, high pH soils. The sometimes long residual activity that has been observed by replanting highly sensitive crops such as sugar beets into sulfonylurea-treated soil is largely due to the extreme sensitivity of these rotational crops and not to an inherently slow rate of breakdown. Soil mobility of a particular sulfonylurea herbicide generally increases with increasing soil pH and decreasing organic matter. As a class, the sulfonylureas are characterized as relatively mobile compounds, and depending on rainfall, net soil water movement and degree of soil drainage, this mobility can be important. However, bensulfuron methyl binds more tightly to soil than do most sulfonylureas resulting in a less mobile and less soil active compound. Within the sulfonylurea chemistry, compounds have been found which undergo very rapid breakdown in soil. Examples include Harmony® (DPX-M6316), which undergoes very rapid breakdown by soil microbes, and Express® (DPX-L5300), which undergoes very rapid chemical hydrolysis in soil. These second generation, short residual products offer substantially greater rotational crop flexibility than many of the earlier sulfonylurea products.

INTRODUCTION

The sulfonylurea herbicides, discovered in 1975 by Dr. George Levitt of Du Pont, have emerged as a major new class of herbicides and an important advance in chemical weed control technology. Worldwide, a total of eight sulfonylurea herbicides have been commercialized (Table 1) and by the mid-1990's it is anticipated that this number could double. With their unprecedented herbicidal activity, use rates have dramatically fallen resulting in application rates of grams rather than kilograms per hectare. Today, a product like Ally® can be applied annually for over 200 years at its recommended use rate of 2 to 8 g/ha before the total dose would equal a single application of many traditional materials now being used at 1 to 4 kg/ha. The need for such broad spectrum, low dosage compounds with greater crop selectivity are important factors contributing to the rapid success of the sulfonylurea herbicides. Equally important are their very favorable toxicological and environmental properties. The acute oral LD_{50} for sulfonylureas in rats is greater than 4000 mg/kg. By comparison, the acute oral LD_{50} of common table salt is 3000 mg/kg.

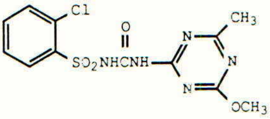
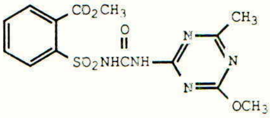
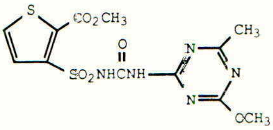
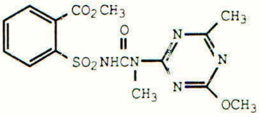
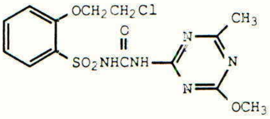
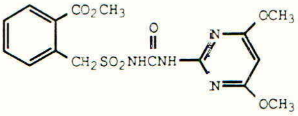
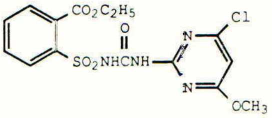
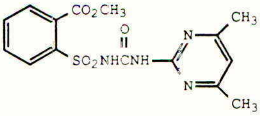
6—5

TABLE 1

Commercialized sulfonylurea herbicides.

TABLE I

SULFONYLUREA HERBICIDES

CHEMICAL STRUCTURE	COMMON/TRADE NAME	PRIMARY USE	APPLICATION RATE (G AI/HA)
	Chlorsulfuron Glean® (Du Pont)	Cereals	4-26
	Metsulfuron Methyl Ally®/Allie®/ Gropper® (Du Pont)	Cereals	2-8
	DPX-M6316 Harmony® (Du Pont)	Cereals	10-35
	DPX-L5300 Express® (Du Pont)	Cereals	5-30
	Triasulfuron Logran® (Ciba-Geigy)	Cereals	10-40
	Bensulfuron Methyl Londax® (Du Pont)	Rice	20-75
	Chlorimuron Ethyl Classic® (Du Pont)	Soybeans	8-13
	Sulfometuron Methyl Oust® (Du Pont)	Noncrop	70-840

Over the past decade, work at Du Pont has concentrated on systematically optimizing the herbicidal activity, crop selectivity and soil residual properties of these molecules. This report, and the one which follows, highlights certain aspects of the soil residual and dissipation properties of these herbicides. For information concerning other aspects, such as mode-of-action and basis of crop selectivity, the reader is referred to a review entitled, 'Sulfonylurea Herbicides' to appear this year in Herbicides: Chemistry, Degradation and Mode of Action, edited by P. C. Kearney and D. D. Kaufman, Vol. 3, Chapter 22, pages 117-189. Marcel Dekker, Inc., New York, NY.

For some time, Du Pont has had a significant commitment to sulfonylurea soils research. The goals of this research are to: (a) develop a fundamental understanding of the key factors important in dissipation and recropping injury, (b) design sulfonylureas with maximum rotational crop flexibility and (c) develop the assay and computer modeling technology needed for defining the soil, weather and recropping patterns where specific sulfonylureas fit best. Significant progress has been made in all of these areas as discussed below. In many instances, other workers have significantly contributed to this progress, especially in areas (a) and (c) above. While only selected references have been cited in this report, a more extensive survey of these contributions can be found in the review cited above. This report will highlight research progress in (a) and (b) above while the subsequent contribution will focus on recent developments in the area of sulfonylurea assay and computer modeling technology.

KEY DISSIPATION PATHWAYS

Chemical Hydrolysis

A major route of sulfonylurea degradation in soil is via chemical hydrolysis of the sulfonylurea bridge. As shown in Fig. 1, sulfonylurea herbicides are weak acids with pK_a's ranging from 3.3-5.2. The neutral form of the sulfonylurea bridge is especially susceptible to hydrolysis, yielding the herbicidally-inactive sulfonamide and amino heterocyclic halves of the parent molecule. Thus, aqueous hydrolysis of sulfonylureas is much more rapid under acidic conditions where a greater proportion of the molecules are in the neutral, hydrolytically susceptible form.

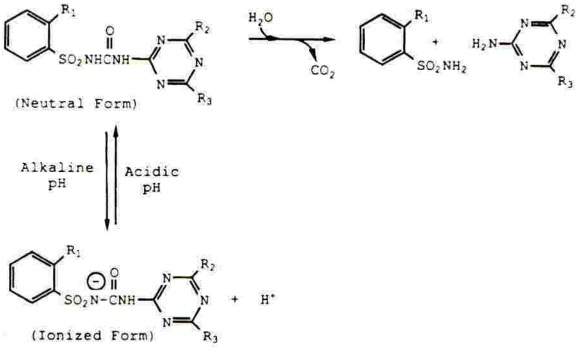


Fig. 1. Sulfonylurea ionization and hydrolysis in water and soil.

The strong influence of pH on sulfonylurea soil degradation is clearly illustrated in Fig. 2. In the ethylene oxide sterilized soils, where microbial degradation is not a factor (top curve in each box), the rate of breakdown by chemical hydrolysis is 15 times faster in the acidic soil (pH 5.9) than the alkaline soil (pH 8.0). The same trend of slower breakdown with increasing pH was observed by Fredrickson and Shea (1986). In a non-sterile, acidic soil (Sharpsburg silty clay loam, pH 5.6, 2.4% organic matter) the degradation half-life of chlorsulfuron at 25°C increased from 1.5 weeks to more than 9 weeks after it was amended with calcium carbonate to increase the pH to 7.5.

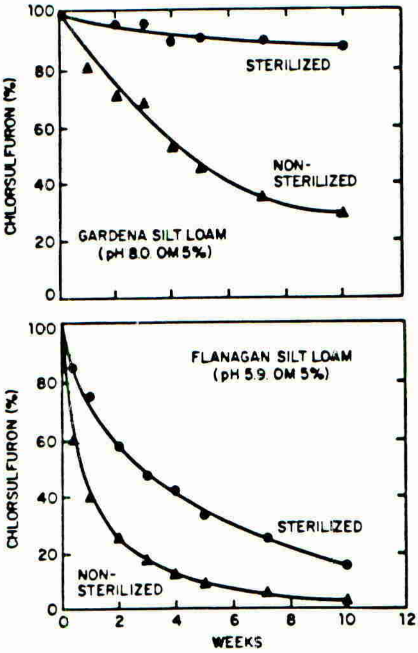


Fig. 2. Chlorsulfuron degradation in sterilized and non-sterilized soils at 30°C (Joshi et al. 1985).

These and numerous related laboratory and field studies have established that chemical breakdown via hydrolysis can be a major factor in the soil dissipation of sulfonylureas. In acidic soils this component is generally a major contributor to total breakdown, whereas in alkaline soils, this component tends to be of minimal importance. To put this in perspective, a single application of 20 g/ha of chlorsulfuron made in the spring of 1982 to an acidic soil (pH 6.3) was found to have no effect the following year on highly sensitive rotational crops. However, in an adjacent area where the soil pH was 7.8, but other conditions were very similar, injury to highly sensitive crops was observed for the following three years (unpublished results). Thus, soil pH and its influence on sulfonylurea chemical hydrolysis has emerged as one indicator for labeling recrop intervals for sulfonylureas with residual activity.

Microbial Degradation

Soil microorganisms also play a very important role in the degradation of sulfonylureas as seen in Fig. 2. Degradation was significantly faster in the non-sterile, microbially-active soils than in soils that had been sterilized. Over the ten week sampling period, microbial breakdown accounted for 79% of the degradation in the non-sterile Flanagan silt loam and 91% in the alkaline Gardena silt loam. Numerous microorganisms including actinomycetes, fungi and bacteria have been isolated from soil and were shown to actively metabolize sulfonylureas in pure culture (Joshi *et al*. 1985). Also, degradation is generally faster in freshly obtained soil samples as compared to soil that has been stored for extended periods.

As expected, warm, moist soil conditions which promote microbial activity also promote sulfonylurea degradation. The effect of temperature on chlorsulfuron degradation in non-sterile and sterilized soils is shown in Table 2. In both acidic and alkaline soils, the first half-life decreases 2 to 4-fold as the temperature is increased from 20°C to 30°C. Increasing temperature promotes both chemical hydrolysis and microbial degradation. Also, note again the marked effect of pH on sulfonylurea soil degradation.

TABLE 2

Effect of temperature on chlorsulfuron soil degradation under laboratory conditions (Joshi, Brown and Van, Du Pont - unpublished results).

	Rochelle, IL Silt Loam		Fargo, ND Silt Loam	
	[pH = 5.7; 4.9% OM]		[pH = 7.5; 5.7% OM]	
Temperature (°C)	Sterile	Non-Sterile	Sterile	Non-Sterile
	(First Half-Life, Weeks)		(First Half-Life, Weeks)	
30	4.3	1.2	33.0	7.8
20	14.0	4.0	69.0	32.0

Mobility

The soil mobility of sulfonylurea herbicides has been extensively studied and correlated with soil and compound properties. Soil thin-layer chromatography R_f values (Table 3) show that sulfonylureas range from those with low mobility and tight soil binding like bensulfuron methyl to those that are relatively mobile like chlorsulfuron and metsulfuron methyl.

TABLE 3

Soil TLC behavior of sulfonylurea herbicides (T. M. Priester, Du Pont - unpublished results).

Compound	Soil Thin-Layer Chromatography R_f Value* Woodstown Sandy Loam (pH 6.6, OM 1.1%)	Cecil Sandy Loam (pH 6.5, OM 2.1%)	Flanagan Silt Loam (pH 5.4, OM 4.3%)	Keyport Silt Loam (pH 5.2, OM 7.5%)
Chlorsulfuron	0.90 (5)**	0.65 (4)	0.59 (3)	0.52 (3)
Metsulfuron Methyl	0.88 (4)	0.74 (4)	0.70 (4)	0.58 (3)
DPX-M6316	0.92 (5)	0.73 (4)	0.44 (3)	0.49 (3)
Sulfometuron Methyl	0.84 (4)	0.59 (3)	0.26 (2)	0.21 (2)
Chlorimuron Ethyl	0.71 (4)	0.59 (3)	0.41 (3)	0.18 (2)
Bensulfuron Methyl	0.46 (3)	0.30 (2)	0.06 (1)	0.05 (1)

* $R_f = \frac{\text{Distance of Compound Migration}}{\text{Distance of Solvent Front}}$; high values indicate mobility.

** U.S. EPA Classification: (1) immobile, (2) low mobility, (3) intermediate mobility, (4) mobile and (5) very mobile.

These data also illustrate that soil pH and organic matter influence the mobility of sulfonylureas. In general, sulfonylurea soil mobility increases with increasing soil pH and decreasing soil organic matter. Like chemical hydrolysis, these results are related to the ionizable character of these compounds. Table 4 presents the pK_a values for 6 sulfonylureas and shows the dramatic effect of pH on octanol/water partition coefficient (lipophilicity) and water solubility.

TABLE 4

Effect of pH on partition coefficient and water solubility of sulfonylurea herbicides.

	Dissociation Constant (pK_a)	Partition Coefficient (octanol-water, at 25°C) pH 5	 pH 7	Water Solubility (ppm at 25°C) pH 5	 pH 7
Chlorsulfuron	3.6	5.5	0.046	60	7000
Metsulfuron Methyl	3.3	1.0	0.014	1100	9500
DPX-M6316	4.0	3.3	0.027	260	2400[a]
Sulfometuron Methyl	5.2	15	0.31	8	70
Chlorimuron Ethyl	4.2	320	2.3	11	1200
Bensulfuron Methyl	5.2	155	4.1	2.9	120

[a] at pH 6

The neutral form of the sulfonylurea molecule (see Fig. 1) is much more lipophilic (less water soluble) than the ionized form. Thus, at pH 5, where a greater proportion of the molecules are in the neutral, undissociated state, the lipophilicity is highest (higher partition coefficient) and the water solubility lowest. Increasing the pH to 7 not only increases the water solubility by 10 to 100-fold but also has a similar dramatic effect on reducing lipophilic character. Consequently, soil pH has a very dramatic effect on overall soil mobility. As the soil pH increases, the equilibrium shifts to favor the more water-soluble ionized form, moving more of the compound from the bound fraction to the soil water phase where it is free to travel with net soil water movement.

In addition to percent organic matter and pH, other soil factors (e.g., porosity, soil type) and environmental factors (e.g., rate of compound application, time of the year, rainfall and soil temperature) can also markedly influence mobility. Using a column packed with a silt loam soil, Nilsson (1985) found that chlorsulfuron moved vertically with rising capillary water. Therefore, during periods of net upward flow of soil water, relatively mobile compounds like chlorsulfuron might reenter the root zone from deeper in the soil profile where it had penetrated during earlier periods of net downward water flow. Our computer model simulations of chlorsulfuron in the U.K. also predict such behavior where net water movement is upward in the spring/summer months in the eastern part of England. Despite the relatively high mobility of some sulfonylureas under certain soil and rainfall conditions, they are very unlikely to pose groundwater contamination problems because of their exceptionally low use rates, low toxicities, and their relatively rapid soil degradation properties.

DISSIPATION UNDER FIELD CONDITIONS

Sulfonylurea degradation under field conditions occurs at rates that are similar to, and often faster than, conventional soil-active herbicides. Palm et al. (1980), when summarizing world-wide field experience, reported that the first half-life of chlorsulfuron in soil is usually between 4 and 8 weeks. For example, under normal growing conditions in Newark, DE, on a Keyport silt loam soil (pH 6.0, 1.4% organic matter), chlorsulfuron was found to have a half-life of about 4 weeks which is comparable to that of metribuzin, somewhat shorter than that of linuron, and about one-half that of bromacil and diuron at the same location.

The disappearance of chlorsulfuron under field conditions in the spring was studied at fourteen locations by J. C-Y. Han and C. Rapisarda (Du Pont - unpublished data). Initial half-lives ranged from 2 to 13 weeks with the slowest rates of degradation occurring in the highest pH soils. Metsulfuron methyl has been shown to degrade at comparable or slightly faster rates than chlorsulfuron under field conditions (Doig et al. 1983, Anderson 1985, Royrvik 1981).

As expected, field degradation of sulfonylurea herbicides in soil has been found to be fastest in warm, moist, light-textured, low pH soils, and slowest in cold, dry, heavy, high pH soils. It must be emphasized that the 4 to 8 week half-life values that have been reported for chlorsulfuron and metsulfuron methyl refer to only the first half-life. Moreover, this value is frequently determined following an application made during the growing season when conditions are most favorable for initial breakdown. Under harsh environmental conditions (e.g., low rainfall and temperatures) or during subsequent years these half-lives can be longer, as is typical for most other compounds in soil. Therefore, it is important to define the conditions under which the measurement has been made. Soil depth is also important since microbial activity often declines below the plow layer.

Despite the relatively rapid soil dissipation of chlorsulfuron and metsulfuron methyl under favorable growing conditions, there have been reports of extended weed control (O'Sullivan 1982) and injury to sensitive following crops under a variety of soil, weather and recropping practices (Foy and Mersie 1984, Brewster and Appleby 1983, Peterson and Arnold 1985). This residual activity is largely due to the unprecedented sensitivity of certain crops and weeds to these herbicides. As seen in Fig. 3, Sweetser et al. (1982) found wheat to be at least 1000 times more tolerant to chlorsulfuron in soil than extremely sensitive plants such as sugar beet. For example, sugar beet root growth can be affected by concentrations of chlorsulfuron and metsulfuron methyl of less than 1 ppb, although soil factors such as organic matter can markedly shift this threshold sensitivity value. In contrast to most other herbicides, where dissipation of 80% of the applied material is normally adequate for rotational crop safety, 99% of the applied chlorsulfuron (>6 half-lives) must dissipate in some situations in order to drop below the threshold soil concentration that can cause injury to such highly sensitive rotational crops. Thus, recrop intervals for sulfonylurea herbicides result from the influence of soil, weather and compound related properties on dissipation coupled with the relative sensitivity of the desired rotational crop.

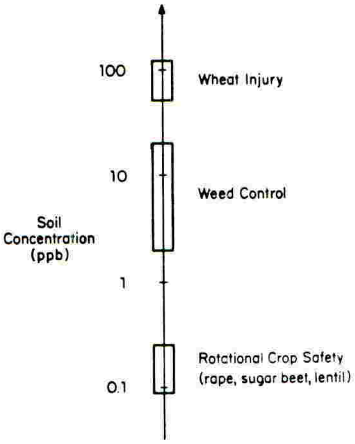


Fig. 3. Schematic representation of relative crop and weed sensitivity to chlorsulfuron in a sandy loam soil, pH 6.5.

SHORT RESIDUAL SULFONYLUREAS

Significant progress has been made in modifying sulfonylurea chemistry to accelerate soil degradation. This is illustrated in Fig. 4 where the degradation rates of the new, short residual cereal herbicides, DPX-M6316 and DPX-L5300 are compared to the established cereal herbicides, chlorsulfuron and metsulfuron methyl. Under identical conditions, DPX-M6316 and DPX-L5300 degrade at initial rates 20 to 50 times faster than chlorsulfuron and metsulfuron methyl. Worldwide recropping studies have confirmed the more rapid dissipation and excellent rotational crop flexibility of these new compounds.

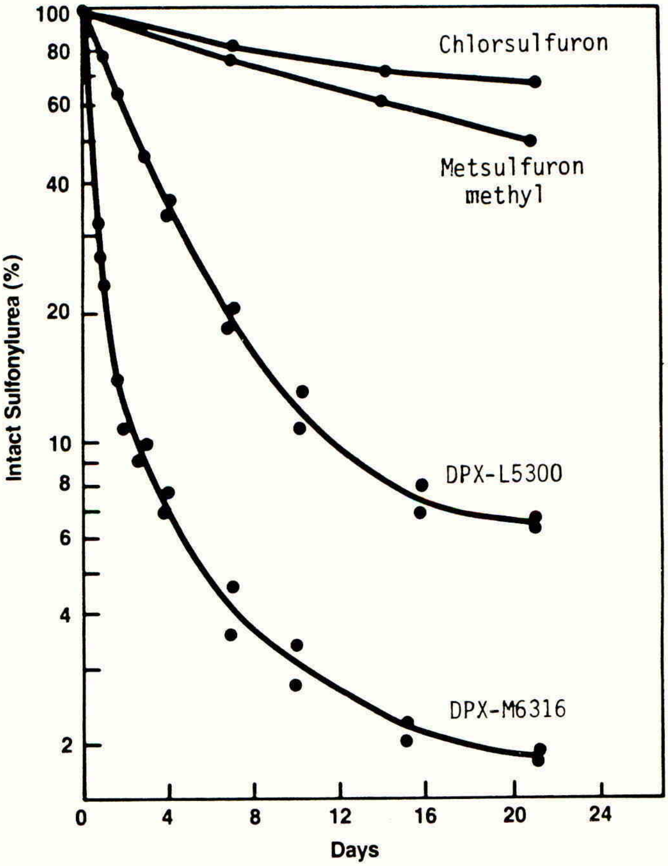


Fig. 4. Relative soil degradation of four sulfonylurea herbicides in non-sterile Gardena silt loam (pH 8.0, 5% OM) at 30°C and 1.0 bar moisture.

The structures for these four cereal herbicides are shown in Table 1. DPX-L5300 is identical to metsulfuron methyl except for the methyl group on the bridge nitrogen. Because of this modification the compound is much more susceptible to chemical hydrolysis. Even in alkaline soils this compound undergoes rapid hydrolysis although alkalinity does have a moderating effect. DPX-M6316 differs from metsulfuron methyl by having a thiophene rather than a phenyl ring. While this change has little effect on chemical hydrolysis, DPX-M6316 is much more susceptible to microbial degradation (Brown et al. 1987).

These recent advances in chemistry and understanding open the way to even more versatile sulfonylurea herbicides for solving many of the world's existing weed problems. With their many attributes, the sulfonylurea herbicides are proving to be a very important advancement in weed control technology.

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PREDICTING SULFONYLUREA HERBICIDE BEHAVIOR UNDER FIELD CONDITIONS

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ABSTRACT

The dissipation of sulfonylurea herbicides has been extensively studied at locations throughout the world. Together with the many laboratory and greenhouse experiments aimed at understanding sulfonylurea soil relations, these data have led to the development of a computer model capable of simulating the behavior of sulfonylurea herbicides in the field. Use of this model to simulate herbicide behavior in the U.K. following an autumn application of 15-20 g/ha chlorsulfuron has provided important insight into why, under certain conditions, sensitive crops like sugar beet cannot be safely planted. Determining exactly when such sensitive crops can be safely planted into treated fields has been aided by the development of a highly sensitive bioassay. In this procedure, lentils are grown under controlled environmental conditions in soil samples taken from treated fields. After several weeks, visual injury ratings are made and used to predict the potential for damage to a given rotational crop. Sugar beet injury projections made using this method to assay field samples were highly correlated with actual sugar beet damage observed in the field.

INTRODUCTION

Establishing the best fit for sulfonylurea herbicides in the marketplace by understanding the influence of soil, weather and recropping patterns has been a major goal of Du Pont's commitment to soils research. An extensive, world-wide field program involving hundreds of locations is at the core of this effort. Equally important are the many laboratory and greenhouse studies aimed at defining the behavior of sulfonylurea herbicides in the soil. These research thrusts have led to recrop intervals which are shortest in regions of warm, moist, light-textured, low pH soil where sulfonylurea herbicide breakdown is fastest. By contrast, rotational crop intervals are longer in cold, dry, heavy-textured, high pH soils where dissipation is slower.

While field recrop tests provide an accurate measure of the duration of biological activity of a compound, they do have some disadvantages. For example, it is impractical to test under all possible combinations of soil, weather and recropping practices; results can often take longer than a year to obtain and the tests themselves are time consuming and costly to conduct. Therefore, reducing the number of field tests that must be performed to reliably predict recrop intervals is an important business objective. Two approaches can be envisioned. Either the residual level of herbicide in the soil can be assayed prior to recropping and then used to assess the risk of injury to sensitive following crops, or the behavior of the herbicide in the field can be simulated by a suitable mathematical model that, given appropriate input data, can be run on a computer to predict injury for any desired scenario. This report will highlight the recent progress that has been made in the assay of residual levels of sulfonylurea herbicides and in the development of predictive mathematical models.

ASSAY OF SULFONYLUREA HERBICIDE SOIL RESIDUES

To predict the impact that residual levels of herbicide may have on a rotational crop, soil samples are obtained from fields previously treated with chlorsulfuron and/or metsulfuron methyl and analyzed prior to recropping. The assay results can be translated into an estimate of following crop injury providing an adequate data base exists which correlates measured residual levels of chlorsulfuron with actual field recrop injury. The challenge of this approach is to develop an assay that is sensitive enough to detect the extremely low residual levels in soil and then to correlate this with the wide range of crop sensitivities.

With regard to assay development, two approaches are possible - analytical and biological. The analytical procedure that has been developed for determining chlorsulfuron residues in soil (Zahnow 1982) uses normal-phase liquid chromatography with photoconductivity detection for the final measurement. Detection limits of 0.2 parts-per-billion have been demonstrated, but conducting routine analyses at these levels is very difficult. Similar HPLC methods are available for metsulfuron methyl and sulfometuron methyl. Beginning with the work of Kelley et al. (1985), Du Pont has continued to develop enzyme-linked immunosorbent assay (ELISA) technology for the determination of chlorsulfuron soil residues. When sensitive rotational crops, e.g., sugar beet, are planted into fields in which chlorsulfuron is detected by either of these methods, injury to that crop will very likely be observed.

Despite their relatively low detection limits, there have been instances where certain highly sensitive crops have been injured by chlorsulfuron residues that were not detected by these analytical methods. Therefore, more sensitive biological techniques have been developed. One such procedure uses lentil, a highly sensitive crop, as the indicator species of a bioassay method for detecting chlorsulfuron and metsulfuron methyl in soil. In this procedure, lentils are planted in the soil to be assayed. The pots are placed in a growth chamber maintained at 75°F during a 16 hour photoperiod and 65°F at night. Pots are watered upon demand twice daily. After 21 days, the soil is gently washed from the roots and a visual injury rating is made versus an untreated control. When making an injury rating, the length and appearance of the secondary roots is more significant than it is for the primary roots. Residues as low as 0.01 parts-per-billion, well below the threshold of injury to sensitive rotational crops, have been measured by this Laboratory Recrop Bioassay. Crops are uninjured when grown in fields from which soil samples have not shown injury in this bioassay. In those cases where injury is observed in the laboratory, empirical correlations have been established which allow the accurate prediction of the risk of injury to sensitive rotational crops grown in the field.

MODELING THE BEHAVIOR OF SULFONYLUREA HERBICIDES

The development of a predictive mathematical model capable of simulating the degradation and movement of sulfonylurea herbicides in the soil as a function of time is a formidable challenge. Three general types of information are required to the dissipation of a compound under field conditions. It is necessary to have information about soil characteristics, weather patterns and properties of the compound and its interaction with the soil as the environment changes from the time of application to recropping. If the goal of the dissipation simulation is to assess the risk of injury to a sensitive rotational crop, the problem is further complicated by the need for a plant response model which is capable of translating the nonuniform distribution of residual herbicide in the soil to a prediction of following crop response. Considering the inherent complexity of this problem, and the stage of development of this technology, it is obvious that any model is of necessity going to be a gross simplification of the real world. Despite the difficulty of this problem, Walker (1987) and Nicholls et al. (1982, 1983) have successfully demonstrated the ability to model the chemical dissipation of several herbicides, including chlorsulfuron (Walker and Brown, 1983), under U.K. conditions.

We too, have sought to develop such a model. The ultimate goal of which is to be able to assess the potential for injury to sensitive rotational crops following application of sulfonylurea herbicides, especially chlorsulfuron. Our model contains a mathematical description of three conceptually independent processes: (1) variation of soil water content and soil temperature over time from the soil surface to the water table, (2) herbicide behavior in the soil (degradation, sorption, leaching, etc.), and (3) plant response to the herbicide. Although physical and biological science forms the core of the model, a great deal of additional software is layered around this core to provide for easy and flexible specification of model inputs, and presentation of the vast amount of model outputs in an understandable, graphical format.

Variations of soil water content and soil temperature are described by partial differential equations. The water table (saturated, and at constant temperature) is the lower boundary condition, while the soil/atmosphere interface is the upper boundary condition.

The latter is more complicated, and more important, for it is through this interface that the soil is coupled to the weather. Daily rainfall and evapotranspiration are required inputs. If these data are not available, a statistically valid sequence of daily rainfall can be generated from monthly total values by a stochastic weather simulator and potential evapotranspiration can be computed from air temperature, humidity, wind speed, and net solar radiation via the Penman equation. Soil hydraulic parameters are computed from textural class. Soil heat conductivity is calculated from soil water potential, with the heat capacity depending on moisture content. The model includes a description of the freeze/thaw cycle, which has a drastic effect on hydraulic conductivity, and a big effect on soil temperatures because the latent heat of fusion is much larger than the heat capacity.

An important feature of the degradation curves obtained from studies with sulfonylurea herbicides in non-sterile (microbially active) soils conducted in our laboratories is the biexponential character of the breakdown process. This behavior is characterized by an initially rapid decay followed by a period of slower degradation. For chlorsulfuron, the transition to the slower breakdown phase occurs after 2 to 4 weeks. In sterilized (microbially inactive) soil, the degradation appears to follow first order kinetics. One way of explaining this observed behavior views the herbicide as partitioning between two compartments in the soil (Figure 1). Following application, the compound is in the "available" compartment where it can undergo degradation by both chemical hydrolysis and microbial breakdown. Concurrently, the compound can also move into a "protected" compartment where it is postulated to be unavailable to soil microorganisms. While in the "protected" compartment, chemical hydrolysis continues but microbial degradation stops until the herbicide returns to the "available" compartment.

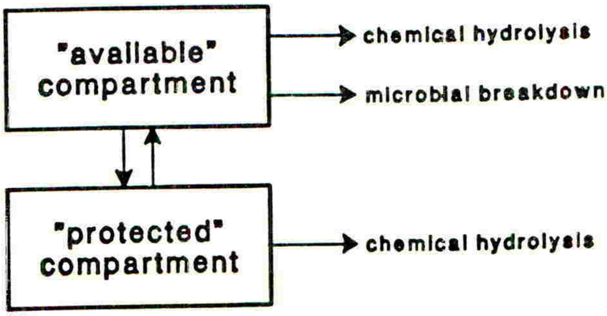

Fig. 1. The two-compartment model of soil degradation.

The mathematical treatment of degradation that is contained in our model makes use of this two compartment description. First order decay takes place at different rates from each compartment, and mass transfer occurs between the compartments. Mass transfer can be modeled either as a diffusion or interface controlled process. In either case, the resulting degradation can be approximated by a biexponential curve. Herbicide transport occurs in the soil water phase by convection, diffusion, and dispersion. This latter term includes the effect of spatial heterogeneity neglected in the one dimensional simulation. Critical to the transport model is the fraction of herbicide in the soil water. In the simplest approach it is assumed that the partitioning between water and soil remains at equilibrium. More realistically this equilibrium state is perturbed by the coupling of the kinetics of sorption, degradation, and soil water flux.

The plant response model is still in the development stage. Currently plant response is computed by averaging herbicide soil water concentration over depth (typically the root zone) and time following recrop. An assessment of the injury potential is obtained from a probit plot that linearly relates percent crop injury and logarithm of herbicide concentration in the soil water.

The complexity of the model and the desire to be able to simulate large numbers of situations makes finding appropriate numerical methods to solve the many equations and designing a computer program with the necessary computational efficiency essential. A stabilized, iterative, Crank-Nicolson scheme was found to reliably solve the differential equations with a reasonable amount of computational effort. The model is currently being run on a Cray 1A supercomputer, where the nearly 5 billion arithmetic operations needed to simulate the fate of a sulfonylurea over a two-year period are performed in less than 2 minutes.

The model was initially validated by simulating recrop injury for over 200 field tests in the United States conducted over a four year period. Application rate, soil properties, recrop interval and weather varied widely among the projections. With continued refinement, good quantitative agreement was eventually obtained between predicted injury and actual recrop injury ratings for the great majority of these validation simulations. The best agreement occurred in cases where observed injury was slight (<20%) or severe (>40%). In cases of intermediate injury, agreement between predicted and actual injury ratings was only fair. On the whole, we believe that the model provides a good assessment of the biological activity of chlorsulfuron residues in the soil.

UNDERSTANDING SUGAR BEET INJURY FROM CHLORSULFURON

In the spring of 1986 and 1987 some sugar beet damage was reported in the U.K. in fields treated with chlorsulfuron in the autumn of 1984 and 1985, respectively. Most of the injury occurred in the eastern sugar beet counties of Norfolk and Lincolnshire with only a few occurrences in the west midlands (e.g., Shropshire). A comparison of features in areas where injury was observed with uninjured regions showed that the main distinguishing feature was net precipitation, i.e., rainfall minus evaporation. In Norfolk the net annual precipitation was about 30 mm while in Shropshire it was six times higher. The many computer simulations that were run have confirmed the greater risk of injury in the eastern sugar beet counties and helped provide an understanding of why the damage occurred.

Little degradation takes place during the fall and winter months immediately following an autumn application of chlorsulfuron. Because the net movement of water is into the soil profile during this period, and since chlorsulfuron is a relatively mobile compound, it is leached out of the root zone. In the spring and summer months when the direction of water flow in the soil is toward the surface, herbicide can be moved back into the root zone where it can injure sensitive rotational crops. Our simulations show that over a period of years in the U.K., chlorsulfuron continually degrades as it moves up and down in the soil.

Because herbicide leaching is a contributing factor to the dissipation of fall applied products, the drainage characteristics of the soil cannot be ignored. Nicholls (1986) was the first to recognize this with regard to understanding the sugar beet injury from chlorsulfuron. In a preliminary survey of locations where sugar beet injury was reported, he found that 47% of the cases occurred on pleosols and stagnogleys which have impeded drainage, 39% of the cases were on gleys which are intermittently waterlogged, and the remaining 14% were on freely draining soils. Our simulations have confirmed that, at sites having alkaline pH and impeded water flow or a high water table, autumn applications of 15 to 20 g/ha of chlorsulfuron can damage sugar beet more than 1 year after treatment.

The behavior of spring applied sulfonylurea herbicides is markedly different to that described above for autumn treatments. Because of the much lower application rate used in the spring vs. the autumn (5-6 g/ha vs. 15-20 g/ha), and because the flow of soil water allows the compound to remain in the warmer, upper layer of soil where more degradation occurs during the first growing season, the potential for injury to sensitive rotational crops is much less. This is apparent when the time interval to reach safety to sugar beet following 5 g/ha Ally® (metsulfuron methyl) in the spring is compared to that needed after a total of 20 g/ha Finesse® (15 g/ha chlorsulfuron + 5 g/ha metsulfuron methyl) in the autumn. As contrasted to fall applied Finesse®, our simulations predict that there will be an adequate safety margin for sugar beet one year after spring treatments of Ally®. The widespread favorable commercial experience with spring applied Ally®, since its introduction in the U.K., confirms the accuracy of these projections.

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THE BEHAVIOUR OF CHLORSULFURON AND METSULFURON IN SOILS IN RELATION TO INCIDENTS OF INJURY TO SUGAR BEET

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ABSTRACT

The rates of degradation of chlorsulfuron and metsulfuron were measured in five soils of different pH and, for two of them, at three depths. Half-lives were very long (up to 627 days) in soils of pH >7. Sodium azide slowed the rate of degradation of metsulfuron more than that of chlorsulfuron which implies that microbial degradation is more important for metsulfuron. To identify the factors involved in the observed herbicide damage to sugar beet crops, the location of incidents were plotted on soil maps. Most cases occurred on sites with impermeable or intermittantly waterlogged subsoil and only a few on apparently free draining sites. Simulations provided evidence that chlorsulfuron applied in autumn can readily leach into subsoils where both microbial activity and hydrolysis of the herbicide could be slow. At sites where drainage is impeded, the tapping of this subsoil by sugar beet and/or return of this water to the topsoil by capillary action could lead to damage.

INTRODUCTION

Several incidents of injury to sugar beet in the summer of 1986 were caused by chlorsulfuron applied to previous crops of winter wheat in the autumn of 1984. This was perhaps surprising for two reasons. Firstly, because Walker and Brown (1983) had measured the half-life of chlorsulfuron in soil at 10°C to be 2 months and had predicted residues 18 months after an October application to be less than 0.2% of that applied. Secondly, Nicholls and Evans (1985) had shown that chlorsulfuron was very weakly adsorbed by soils of normal pH and so it was expected to be leached below the root zone of the crop during two winters in the field. So *a priori*, incidents of failure to control weeds, when uptake from soil was required, was considered much more likely than incidents of crop injury because of the risk of herbicide being leached away from weed roots. Nevertheless Richardson *et al* (1981) had warned that residues of chlorsulfuron toxic to beet could persist for more than 53 weeks in soil.

Chlorsulfuron is aplied at such low rates that analysis of residues from commercial applications was not possible with conventional instrumental techniques and bioassays had not been sufficiently developed in the U.K. at the time. Therefore simulation was an important method for developing an understanding of the behaviour of chlorsulfuron in field soils. The present work attempts to explain how residues can persist at concentrations which are toxic to sugar beet for up to two years after autumn applications.

MATERIALS AND METHODS

Rates of degradation

The properties of the soils used are given in Table 1. The herbicides were wettable powder formulations (80% ai). All experiments involved soils incubated at 20°C and the water content indicated in the Table. The initial concentration of herbicide was 5.0 mg/kg and residual concentrations were measured by HPLC. The herbicides were extracted from soil in methanol + water (80 + 20 by volume) containing 0.1% acetic acid. The HPLC mobile phase was methanol + water (70 + 30 by volume) containing 0.1% acetic acid. The column used was Lichrosorb RP-18 and detection was at 245 nm. All incubations lasted from 84 to 104 days. In the incubations involving sodium azide, the inhibitor was mixed into soil at 800 mg/kg prior to incorporating the appropriate herbicide.

Adsorption

Adsorption coefficients were measured by the method given in Nicholls and Evans (1985).

Leaching study

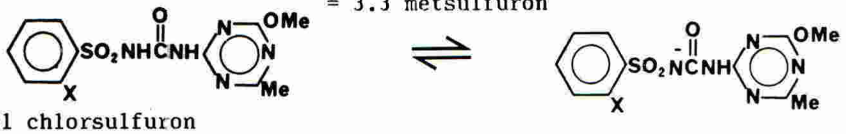
Measurements were made on fallow plots at Rothamsted and Woburn. The properties of the soils were given in Nicholls and Evans (1985) and the experimental method described by Nicholls *et al* (1983). Technical-grade chlorsulfuron was applied at the rate of 420 g ha^{-1} and analysed by the HPLC method given above.

Simulations

Simulations were made using the model CALF as described by Nicholls *et al* (1982), which uses the empirical concept of mobile and immobile water categories. Values for the water content at field capacity and -2×10^{-5} Pa (-2 bar) were 0.29 and 0.17 $\ell\ kg^{-1}$ respectively. Adsorption coefficients are given on the figures. Rates of degradation in the topsoil (0-30 cm) were calculated using the equations of Walker and Barnes (1981) from the coefficients given by Walker and Brown (1983). In order to simulate slow rates of degradation in the subsoil (>30 cm), for the data in Figure 4 and Table 2, rates were arbitrarily set at one tenth of those which would have occurred in topsoil. Measurements of rainfall, evaporation from an open water surface and maximum air temperature were those measured daily at 09.30 at Rothamsted.

PHYSICO-CHEMICAL PROPERTIES

pK_a = 3.7 chlorsulfuron
= 3.3 metsulfuron



X = Cl chlorsulfuron
= $COOCH_3$ metsulfuron

Chlorsulfuron and metsulfuron, when unionised, are moderately polar (log K_{OW} = 1.5 and 0.8 for chlorsulfuron and metsulfuron respectively) but are weak acids being almost completely ionised at normal soil pH (6-8). Adsorption of chlorsulfuron to soil is weak (Fig. 1). Anions are more polar than the unionised molecule by 3-4 log K_{OW} units and because the balance of charge at soil surfaces is negative, anions are more weakly adsorbed than the unionised parent molecule. The consequence of such weak adsorption is a great potential for movement through soil.

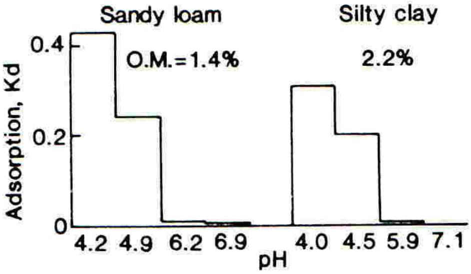


Fig. 1. Adsorption of chlorsulfuron on soils of different pH

DEGRADATION

Degradation of chlorsulfuron in soil is by acid-catalysed hydrolysis so that persistence increases with pH. This is illustrated in Table 1b where, in general, soil half-life increases with soil pH. The relationship is better seen in the depth samples of Soakwaters soil which have similar organic matter content but degradation in the deepest layer which has a high pH, is about 30 times slower than that in the top layer. The rate of degradation from the deepest layer in the Wharf Ground soil was also slow but in this soil, although pH was slightly higher, organic matter content and hence probably microbial activity was low.

Degradation rates for metsulfuron were almost identical to those of chlorsulfuron. Sodium azide, which inhibits microbial activity, increased the persistence of metsulfuron more than that of chlorsulfuron. This indicates microbial activity is more important for the degradation of metsulfuron than of chlorsulfuron.

TABLE 1

Soil properties and rates of degradation of chlorsulfuron and metsulfuron at 20°C. The half-lives shown in parentheses are extrapolations from the observed data since the residual concentration did not fall to 50% of the intial amount during the incubation period. The half-lives marked * were obtained in the presence of the microbial inhibitor sodium azide.

		Organic matter (%)	pH	Water content at 0.33 bar (%)	Half-life in soil (days)	
					Chlorsulfuron	Metsulfuron
(a) Depth samples						
Soakwaters	0-20	2.01	5.8	11.9	21	23
	20-40	1.86	5.6	9.7	22	24
	40-60	1.85	7.5	10.1	(627)	(303)
Wharf Ground	0-20	2.49	6.2	12.8	60	75
	20-40	2.08	6.2	12.4	58	66
	40-60	1.64	6.7	12.2	91	94
(b) Different soils with pH range						
Soakwaters		2.01	5.8	11.9	25 (129)*	29 (420)*
Wharf Ground		2.49	6.2	12.8	73 (149)*	84 (1349)*
Hinton		1.49	6.4	9.9	27 (174)*	32 (111)*
Sutton Scotney		6.66	7.2	32.8	(120) -	75 -
Kirton		3.45	7.8	19.0	(163) (292)*	(190)(1000)*

LEACHING

Chlorsulfuron applied at high rates to the soil surface was leached considerably by the rain that fell in autumn and winter (Figure 2). Concentrations near the surface only one month after application were very small especially for the latest application.

Simulations, using measured values of the adsorption coefficient and degradation coefficients given by Walker and Brown (1983), indicate that the Rothamsted-NVRS model predicted distributions with moderate precision.

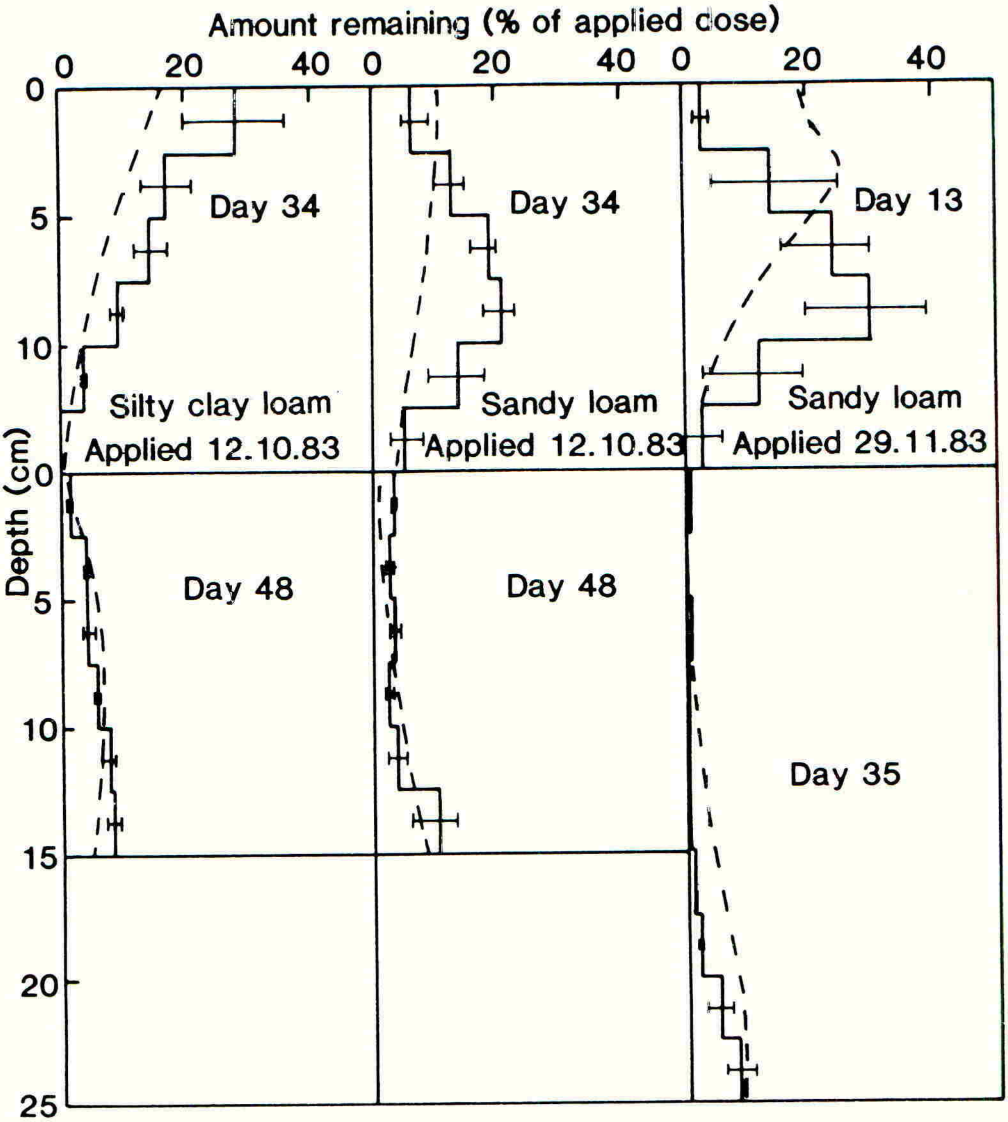


Fig. 2. Distribution of chlorsulfuron: ——— measured values (bars represent range of duplicate measurements), - - - simulated values. Measured values of the adsorption coefficient (K_d) used in the simulation were 0.005 and 0.067 for the sandy and silty clay loam respectively.

WEATHER

The distribution of chlorsulfuron in soil is a product of leaching and degradation, and these in turn are dependent on weather. The data for the weather which occurred after applications in autumn 1984 and 1985 are given in Figure 3. Rainfall occurred randomly throughout the period and so was impossible to predict. However evaporation of water is consistently large in summer and very small in winter. Consequently, rainfall exceeds evaporation in winter enabling leaching to occur whilst in summer evaporation of water exceeds rainfall giving net upward movement of water and of herbicide. Not surprisingly, soil temperature follows a similar seasonal pattern to that of evaporation.

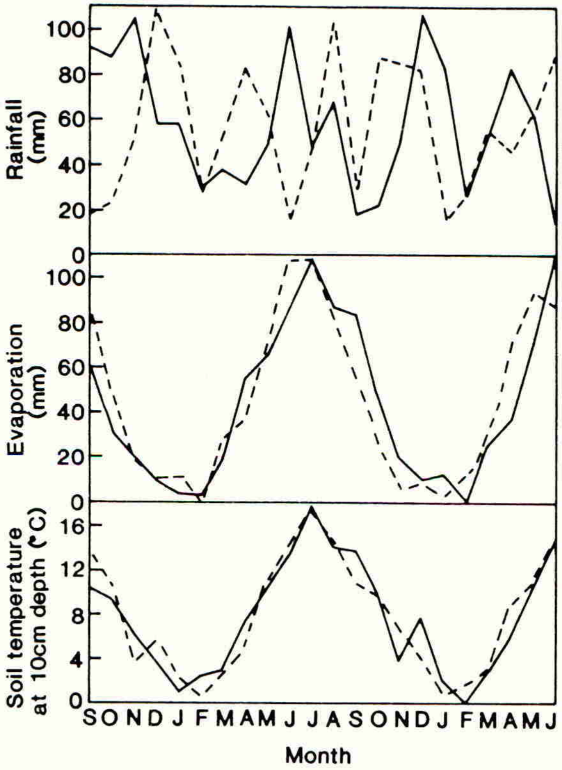


Fig. 3. Weather data. ——— starting September 1984, --- starting September 1985.

SIMULATIONS

Simulations (Figure 4) indicate that in a free draining soil chlorsulfuron might leach to more than one metre depth within 18 months of application. Although sugar beet can root down to one metre depth, damage in these circumstances is difficult to envisage. However, there are three types of drainage in soil profiles:- free draining, intermittantly water logged and impermeable.

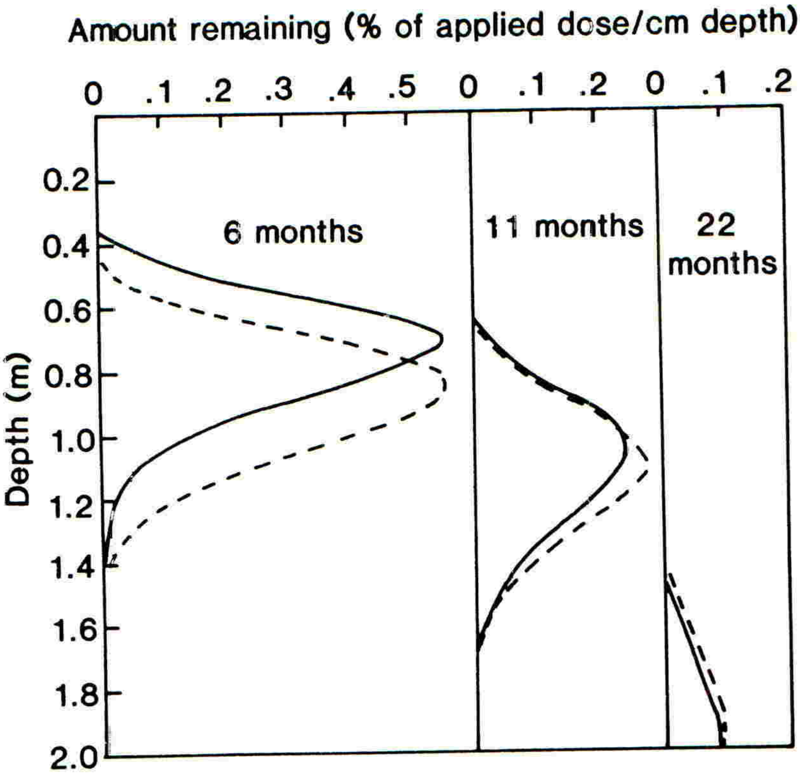


Fig. 4. Simulated distributions of chlorsulfuron using adsorption coefficient K_d = 0.02, ---- applied October 1984, applied October 1985

In an impermeable subsoil, residues will be prevented from leaching by the slow rate of permeation and if that subsoil were of high pH then residues could persist. In an intermittantly waterlogged soil, leaching would become slow as the water table was approached and the hydraulic head became small and there would be the possibility of residues being returned to the surface as soils dried (Phillips 1964). It would clearly be futile to simulate leaching in an impermeable soil but it is important to investigate the persistence of residues where there is a permeable subsoil in which degradation is nevertheless slow. The model CALF was set to calculate rates of degradation in topsoil (<30 cm depth) using rate constants measured by Walker and Brown (1983). Furthermore slow degradation of herbicide in subsoil was modelled by setting rates of degradation of herbicide which had leached below 30 cm depth to only one tenth of those which were set to occur in the topsoil. One tenth is an arbitrary value which lies between the values measured for Soakwaters and Wharf Ground. The simulations (Table 2) indicate that total soil residues are much greater after an autumn application than after spring application. This is because in autumn herbicide can be rapidly leached into subsoil where it can persist because of cooler conditions, high pH and/or lower microbial activity (Anderson and Humburg 1987). After spring applications, residues stay near the surface where higher soil temperatures during summer and high microbial activity favour rapid degradation. Residues from spring applications are therefore quite small by the time winter rain can leach them away.

TABLE 2

Simulation of chlorsulfuron or metsulfuron residues in a silty clay loam assuming adsorption $K_d = 0.02$

Time after application	Autumn application		Spring application	
	1-10-84	1-10-85	1-4-84	1-4-85
6 months	51	48	10	6
12 months	38	36	6	4

REPORTS OF DAMAGE TO FOLLOWING CROPS

Reports of injury to sugar beet where chlorsulfuron had been used previously were plotted on soil survey maps (Anon 1983) to discern a relationship between sites of injury and the type of subsoil. The results are given in Table 3.

TABLE 3

Subsoil type at location of reported sugar beet damage

		1986	1987
Impermeable	pelosols stagnogleys	80	55
Intermittently waterlogged	gleys	55	60
Clay or clay-enriched subsoil	argillic	6	16
Peat		4	1
Free drained		12	30

The majority of incidents occurred on impermeable or intermittently waterlogged subsoils. Many incidents occurred in the Fens and the Norfolk Broads and in other low lying sites close to rivers or streams. Few incidents were reported from sites with free draining subsoils, such as those in the sugar beet growing areas due north of Bury St Edmunds or on the Lincolnshire or Yorkshire Wolds. Caution must be used in studying these figures because diagnosis of injury and its attribution to sulphonylureas is difficult although the reports were made by independent specialists of the British Sugar Corporation.

CONCLUSIONS

Chlorsulfuron and metsulfuron can persist in soils of high pH and low microbial activity where half-lives of at least 18 months are possible. It is significant that lime is usually applied to fields where sugar beet is grown and often this is done before the preceding cereal crop is sown. This means that these herbicides applied before beet crops will almost inevitably be applied to soils of high pH and hence will have a high probability of persisting.

Chlorsulfuron and metsulfuron are potentially highly mobile in soil and autumn applications are rapidly leached into the subsoil of a free draining profile. Spring applications tend to stay in the topsoil where they degrade faster because microbial activity and soil temperature are greater. This is especially important for metsulfuron which is applied in spring and is apparently more susceptible to microbial degradation than chlorsulfuron.

Incidents of injury to following crops from autumn applications of chlorsulfuron are most likely in soils of high organic matter content or those which are imperfectly drained or at low-lying sites with a high water table. At these sites, the tapping of subsoil by a deep rooted and highly sensitive crop such as sugar beet and/or the return of the water to the topsoil by capillary action can lead to appreciable damage.

With the recent trend to autumn sowing of cereals, the possibility exists of similar incidents of damage to following crops with other acidic herbicides. The appearance of such chemicals in drainage water following leaching is also possible.

ACKNOWLEDGEMENTS

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SESSION 7A

HERBICIDE BEHAVIOUR IN SOIL: II

CHAIRMAN	DR I. J. GRAHAM-BRYCE
SESSION ORGANISERS	DR A. WALKER DR K. S. KILLHAM
INVITED PAPERS	7A-1 & 7A-6
RESEARCH REPORTS	7A-2 to 7A-5 & 7A-7

LEACHING OF HERBICIDES TO GROUND WATER: A REVIEW OF IMPORTANT FACTORS AND OF AVAILABLE MEASUREMENTS

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ABSTRACT

The fraction of a herbicide dose (applied to the soil surface) that leaches to ground water is the result of the following processes: transformation in soil, plant uptake, distribution over the three phases in soil (solid-gas-liquid) and transport in soil. The major factors influencing leaching to ground water are: the sorption coefficient, the transformation rate, the excess of rainfall or irrigation over evapotranspiration, the season of application and the uniformity of water flow in soil. Ten herbicides have been detected to be leached out of the root zone for non-irrigated soils and five herbicides for irrigated soils. The concentrations found in the ground water are usually in the order of 1 mg/m^3 or lower for non-irrigated soils and in the order of 10 mg/m^3 or lower for irrigated soils. The fraction of the dose leached is usually in the order of 1 % or less.

INTRODUCTION

In the U.S.A. and in most West-European countries ground water is a major source of drinking water. Interest in possible contamination of ground water with pesticides has increased drastically since, in 1979, residues of the nematicides aldicarb and 1,2-dibromo-3-chloropropane were found in ground water in various states in the U.S.A. (Cohen *et al*., 1984) although already in 1974 atrazine was detected in drinking water of Iowa cities which used well systems as sources of water (Richard *et al*. 1975). In this paper I attempt to give an overview of our current knowledge of the processes and factors determining the fraction of the dose that leaches to the ground water and of the available measurements of herbicide leaching to ground water.

PROCESSES AND FACTORS DETERMINING THE LEACHING OF HERBICIDES TO GROUND WATER

The fraction of a herbicide dose (applied to the soil surface) that leaches to the ground water is the result of all important processes to which the herbicide is subjected in the soil system:

1. transformation (photochemical transformation at the soil surface and chemical and microbial transformation in the soil system)
2. plant uptake
3. distribution over the three phases (solid-liquid-gas) in soil
4. transport in the liquid phase via diffusion and via convective flow with the water in soil and in the gas phase via diffusion.

The processes are influenced by many factors. These factors may be divided into five categories:

1. factors determining the boundary condition at the soil surface (weather conditions such as rainfall, potential evapotranspiration, solar radiation and wind speed and irrigation schedule)

2. properties of the soil-plant system (for instance soil structure, soil hydraulic properties and root development)
3. properties of the herbicide (for instance solubility, saturated vapour pressure, pK_a, diffusion coefficients in water and air) and properties of the formulation (leading to, for instance, slow release of the herbicide)
4. properties of the herbicide-soil-plant system (for instance sorption coefficient, transformation rate coefficient as a function of temperature and moisture content, transpiration-stream-concentration factor)
5. time of application (for instance, spring or autumn) and mode of application (for instance spraying onto the soil surface or injecting at 10 cm depth).

Factors from each of the five categories may have an influence (directly or indirectly) on the relative importance of each of the four groups of processes described before. These interrelationships may be illustrated with a few examples. Solar radiation influences soil temperature and thus the transformation rate in soil and the distribution over the three phases in soil. Potential evapotranspiration influences plant transpiration and thus herbicide uptake. Rainfall rate influences the transport rate in soil because it influences the flow rate of the water in soil. Soil hydraulic properties have an influence on the volume fraction of liquid which has an influence on the heat conductivity. Thus indirectly the soil hydraulic properties influence soil temperature and thus the transformation rate in soil. These few examples of complex interrelationships may be amplified with many others.

To describe $\underline{f}_l$, i.e. the fraction of the dose eventually leached to the ground water, we need to account only for those processes resulting in loss from the soil system:

$$\underline{f}_l = 1 - \underline{f}_t - \underline{f}_u - \underline{f}_v \qquad (1)$$

where $\underline{f}_t$ is the fraction of the dose eventually transformed, $\underline{f}_u$ is the fraction eventually taken up by plants and $\underline{f}_v$ is the fraction eventually volatilized at the soil surface. However, the eventual distribution of a certain herbicide dose over $\underline{f}_l$, $\underline{f}_t$, $\underline{f}_u$ and $\underline{f}_v$ is in principle a function of all the factors mentioned above. It is difficult to predict the effect of a certain factor on $\underline{f}_l$ because all processes act simultaneously and interact with each other. The principles of leaching of herbicides to ground water are thus very complex and can only be assessed via a system analysis. Theoretically this could be done by studying the effect of all factors independently by experiments in actual field systems. In real life this is very difficult because it would imply a tremendous experimental effort for a single herbicide. An attractive alternative is to use simulation models in which all processes being considered as relevant, are incorporated. The influence of the various factors may be assessed with such a model via a sensitivity analysis. From results of such simulation studies (Leistra & Dekkers 1976, Leistra 1975, Leistra 1985), the following factors have so far been identified as being of major influence on the fraction that leaches to the ground water:

1. the sorption coefficient (i.e. the slope of a linearized sorption isotherm)
2. the transformation rate coefficient (assuming first-order transformation)
3. the excess of rainfall or irrigation over evapotranspiration
4. the time of application
5. the uniformity of water flow in soil.

The effect of the sorption coefficient on the fraction of the dose leached may be illustrated by results of a simulation study for a soil cropped with potatoes carried out by Leistra & Dekkers (1976). They found that the fraction of the dose leached below 1 m depth is not a continuously decreasing function of the sorption coefficient, but goes through a maximum at values between 0.1 and 1 dm^3/kg (see their Table 1). As discussed by Leistra & Dekkers (1976) the increase of the fraction leached with increase of sorption at low values of the sorption coefficient is the result of a substantially reduced plant uptake with increasing sorption. Such an effect thus occurs only if a crop is present and its magnitude will depend on the parameters in the sub-model for plant uptake of the herbicide. This illustrates again the complex interrelationships between the different processes in the system. Nevertheless the results obtained by Leistra & Dekkers show that herbicide-soil-plant systems with sorption coefficients in the order of 0.1 and 1 dm^3/kg exhibit more leaching than systems with higher sorption coefficients. Thus, as a general rule, one may expect more leaching in systems with low sorption coefficients than in systems with high sorption coefficients.

The effect of the transformation rate coefficient on the fraction of the dose leached may also be illustrated by the results calculated by Leistra & Dekkers (1976). They showed that the effect of the transformation rate is straightforward (see their Table 1): the fraction leached decreases continuously with an increasing transformation rate coefficient. Thus, as a general rule, one may expect persistent herbicides to leach more than labile herbicides.

The effect of rainfall on leaching may be illustrated by results of calculations with a model I developed recently for a sandy soil cropped with maize. The model is based on the concepts described by Leistra & Dekkers (1976). Sorption was set to zero and the first-order transformation rate coefficient used was 0.02 d^{-1} at 15 °C in the top layer. The model parameters may be considered realistic for the herbicide bentazon in this soil system. The standard calculation was performed with rainfall data as measured in 1984 and 1985 in an area with intensive maize cropping in the south of the Netherlands (location: Eersel). Increasing the rainfall by 50 % had a considerable effect: the fraction leached below 1 m depth was 0.1 % in the calculation with normal rainfall and was 0.8 % in the calculation when rainfall was increased by 50 %.

The effect of application time on leaching may be illustrated by results of two calculations carried out for the same system as in the preceding paragraph (i.e. bentazon in a sandy soil cropped with maize). In the two calculations the herbicide was applied at the end of May (normal application time) and at the end of September after crop harvest. The effect of application time was enormous for this herbicide-soil-plant system: the fraction leached below 1 m depth was increased from 0.1 % for application in spring to 48 % for application in autumn. This increase is mainly the result of the uptake by the maize crop after application in autumn being negligible (10^{-7} % of the dose) wherease uptake was calculated to be 50 % after application in spring.

The effect non-uniform water flow in soil on leaching may be illustrated by results obtained by Leistra (1985) in a simulation study for a greenhouse soil. Leistra calculated the leaching of the insecticide methomyl from a 0.7 m deep soil system with a model in which water flow was uniform and with two models in which water flow was non-uniform (the non-uniform water flow was assumed to be the result of a spatially variable infiltration rate at the soil surface). The assumption of non-uniform water flow resulted in much higher fractions of the dose leached than did uniform flow (typical example: 2.1 % eventually leached for non-uniform flow compared with 0.2 % for uniform flow).

AVAILABLE MEASUREMENTS OF HERBICIDE LEACHING TO SUBSOILS AND GROUND WATER

Tables 1 and 2 show an overview of available measurements in which herbicides were detected in measurable concentrations in the liquid phase below the root zone of soils to which herbicides were applied. The liquid phase was collected usually from drainage water (with the exception of a. Edwards & Glass 1971, Glass & Edwards 1974 1979 and Stoller et al. 1975 which collected the liquid phase from lysimeters; b. Wehtje et al. 1984 which collected the liquid phase from vacuum extractors at 1.5 m depth and from bores at 4-6 m depth, and c. Loch et al. 1986 which collected the liquid phase from bores). The doses were usually normal from an agricultural point of view, although in a few cases intentionally higher doses were used for scientific purposes (Edwards & Glass 1971, Glass & Edwards 1974, Stoller et al. 1975, Hebb et al. 1978, Wehtje et al. 1984). As shown in Tables 1 and 2, most soils were sandy loams and only a few measurements have been done for sands and clays. The sampling depth was usually around 1 m (range 0.6-6 m) and the length of the measuring period ranged from a few weeks to four years.

Table 1 shows the results for soils exposed to natural rainfall only. By far the highest concentrations are for bromacil below a sand soil low in organic matter after application of an extremely high dose (22 kg/ha). As shown by Table 1 atrazine and its transformation products desethylatrazine and desisopropylatrazine have been detected in several studies in drainage water and ground water at average concentrations usually between 0.1 and 10 mg/m^3, corresponding with fractions of the dose leached below about 1 m depth between the order of 0.1 and 1 %. The highest fractions of atrazine leached are for clay soils. As shown by Table 1 around ten other compounds have been detected at average concentrations between the order of 0.01 and 1 mg/m^3, the highest values (5-10 mg/m^3) being found for dinoseb applied at a comparatively high dose of 8 kg/ha (used for killing foliage of potatoes).

In view of the concentrations in Table 1 being usually below 1 mg/m^3, leaching studies under natural rainfall with detection limits well above 1 mg/m^3 (e.g. Jarczyk 1983) are of little scientific value.

It would be very useful to be able to interpret the results of the leaching studies reported in Table 1 in terms of the processes in soil. In theory, the measurements might be explained by calculations with simulation models. However, the input data for such models (e.g. rainfall, potential evapotranspiration, root development, course of organic matter content with depth) are not available. Thus these measurements can only be interpreted very roughly. In a first attempt to explain the measurements, only the properties of the herbicide-soil system were considered: sorption and transformation. Data on sorption and transformation were collected from the literature for the herbicides reported in Table 1. Sorption was characterized by the quantity K_{om} (m^3/kg) which is defined as

$$K_{om} = S/m_{om} \qquad (2)$$

TABLE 1

Concentrations of herbicides (and of some of their transformation products) found in the liquid phase below the root zone in field soils exposed to natural rainfall. For the transformation products, the fraction of the dose refers to the parent compound.

Chemical	Annual dose (kg of a.i. per ha)	Soil type (plough layer)	Sampling depth (m)	Length of measuring period in months	Concentration (mg/m^3) (only positive concentrations taken into account)		Fraction (%) of dose leached below sampling depth	Reference
					average	range		
Atrazine	2	clay	0.9	9	20	9 - 33	1	Schiavon & Jacquin 1973
Atrazine	2	loam	0.9	9	13	6 - 26	0.4	Schiavon & Jacquin 1973
Atrazine	3	sandy loam	1.2	9	0.9	0.06 - 11	0.07	Muir & Baker 1976
Atrazine	1	clay	0.7	48	2	0.6 - 4	0.6	Von Stryk & Bolton 1977
Atrazine	1	loamy sand	0.6-1.5	24	0.3	0.1 - 0.6		Loch et al. 1986
Atrazine	1	sandy loam	0.8-1.0	26	0.6	0.2 - 2		Hurle et al. 1987
Desethylatrazine		sandy loam	1.2	9	1.1	0.4 - 8	0.09	Muir & Baker 1976
Desethylatrazine		sandy loam	1.3	9	0.7	0.2 - 4	0.1	Muir & Baker 1976
Desethylatrazine		sandy loam	0.8-1.0	5	0.05	0.02 - 0.2		Hurle et al. 1987
Desisopropylatr.		sandy loam	1.2	9	0.08	0.02 - 0.8	0.08	Muir & Baker 1976
Desisopropylatr.		sandy loam	1.6	9	0.2	0.02 - 0.6	0.09	Muir & Baker 1976
Bromacil	22	sand	5 -6	22	70	0.1 - 1200		Hebb et al. 1978
Cyanazine	3	sandy loam	1.6	9	0.4	0.1 - 1.1	0.0006	Muir & Baker 1976
Cyanazine	2	sandy loam	1.6	6	0.02	0.003- 0.1	0.0008	Yoo et al. 1981
Cyanazine-amide		sandy loam	1.6	9	0.8	0.1 - 3	0.012	Muir & Baker 1976
Cyanazine-amide		sandy loam	1.6	6	0.05	0.02 - 0.1	0.003	Yoo et al. 1981
Dicamba	6	silt loam	2.4	12	0.4	0.2 - 0.7		Glass & Edwards 1979
Dinoseb	1-8	loamy sand	0.7-1.5	24	2	0.1 - 10		Loch et al. 1986
Metribuzin	0.6	clay/sand	1.2	9	0.6	0.02 - 2	0.013	Muir & Baker 1976
Picloram	2	silt loam	2.4	12	0.9	0.5 - 1.2	0.1	Glass & Edwards 1974
Simazine	0.5	sandy loam	0.8-1.0	11	0.4	0.07 - 1.2		Meinert & Häfner 1987
2,4,5-T	11	silt loam	2.4	14	0.2	0.1 - 0.5		Edwards & Glass 1971
Terbuthylazine	0.7	sandy loam	0.8-1.0	11	0.4	0.03 - 1.0		Meinert & Häfner 1987
Terbuthylazine	1	sandy loam	0.8-1.0	2	0.5	0.06 - 2		Hurle et al. 1987
Desethylterbuthyl.		sandy loam	0.8-1.0	2	0.05	0.02 - 0.07		Hurle et al. 1987

where S is the sorption coefficient (m^3/kg) and m_{om} is the mass fraction (1) of organic matter. The transformation rate was characterized by the time necessary for disappearance of 50 % of the dose (DT_{50}) in laboratory experiments with moist soil at 20 °C. Fig. 1 shows the estimated K_{om}-DT_{50} combinations for the herbicides of Table 1. It must be realized that the location of a herbicide in Fig. 1 indicates only the average K_{om} and DT_{50}: K_{om} values of a given herbicide may vary a factor of 2-3 for different soil types and DT_{50} values may vary a factor of 4 for different soil types. As shown in Fig. 1, the herbicides found in ground water cover a wide range of K_{om}-DT_{50} combinations. Thus classification of herbicides with respect to K_{om} and DT_{50} may not be very useful to ascertain whether or not they may leach out of the root zone at the concentration levels shown in Table 1.

Table 2 shows the measurements for irrigated soils. Fractions of the dose leached for atrazine and dicamba on a clayey soil (Schwab et al. 1973) were much higher than found for the same herbicides in non-irrigated soils in Table 1. Schwab et al. (1973) report that most of the leaching occurred after applying 80 mm irrigation water within 1-2 d after spraying of the herbicides. Also the 2,4-D and terbacil measurements described by Mansell et al. (1978 1980) and Wheeler et al. (1978) were carried out in a short period (2 weeks) after applying 80-160 mm of irrigation water within 1 d after spraying. If leaching occurs so rapidly, the transformation process is of minor influence, and the fraction leached is almost fully controlled by the transport rate in soil. Application of such large amounts of irrigation water leads probably to non-uniform water flow in soil. If water flow is non-uniform, irrigation immediately after spraying results in a comparatively high fraction leached (see the simulation study by

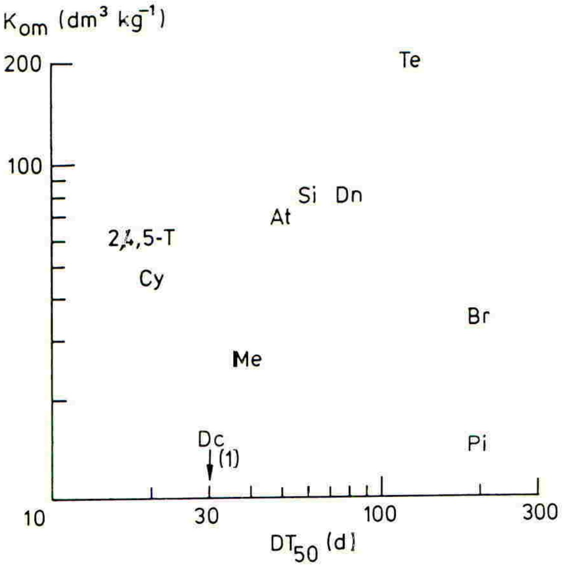

Fig. 1. Average K_{om} and DT_{50} values of the herbicides of Table 1 as found in the literature. At = atrazine, Br = bromacil, Cy = cyanazine, Dn = dinoseb, Dc = dicamba, Me = metribuzin, Pi = picloram, Te = terbuthylazine, Si = simazine.

TABLE 2

Concentrations of herbicides found in the liquid phase below the root zone in field soils exposed to natural rainfall plus irrigation.

Chemical	Annual dose (kg of a.i. per ha)	Soil type (plough layer)	Sampling depth (m)	Length of measuring period in months	Concentration (mg/m^3) (only positive concentrations taken into account)		Fraction (%) of dose leached below sampling depth	Reference	
					average	range			
Atrazine	3	silty clay	0.9	36	90		4	Schwab et al.	1973
Atrazine	4	sandy loam	1.5	4	0.8	0.1- 2	0.008	Wehtje et al.	1984
Atrazine	2	sandy loam	1.5	4	0.3	0.1- 1.1	0.007	Wehtje et al.	1984
Atrazine	2-4	sandy loam	4 - 6	19	0.9	0.4- 1.5		Wehtje et al.	1984
Bentazon	3	silt loam	1.0	7	10	2 - 11	0.1	Stoller et al.	1975
Bentazon	3	silt loam	1.0	7	5	1 - 11	0.2	Stoller et al.	1975
Bentazon	3	silt loam	1.0	7	10	1 - 20	0.5	Stoller et al.	1975
Bentazon	3	silt loam	1.0	7	20	1 - 50	0.9	Stoller et al.	1975
2,4-D	4	sand	1.1	½	10	1 - 20	0.1	Wheeler et al.	1978
Dicamba	0.1	silty clay	0.9	36	2		5	Schwab et al.	1973
Terbacil	4	sand	1.1	½	50	40 - 70	0.6	Mansell et al.	1978
Terbacil	4	sand	1.0	½	70	10 -170	0.1	Mansell et al.	1980

Leistra 1985). In the experiments with bentazon (Stoller et al. 1975) non-uniform water flow may also have been the cause of the leaching: Stoller et al. applied 600 mm of irrigation at regular intervals in the first two months after spraying and detected bentazon at 1 m depth in the leachate of soil lysimeters after percolation of about only 10 mm of water.

As shown in Table 2, Wehtje et al. (1984) found much lower fractions of the atrazine dose leaching out of the root zone than Schwab et al. (1973). This may have been caused, in part, by the amount of water percolated below 1.5 m depth being abnormally low (40 mm in 4 months) in the study of Wehtje et al. (1984). This low amount of percolation may also explain the reasonable correspondence between the concentrations of atrazine found by Wehtje et al. (1984) and those found by Muir & Baker (1976) and Hurle et al. (1987) for a similar non-irrigated soil (see Table 1).

GENERAL DISCUSSION

As shown by Table 1, fractions of herbicides measured to be leached below the root zone of non-irrigated soils are usually in the order of 1 % or less resulting in concentrations in the liquid phase in the order of 1 mg/m^3 or less. Although simulation models are useful to assess whether or not a large fraction of the dose leaches to ground water, the models currently available are not accurate enough to predict whether in a specific field situation a very low fraction (e.g. 0.1 % or 0.001 %) leaches out of the root zone. Estimating a leaching fraction of 0.1 % accurately implies that the model has to account for the behaviour of more than 99.99 % of the herbicide molecules in the soil system. In field tests of simulation models, usually measured and calculated profiles of the total concentration in the soil system are compared (see, for instance, Nicholls et al. 1982 or, for a review, Boesten 1986). Such tests consider the behaviour of the bulk of the herbicide and are not very sensitive to leaching of very low fractions of the dose to the ground water. If we want to test whether or not 0.1 % of the dose leaches to the ground water, the fraction of the herbicide molecules moving most rapidly through the root zone has to be measured directly. This may be done by measuring the course over time of the concentration in the liquid phase at a certain depth (for instance, via experiments with lysimeters or via sampling of ground water).

The behaviour of the 'fastest 0.1 %' of the herbicide molecules may be influenced by processes which are not relevant for the bulk of the molecules (for instance, rapid movement of a very small fraction through worm holes during heavy rainfall). Thus models currently used to simulate field behaviour, may need to be extended to be able to simulate accurately low leaching fractions. Before models are able do so, they have to be validated for the range of herbicide-soil-plant systems. This is a tremendous experimental task. It is therefore recommended that in future leaching studies all data be recorded that are necessary to be able to use the results of the studies for model tests.

Leaching of a herbicide to ground water does not directly imply that it will also occur in drinking water: travel times from the ground water table to the point where the drinking water is collected, may be in the order of tens of years. Thus concentrations eventually occurring in drinking water may be much lower than those just below the ground water table as a result of transformation in the saturated zone. Only little is currently known about transformation rates of herbicides in the saturated zone and about transformation products formed in this zone.

At the moment, the significance of herbicide concentrations found in ground water (Tables 1 and 2), is a point of discussion. According to an European Cummunities directive relating to the quality of water intended for human consumption adopted in 1980, the maximum admissible concentration (MAC) of any pesticide is 0.1 mg/m^3 and the MAC for the sum of all pesticides is 0.5 mg/m^3 (Smeets & Amavis 1981). These MAC values are based on the idea that contamination of drinking water with pesticides should be completely prevented and they are not based on toxicological considerations (see Aurand 1987 for a historical note on the European Communities directive). Guth & Hörmann (1987) suggested to develop MAC values based on toxicological considerations in the same way as for food. In the U.S.A., the Environmental Protection Agency is currently developing MAC values for a number of pesticides in drinking water based on toxicity data (Stara et al. 1986).

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THE PERSISTENCE AND MOBILITY OF AC 222,293 IN CROPPED AND FALLOW SOILS

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ABSTRACT

An experiment was set up to study the persistence and mobility of AC 222,293 in cropped and fallow sandy loam and clay sieved top soil contained in 40 l, 30 cm deep plastic tanks. Winter wheat was sown in half of the containers and at GS12 AC 222,293 was applied at 1.0 kg/ha (twice the field rate). Residual herbicide activity was determined for 8 sampling depths up to 20 cm and 4 time intervals up to 7 months post-application by bioassay using sugar beet. In fallow soil, herbicide activity persisted longer in the sandy loam (35% of the amount applied remaining at the end of the study compared with 20% in the clay soil). In the sandy loam the presence of a crop reduced the persistence of the compound. In the clay soil the crop had no effect on the persistence of AC 222,293. The herbicide was evenly distributed in the top 20 cm of cropped and fallow samples of the clay soil 6 months post-application and of the fallow sample of the sandy loam soil 7 months post-application. In the cropped sample of the sandy loam no herbicide was detected in the top 10 cm. Although the study employed sieved top soil rather than field monoliths and should not be extrapolated to field situations, the results illustrate differences between both fallow and cropped soil and sandy loam and clay soils.

INTRODUCTION

AC 222,293 (trade mark 'Assert'[3] or 'Dagger'[3]) is a post-emergence herbicide discovered by American Cyanamid Company for the control of *Avena* spp., *Alopecurus myosuroides* Huds., and certain broad-leaved weeds in wheat and barley (Kirkland & Shafer, 1982). The herbicide is a mixture of methyl 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-*m*-toluate and the *p*-toluate isomer. Pillmoor & Caseley (1984) demonstrated that the compound is active against *A. fatua* and *A. myosuroides* via both the foliage and roots. Entry via the soil plays a key role in the control of *A. myosuroides* (Pillmoor & Caseley, 1984). Therefore the location, persistence and availability of AC 222,293 residues in soil are direct relevance to its phytotoxic action.

The objectives of this investigation were to a) determine the location of AC 222,293 residues in soil during the initial period of weed control following application and b) investigate the subsequent mobility and persistence of AC 222,293 residues in two cropped and fallow soils.

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[3] Trademarks of American Cyanamid Company

MATERIALS AND METHODS

Soils and plant material

Begbroke sandy loam and Wytham clay top soils were each air dried in a glasshouse, sieved (5 mm mesh) and supplemented with nitrogen, phosphorus, potassium and trace elements. Table 1 shows the properties of the soils. Organic carbon was determined by a dichromate titration method; soil pH by a glass electrode using a 1:2.5 suspension of soil in 0.01M $CaCl_2$ solution; particle size distribution by a pipette/sedimentation method. Adsorption of AC 222,293 was measured by shaking 1.0 g amounts of each soil with aqueous solutions of the herbicide in 0.01M $CaCl_2$ (10 ml containing AC 222,293 in the range 2-16 µg/ml) overnight. The samples were centrifuged and the concentration of AC 222,293 in the resultant solution determined by reversed-phase isocratic hplc. A stainless steel column (100 mm x 3.0 mm i.d.) packed with Chrompak C-18 was used and the elution solvent was methanol:water (7:3 by volume) at a flow rate of 0.5 ml/min controlled by a Tracor 955 hplc pump. The herbicide was determined using a Cecil 212 u.v. detector set at 235 nm. Twenty µl injections were made and the peak heights obtained were compared with those from similar injections of solutions containing known concentrations of the herbicide. All adsorption measurements are the mean of three replicates. Measurements of AC 222,293 adsorption were characterised using the Freundlich relationship:

$$C_a = k_f . C_w^{(1/n)}$$

where C_a is the concentration of herbicide adsorbed (µg/g), C_w is the equilibrium concentration of herbicide in solution (µg/ml) and k_f and (1/n) are constants.

The soils were packed into 16 plastic tanks (40 l capacity, 30 cm deep). Half of the tanks were filled with Begbroke sandy loam and half with Wytham clay top soil to bulk densities of 1.4 and 0.7 g/ml respectively. Winter wheat (cv Fenman) was planted 1.5 cm deep in 4 containers of each soil immediately after filling. All containers were kept in a frost free greenhouse and watered to keep the soil close to field capacity until herbicide application, approximately 1 month after filling the tanks.

Herbicide application

A suspension concentrate formulation of AC 222,293 (300 g a.i./l) was used. When the wheat had reached GS12 AC 222,293 was applied at 1 kg a.i./ha (twice the recommended field rate) using a laboratory pot sprayer fitted with a single Spraying Systems 8001 'T-jet' nozzle delivering 200 l/ha. Begbroke sandy loam was sprayed on 7 December 1984 and Wytham clay on 10 January 1985.

Measurement of AC 222,293 persistence and mobility

Following herbicide application the containers were transferred to a well-drained area outside and received natural precipitation. Leachate was allowed to drain from the containers. The spaces between the containers were packed with sand, and a layer of 'guard-containers' of control soil was placed around the perimeter of the others. This was done to ensure that the soil temperature in the containers of treated soil was as near as possible to normal field temperatures. Daily maximum and minimum air temperatures and rainfall were recorded for the duration of the study. Evaporation from soil was calculated using a modified form of the Penman equation (Simmons & Jenkins, pers. comm.). A summary of the weather during the period of the experiment is given in Table 2.

Following application one cropped and one fallow container were sampled at the intervals shown in Table 3. On each occasion 12 plastic tubes (25 cm x 6.5 cm i.d.) were driven into each container. Each soil column was cut into 8 sections (0-1, 1-2, 2-3, 3-5, 5-7, 7-10, 10-15 and 15-20 cm except the final sampling interval when each column was cut into eight 2.5 cm sections). The samples for each depth were bulked together and soil moisture contents determined. Shoot dry weights of cropped samples were also determined.

Residual herbicide activity in each sample was measured using a bioassay based on shoot growth of sugar beet. The minimum detectable concentration was 12.5 µg/kg in both soil types. The mean dose causing 50% fresh weight reduction (ED50) was 43.7 and 52.5 µg/kg in the sandy loam and clay soils respectively. ED50 values for _A. fatua_ and _A. myosuroides_ were 57.4 and 66.0 µg/kg in the sandy loam and 80.0 and 102 µg/kg in the clay soil respectively.

RESULTS

Soil moisture content and crop dry weight

Average moisture contents of the soil samples taken from the top 20 cm of each container and crop dry weights are given in Table 3. Soil moisture contents of cropped and fallow soils were similar for both soils during the period up to 12 March. However at the two later sampling intervals the soil moisture contents of cropped soils were between 35 and 50% of those of fallow soils. This reduction in soil moisture content corresponded with an increase in shoot dry weights of up to 60 fold.

Persistence of AC 222,293 in soil

Results from the measurements of AC 222,293 persistence are shown in Figure 1. In fallow soil, herbicide activity persisted longer in Begbroke sandy loam than in Wytham clay. Respective times for 50% loss were approximately 155 and 105 days. The effect of a winter wheat crop on the persistence of AC 222,293 activity varied with soil type. In the lighter sandy loam the presence of a crop reduced persistence, the time for 50% loss being approximately 120 days. The difference was even more evident over the period from 12 March to 2 July where times for 50% loss in fallow and cropped soil were approximately 85 and 45 days respectively. In the heavier clay soil the crop had no effect on the persistence of AC 222,293.

Mobility of AC 222,293 in soil

The distribution of AC 222,293 in the profiles of Begbroke sandy loam and Wytham clay are shown in Figures 2 and 3 respectively. In Begbroke sandy loam the presence of a winter wheat crop had little effect on the distribution of herbicide activity in the top 20 cm of the soil profile for the first three months following application of AC 222,293.

TABLE 1
Properties of soils and Freudlich k_f and (1/n) values for the adsorption of AC 222,293

Soil	Organic carbon %	pH	Particle size distribution <2 µm %	2-60 µm %	60-2000µm %	Freudlich constants k_f	(1/n)
Sandy loam	2.2	6.5	22	7	71	1.2	0.89
Clay	4.0	6.1	49	11	40	6.6	0.76

TABLE 2

Weather during period of experiment

	Dec. 1984	Jan. 1985	Feb. 1985	Mar. 1985	Apr. 1985	May 1985	June 1985	July 1985
Mean air temp Max. (°C)	7.7 (7.2)	3.3 (6.2)	4.9 (6.0)	8.1 (8.9)	12.1 (12.0)	14.4 (15.5)	16.1 (19.4)	20.8 (22.5)
Min. (°C)	1.9 (1.4)	-1.7 (0.2)	-1.6 (3.6)	0.8 (2.0)	3.8 (3.3)	6.0 (5.7)	7.6 (9.0)	10.3 (11.3)
Rainfall (mm)	39 (56)	31 (47)	21 (39)	55 (63)	34 (30)	102 (48)	110 (38)	72 (26)
Evaporation deficit at end of each month (mm)	-28	-41	-41	-52	-18	-23	-44	-34

Values in parentheses are previous 10 year averages.

TABLE 3

Average soil moisture contents of samples taken from the top 20 cm of each container and the dry weights of plant material harvested at each occasion.

Date	Soil moisture contents				Wheat shoot dry weights	
	Sandy loam		Clay		Sandy loam	Clay
	fallow (%)	cropped (%)	fallow (%)	cropped (%)	(g)	(g)
7 January	23.0	19.8	-	-	4.4	-
7 February	-	-	63.0	59.5	-	2.8
12 March	26.4	26.1	39.5	40.3	16.0	4.5
8 May	18.7	6.5	40.2	19.0	103	50.9
2 July	21.3	10.7	43.0	18.8	357	264

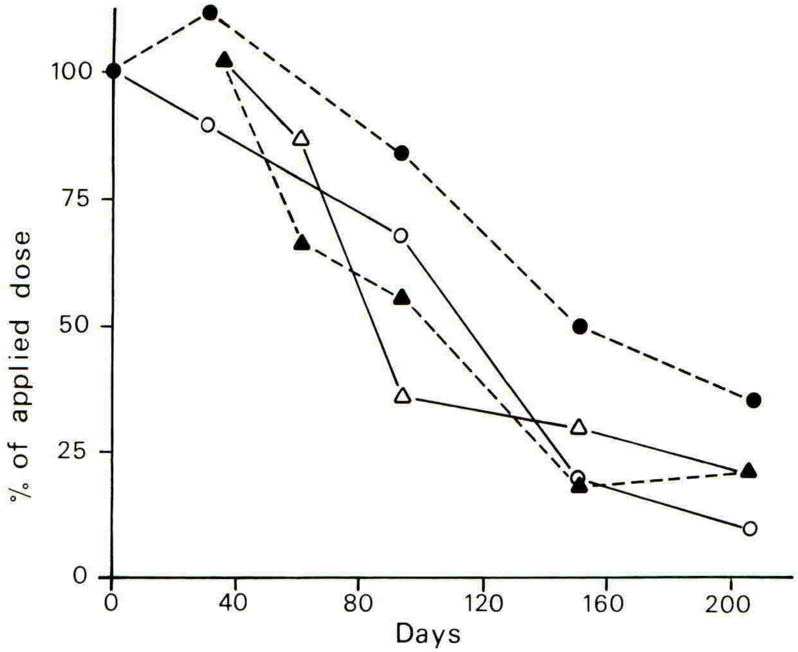

Fig. 1. Persistence of AC 222,293 in cropped (∘) and fallow (•) sandy loam soil following application on 7 December 1984 and in cropped (Δ) and fallow (Δ) clay soil following application on 10 January 1985.

One month following application over 75% of the activity remaining in the soil was located in the top 5 cm of the profiles of both cropped and fallow soil. Three months following application no herbicide was detected in the top 2 cm of the two profiles. The majority of the herbicide activity remaining was situated in a zone 2 to 10 cm below the soil surface. Five and 7 months following application AC 222,293 was relatively evenly distributed in the top 20 cm of the fallow soil. Soil sampled on 8 May contained herbicide activity equivalent to 11% of the amount applied (18% of that remaining) in the top 2 cm. This apparent net movement upwards corresponded with a period when evaporation exceeded rainfall (Table 2). However, in cropped soil the majority of herbicide activity remaining 5 and 7 months post-application was found in zones 7 to 15 and 10 to 20 cm below the soil surface respectively. At the last sampling interval no herbicide was detected in the top 10 cm of cropped soil.

In Wytham clay soil the crop appeared to have no effect on the distribution of AC 222,293 residues for the duration of the experiment. One month post-application over 55% of the activity remaining in the soil was located in the top 5 cm of both cropped and fallow soil. Two months following application the majority of the herbicide activity was located in the top 10 cm with the highest concentrations in a zone 2 to 5 cm below the soil surface. Four and 6 months post-application AC 222,293 residues were relatively evenly distributed in the top 20 cm of both fallow and cropped soil.

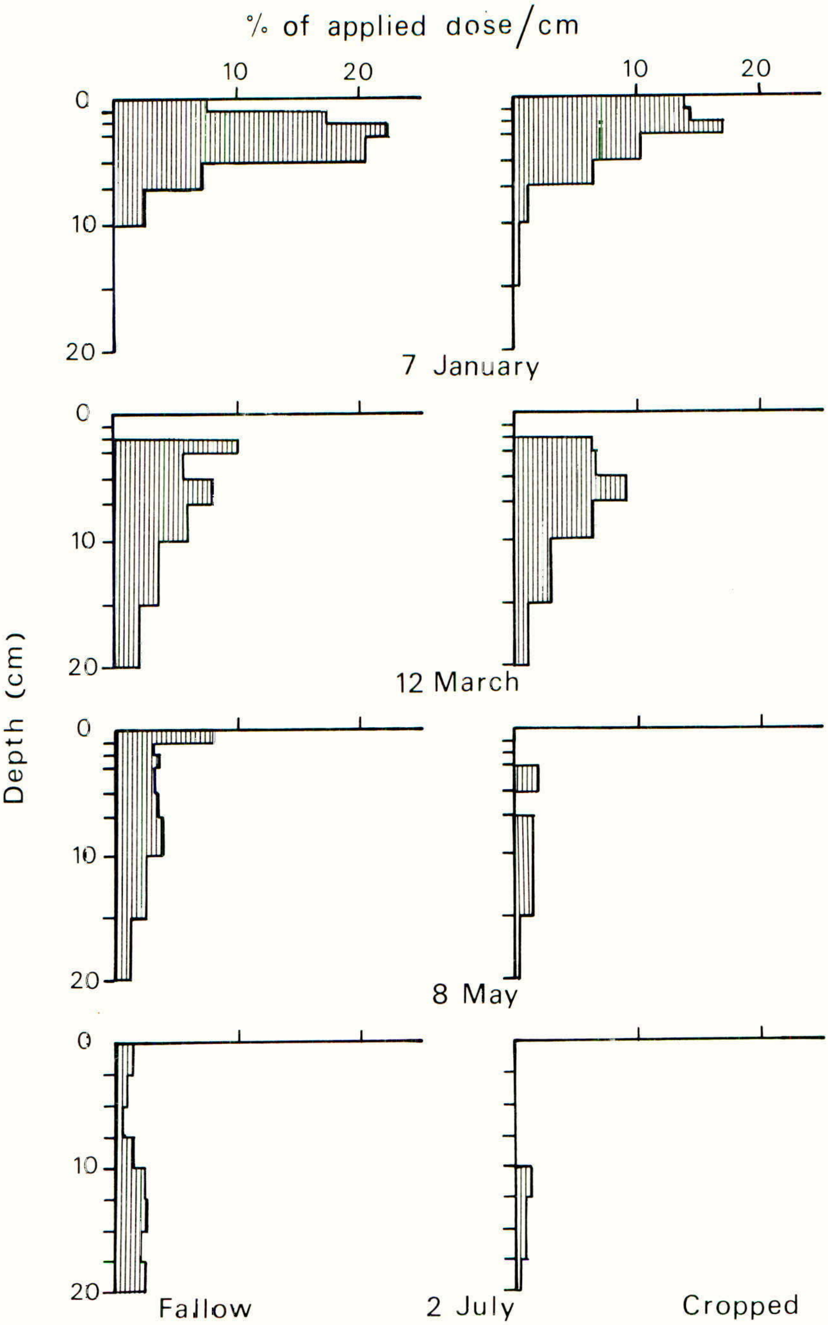

Fig. 2. Distribution of AC 222,293 residues in sandy loam soil following application on 7 December 1984.

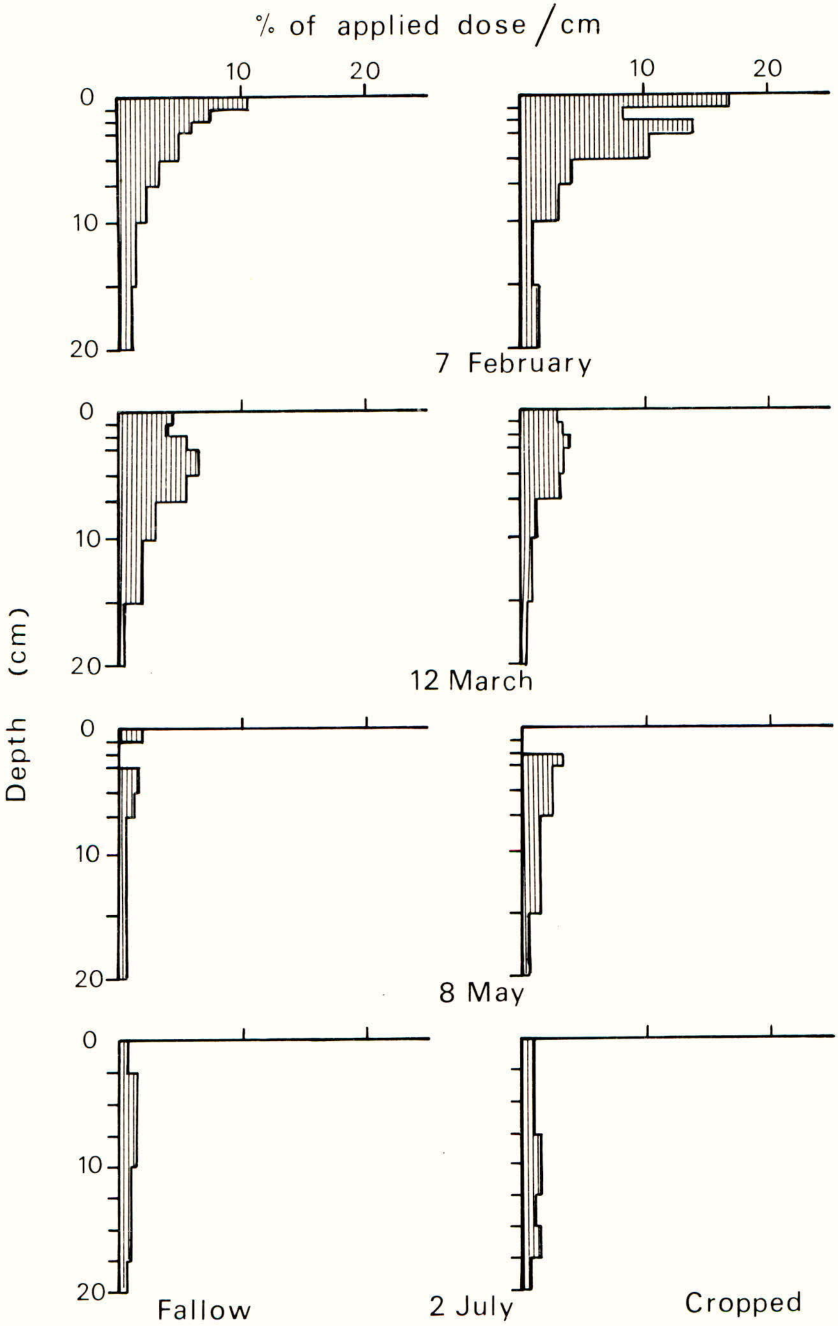

Fig. 3. Distribution of AC 222,293 residues in clay soil following application on 10 January 1985.

DISCUSSION

Persistence of AC 222,293 residues in the top 20 cm varied with soil type. The reasons for the faster rate of loss of activity in the heavier clay soil with increased organic carbon content have not been investigated. However, based on results from glasshouse and controlled environment studies (Richardson et al., 1982; Pillmoor & Caseley, 1984), residue levels in the top 20 cm of both soils are high enough to maintain control of A. myosuroides and A. fatua throughout the period from autumn to spring. The persistence and location in the soil profile of these residues in the first months post-application probably account for the effective residual activity against spring germinating Avena spp. following autumn applications as reported by Hudson & Townsend (1985).

The effect of a winter wheat crop on persistence again varied with soil type. Reduced persistence in the lighter sandy loam may have resulted from relatively low adsorption to soil particles ($k_f = 1.2$) compared with the clay soil where adsorption was greater ($k_f = 6.6$) and the crop had no effect on persistence. Caseley (1982) also found that the persistence of chlorsulfuron in Begbroke sandy loam was reduced in the presence of a winter wheat crop. However, direct evidence for loss of residues by uptake by the crop is not available.

The use of large containers in persistence and mobility studies allows for comparison between different soils under the same climatic conditions with fallow and crop situations. However, such a system does not completely simulate a field soil profile, particularly with regard to the properties of the subsoil. For example, in this study as the soil profile is composed entirely of top soil, the distribution of AC 222,293 in the 10-20 cm zone of the profile may well deviate from that in a field subsoil. Residues in the latter need to be studied in monoliths or the field.

ACKNOWLEDGEMENTS

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7A—3

BENAZOLIN-ETHYL - A CASE STUDY OF HERBICIDE DEGRADATION AND LEACHING

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ABSTRACT

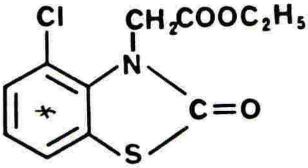
The degradation and leaching of the herbicide benazolin-ethyl have been investigated both in the laboratory and outdoors using [^{14}C]-benzyl ring-labelled compound. Rapid degradation of the parent molecule occurred via ester hydrolysis to the corresponding acid (benazolin) which was then further degraded resulting, ultimately, in mineralisation to $^{14}CO_2$. Theoretical calculations based on the octanol/water partition coefficients of benazolin-ethyl and benazolin indicated that the acid would be potentially mobile in soils, particularly those soils with low organic matter content. Results from soil adsorption/desorption studies have also pointed to the potential leachability of benazolin. Mobility of benazolin was substantiated in early laboratory leaching studies using soil columns and soil thick-layer plates.

However, when the competing mechanisms of degradation and leaching are combined, as in an aged leaching study, benazolin was more readily degraded than leached and was only detected in the leachate of very sandy soils. More definitive evidence of the preferential degradation of benazolin was obtained from outdoor lysimeter studies. Following treatment of 1 metre intact sandy soil cores with radiolabelled benazolin-ethyl, benazolin was again formed although none was detected in the leachate. The majority of the benazolin remained in the top 20 cm where it was further degraded.

It is concluded therefore, that predictions of herbicide behaviour in soil based solely on laboratory studies and theoretical calculations are of limited value. A more realistic assessment may require outdoor investigations.

INTRODUCTION

Benazolin-ethyl is a readily translocated broad spectrum herbicide with auxin type plant growth regulator properties. It is mainly used for weed control in cereals and oil seed rape.



* position of [^{14}C] radiolabel

Ethyl 4-chloro-2-oxobenzothiazolin-3-ylacetate

Fig 1 Benazolin-ethyl structure and nomenclature

The degradation and leaching of benazolin-ethyl have been fully investigated as part of the environmental impact assessment. The potential mobility of the parent compound and its major metabolite benazolin has been estimated from physico-chemical properties and compared with experimental results both in laboratory and field situations.

DEGRADATION UNDER LABORATORY CONDITIONS

Methods

Radiolabelled benazolin-ethyl was applied to two soils, a silt loam (Shippea Hill, pH 7.5, organic carbon 3.8%) and a sandy loam (Shelford, pH 5.8, organic carbon 3.4%) at a rate equivalent to 0.6 kg a.i./ha. The soils were incubated at 25°C and 50% moisture holding capacity (MHC) in a continuous flow-through system. Volatile products evolved were collected in a series of 'trapping' solutions.

The treated soils were analysed immediately after treatment, after 2 hours and at intervals up to 1 year. Soils were soxhlet extracted with dichloromethane and methanol/water (9:1), or acetonitrile/water (4:1). Radioactivity in the volatile trapping solutions and solvent extracts were quantified by liquid scintillation counting (LSC). Soil extracts were concentrated by rotary evaporation under reduced pressure and aliquots analysed by thin layer chromatography. Non-extractable radioactivity ('bound') was quantified by combustion followed by LSC.

Results

The primary degradative route of benazolin-ethyl under aerobic conditions was by rapid hydrolysis (half life <1 day) of the ethyl ester to form benazolin (4-chloro-2-oxobenzothiazolin-3-ylacetic acid). Degradation of benazolin then occurred (half life 2-4 weeks) with cleavage of the acetic acid moiety to form BTS 18 753 (4-chlorobenzothiazolin-2-one). Further degradation via ring opening led to mineralisation of the radiolabelled carbons with up to 35% evolved as $^{14}CO_2$ in one year. Up to 66% of the applied radioactivity remained unextracted from the soil (bound residue), although there was some evidence of further mineralisation of the residue to $^{14}CO_2$.

MOBILITY OF BENAZOLIN-ETHYL, AND ITS DEGRADATION PRODUCTS

Predicted mobility

The mobility of a pesticide in soil has been shown to be related to its octanol/water partition coefficient (Log P) and the soil organic matter content (Briggs, 1981) and can be expressed either by the degree of adsorption to the soil, the Kd value, or terms of movement on a chromatographic plate (Helling, 1971).

Measured Log P values for benazolin-ethyl and benazolin were 2.7 and 0.8 respectively. Using these values, benazolin was predicted to be weakly adsorbed to soil and of relatively high mobility in comparison to the ethyl ester.

Measurement of the adsorption coefficient (Kd)

The adsorption and desorption characteristics of both radiolabelled benazolin-ethyl and benazolin in two soil types were used to obtain the ratio between the amount of chemical adsorbed to the soil and the amount remaining in solution i.e. the adsorption coefficient Kd. Four concentrations in the range 0.15μg a.i./ml 0.01M calcium chloride to 1.53 μg a.i./ml were equilibrated in a soil solution ratio of 1:5.

The Kd values obtained from the initial slope of the Freundlich isotherm were 15 and 8 for benazolin-ethyl and 1 and 0.4 for benazolin in sandy loam and clay loam soils respectively. These results showed that benazolin was less readily adsorbed than benazolin-ethyl and was likely to be of relatively high mobility. The comparison of predicted (calculated) Kd values with measured values is shown in Table 1. Measured values in fact showed higher Kd values and therefore lower mobility.

TABLE 1

Comparison of calculated Kd values with measured values

Soil type and organic matter content		Benazolin-ethyl	Benazolin
Sandy loam (5.9%)	Calculated	7.0	0.64
	Measured	15	1
Clay loam (1.9%)	Calculated	2.3	0.21
	Measured	8	0.4

Measurement of mobility in the laboratory

Radiolabelled benazolin-ethyl was applied to soil thick-layer plates comprising of four contrasting soil types and the relative mobility measured using radiochemical techniques. According to the Helling index benazolin-ethyl was classified as immobile in sandy loam, clay and silty loam soils and of intermediate mobility in a sand with low organic matter (0.6%). The rapidly formed benazolin ranged in mobility from immobile in the clay to mobile in the low organic matter sand. Virtually no BTS 18 753 was found. These results are shown in Table 2 together with the predicted mobility index calculated from the octanol/water (log P) partition coefficient. Radiolabelled atrazine was used as a comparative standard and was found to have the expected intermediate mobility classification (class 3) in three of the four soil types and was very mobile (class 5) in the low organic matter sand. In general the calculated results tend to overestimate the mobility compared with the measured values.

TABLE 2

Comparison of calculated with measured values using Helling index*

Soil type	% Organic matter	Benazolin-ethyl Calculated	Benazolin-ethyl Measured	Benazolin Calculated	Benazolin Measured
Silty clay loam	5.2	2	1	3	2
Clay	5.9	2	1	3	1
Sand	0.6	3	3	5	4
Sandy loam	2.9	2	1	4	2

* Helling index range : 1 (immobile) to 5 (highly mobile)

In a further study, the leaching of both radiolabelled benazolin-ethyl and benazolin was investigated in 30 cm long x 5 cm i.d. columns using two contrasting West German (Speyer) sandy soils (2.1 and 2.2) containing 1.8% and 4.5% organic matter (o.m.) respectively. The soils were leached with 393 ml of 'rain' over a 48 hour period with 24% and 4% of the applied radioactivity being recovered in the leachate from the benazolin-ethyl treated 2.1 and 2.2 soil columns respectively. Corresponding figures for the benazolin treated columns were 74% and 41%, indicating that benazolin was considerably more mobile than benazolin-ethyl.

In the case of the benazolin-ethyl treated columns rapid hydrolysis to benazolin and then movement of benazolin occurred.

COMBINED DEGRADATION/LEACHING IN THE LABORATORY

Radiolabelled benazolin-ethyl was 'aged' for 30 days in a sand (3.1% o.m.) and a sandy loam (6.8% o.m.) using a flow-through incubation system. The treated soil was then applied to the top of 30 cm columns of similar soil type and the equivalent of 800 mm 'rain' was applied at a rate of c. 20 ml per day for 45 days.

At commencement of leaching, most of the radioactivity in the sand soil applied to the columns was benazolin (55%) compared with 20% in the sandy loam (see Table 3).

At the end of the leaching period, benazolin was only detectable in the sand leachate (23% compared with 55% applied). By comparison less than 1% of the radioactivity was leached from the sandy loam (see Table 4). Negligible amounts of benazolin remained in both soils.

TABLE 3

Composition of 'aged' soil extracts at Day 30

Radioactivity characterised	% applied radioactivity Sandy loam	Sand
Benazolin-ethyl	3.5	1.7
Benazolin	19.6	55.3
BTS 18 753	21.7	10.4

TABLE 4

Distribution of radioactivity in laboratory soil columns

Soil section	Sandy loam Total extracted	 Unextracted 'bound'	Sand Total extracted	 Unextracted 'bound'
Treated soil	10.7	39.6	1.5	7.7
0-5 cm	4.3	10.7	3.2	9.6
5-10 cm	0.7	3.1	2.1	6.8
10-15 cm	0.1	0.6	1.3	5.2
15-20 cm	0.1	0.2	1.2	5.7
20-25 cm	0.1	0.1	1.1	4.6
25-30 cm	<0.1	<0.1	2.2	4.4
Drainage sand	<0.1	<0.1	0.3	<0.1
Leachate	0.88%		28.2%	

Figures are % of applied radioactivity.

OUTDOOR LYSIMETER STUDIES

Although mobility of benazolin in sandy soils had been demonstrated in laboratory studies, in order to assess the implications of this in the field situation further investigations were carried out using soil lysimeters.

Intact soil cores (10.5 cm i.d. x 1 m) were collected from two field sites comprising of sandy loam (3.0% o.m.) and a sand (1.7% o.m. at surface and 0.6% at 20 cm). The base of each core was fitted with a water tight buchner funnel and suspended in a large tank containing drain holes. The cores were supported in the tank by sand. Each 'lysimeter' was treated with [^{14}C]-benazolin-ethyl (0.69 kg ai/ha) in December 1985 and leachate was collected from natural rainfall (200 mm) until May 1986.

No radioactivity was detected in the leachates over this time. Subsequent analysis of 10 cm soil segments from each lysimeter showed that the majority of the applied radiochemical was present in the top 20 cm with no detectable penetration beyond 30 cm in the sandy loam and 60 cm in the sand respectively, see Table 5. A substantial proportion (up to 60%) of the applied radiochemical remained unextractable ('bound'). However, analysis of extractable radioactivity showed that the top 10 cm segments comprised mainly of BTS 18 753 (3 and 32%) and benazolin (3 and 22%) in the sand and sandy loam respectively. Below 10 cm, the principle metabolite was BTS 18 753 which accounted for 10% of applied radioactivity. Below 20 cm there was less than 1% benazolin in total in either of the soil types. No attempt was made to measure mineralisation rate by collection of $^{14}CO_2$.

Results thus indicate that following treatment of the soil with benazolin ethyl, hydrolysis to benazolin had occurred. Although mobile in soil, benazolin was not present in significant amounts below 20 cm having been further degraded to the relatively immobile product BTS 18 753.

TABLE 5

The distribution of radioactivity within the lysimeter cores

	% of applied radioactivity	
Segment	Sandy loam	Sand
1	45.7	25.3
2	21.7	57.0
3	1.7	5.7
4	<0.5	2.8
5	<0.5	1.7
6	<0.5	0.5
7	<0.5	<0.5
8	<0.5	<0.5
9	<0.5	<0.5
10	<0.5	<0.5
Leachate	<0.01	<0.01

Limit of reliable determination 0.5% of applied radioactivity in lysimeter segments. Results are a mean of 3 lysimeters per soil type and include both extractable and unextractable ('bound') radioactivity.

The laboratories studies have shown that benazolin-ethyl is rapidly degraded via ester hydrolysis to benazolin. Although by both predictive methods and laboratory experiments benazolin appeared to be a potential contaminant of ground water when applied to very sandy soils with low organic matter, lysimeter studies under outdoor conditions have shown that this is not necessarily the case. Under outdoor conditions benazolin is degraded during leaching via loss of the acetic acid moiety to form the relatively immobile BTS 18 753.

CONCLUSION

Predictions of herbicide behaviour based solely on laboratory studies, whilst high-lighting the potential for ground water contamination should not be considered in isolation from field studies where other mechanisms also affect the fate of the chemical in the soil.

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LEACHING BEHAVIOUR OF AGED PESTICIDES: STANDARDIZED SOIL COLUMN EXPERIMENTS WITH ^{14}C-METAMITRON AND ^{14}C-METHABENZTHIAZURON

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ABSTRACT

The leaching behaviour of [phenyl-UL-^{14}C]metamitron and [benzene-U-^{14}C]methabenzthiazuron after 0, 30, and 105 days of incubation was studied in two soils, a degraded loess soil and a humic sand, with two application rates. In this experimental approach the standardized test methods as recommended by the Biologische Bundesanstalt (Federal German Biological Agency) for studying degradation and mobility of pesticides in soil were combined: Degradation at 21°C and 40% of the maximum water holding capacity of the soil and leaching applying 200 mm of simulated precipitation within 48 hours.

In case of metamitron up to 17,5% of the applied ^{14}C was mineralized to $^{14}CO_2$ in the sandy soil and up to 26.4% in the loess soil within 105 days of aging. In the sandy soil 6.5% of the applied ^{14}C were found in the leachate when irrigated at day 0. This portion was reduced to 4.3% after 30 days and to 1.3% after 105 days of soil incubation. In the loess soil the leachate of the 30 cm soil columns contained only 1.6% at day 0 and after aging less than 1%. Unchanged metamitron was detected in all leachates which contained more than 1% of the applied ^{14}C.

In case of methabenzthiazuron between 0.4 and 1.0% of the applied ^{14}C was mineralized to $^{14}CO_2$ within 105 days of incubation. After the leaching procedure more than 99 % of the radioactivity added to top 2 to 4 cm of the soil columns was retained in the upper 10 cm. In the sandy soil 0.3% of the applied radioactivity was detected in the leachate after 105 days of aging slightly increasing with increasing time of incubation, whereas in the loess soil generally less than 0.1% was found in the leachates.

The data will be discussed and compared with data obtained in long-term lysimeter experiments.

INTRODUCTION

The soil as a sink for chemicals, and not only for organic agricultural chemicals, has been a central topic in ecological research for several years, in which context major emphasis is placed on problems of the long-term behaviour in the soil of pesticides applied year after year. Interest is mainly concentrated on degradation behaviour and bioavailability, and in addition, leaching behaviour has come into focus due to EC initiatives (EG, 1980).

Within this framework, extensive field lysimeter experiments with a degraded loess soil were started in 1983 and 1984 by Hansper (1986) and Kubiak (1986). These were intended on the one hand to study in detail the long-term behaviour of pesticide residues in the soil with respect to degradation, plant availability and translocation, and on the other hand to investigate the problem of the extent to which results from field lysimeter experiments can be transferred to the real field situation. For this purpose the herbicide metamitron (active ingredient in Goltix[R]) was applied pre-emergence to sugarbeet, and methabenzthiazuron (active ingredient in Tribunil[R]) post-emergence to winter wheat in the form of ^{14}C-labelled compounds in the application quantities used in practice (see Fig. 2 and 3).

During the first two years after spray application, field experiments with inactive substances were

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[R] registered trademark of Bayer AG

carried out parallel to the lysimeter experiments. A comparison showed that the results obtained from the lysimeter experiments were almost identical to the data obtained under real field conditions (Kubiak et al., 1987). This is demonstrated both by the soil temperature and soil moisture curves recorded in the two experimental units (Kubiak, 1986), as well as the degradation and translocation behaviour of the active ingredients studied (Kubiak, 1986) and the residue situation in the plants (Hansper, 1986).

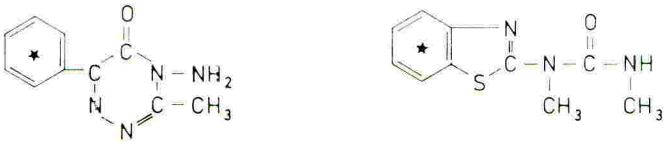
Current intensive discussions about the possibility of groundwater contamination by pesticide residues from the soil played a major role in continuing the lysimeter experiments for a further period of three years. In order to assess the mobility of active ingredients in the soil, the Biologische Bundesanstalt stipulates the implementation of a standard leaching experiment with soil columns as part of the licensing procedure for pesticide active ingredients (BBA, 1986b).

The present paper is concerned with the question of the extend to which the results obtained from such soil column experiments are able to reflect the real situation in the field and whether conclusions may be drawn about actual processes in the field. Standardized soil column experiments were therefore used to study the leaching behaviour of [phenyl-UL-^{14}C]metamitron (MAT) and [benzene-U-^{14}C]methabenzthiazuron (MBT) after 0, 30 and 105 days of incubation in two soils. The results of these experiments are presented and dicussed by means of a comparison with data obtained under realistic conditions from the lysimeter experiments mentioned above.

MATERIALS AND METHODS

Chemicals

The technically pure and ^{14}C-labelled active ingredients were supplied by Bayer AG as part of cooperative work (Fig. 1).



[phenyl-UL-^{14}C]metamitron [benzene-U-^{14}C]methabenzthiazuron

Fig. 1. The herbicidal active ingredients studied showing the location of ^{14}C-labels.

Soils

The experiments were carried out with two soils, namely a humic sand (standard soil 2.1 as rcommended by BBA) and a clayey silt (degraded loess soil Merzenhausen). The major chemical and physical properties of these soils are compiled in Table 1.

Table 1
Chemical and physical properties of soils used

Soil	pH_{KCl}	C_{org} %	Total N %	S-value mval $100g^{-1}$	clay %	silt %	sand %
sandy soil	5.8	0.7	0.04	2.5	1.4	9.2	89.4
clayey loess soil	6.6	1.3	0.08	9.5	9.7	83.8	6.5

Degradation Study

The active ingredients were applied in amounts corresponding to half the maximum quantity and also the maximum quantity recommended in practice, both in the degradation study and lysimeter experiment. For metamitron this is 3.5 and 7 kg a.i. ha^{-1} respectively, and for methabenzthiazuron 2 and 4 kg a.i. ha^{-1} respectively. Assuming a uniform distribution on the soil surface the applied herbicide quantities in the degradation experiment amounted to 6.8 and 13.7 mg kg^{-1} soil respectively in case of MAT and 2.7 and 5.5 mg kg^{-1} soil respectively in case of MBT. ^{14}C-labelled and unlabelled active ingredients were mixed and then incorporated into the soil which had been sieved to 1 mm grain size. Samples of 100 g soil (relative to the dry weight) were weighed into Erlenmeyer flasks, moistened to 40% of the maximum water-holding capacity, closed with a special trap to bind $^{14}CO_2$ and other radioactive volatile compounds, and incubated in the dark at 21°C and 80-90% relative humidity. All experimental steps are in accordance with the official BBA guidelines for testing of pesticides section 4-1 (BBA, 1986a). Three replicates were prepared for each experimental variant. Two replicates were used in the leaching experiment and the third batch served to analyze for extractable unchanged active ingredient and metabolites.

Leaching Experiments

The leaching experiments were carried out in accordance with the guidelines for the official testing of pesticides section 4-2 (BBA, 1986b) after 0, 30 and 105 days of aging the herbicides in the soil. The air-dried soil, sieved to a grain size of 1 mm (2 mm in case of the loess soil), was added to the glass columns (30 cm in height, 5 cm diameter) by shaking to a height of 26 cm and saturated with distilled water by accumulation. After placing the soil pre-incubated with active ingredient on top of the glass columns, the soil was then uniformly irrigated via a glass filter with 393 ml of water equivalent to 200 mm of precipitation over a period of 48 hours. The average period of spray irrigation for the clayey loess variants amounted to 78 hours. The leachate was collected in two fractions of 200 ml each (fraction I and II). The soil columns were separated into 2 cm segments and the radioactivity translocated was determined.

Methods of Extraction and TLC

The incubation batches and the leachate from the experimental variants treated with metamitron were processed according to the extraction method published by Jarczyk (1986). Methabenzthiazuron and its metabolites were extracted according to a method discribed by Kubiak (1986). In general, only those leachate fractions containing 1% of the applied radioactivity were analyzed further. The radioactive compounds in the organic and aqueous extracts were separated on silica gel plates (silica gel 60 F-254, Merck) by means of TLC. The unchanged active ingredient still present and the resulting metabolites were identified by a combination of radioactivity measurements (Automatic TLC Linear Analyzer LB-2842, Berthold), autoradiography and a comparison of radioactive zones on the TLC plates with the zones of reference compounds visible under UV light.

RESULTS AND DISCUSSION

Leaching Experiments with Metamitron (MAT)

During an incubation period of 105 days, about 17% of the ^{14}C-labelled compound was mineralized to $^{14}CO_2$ in the sandy soil and 18% in the loess soil (Table 2). It was possible to determine MAT in the extracts of the two soils after 30 and also after 105 days of incubation. At 105 days, 10% of the radioactivity applied to the sandy soil still represented MAT and 4% in the loess soil. Furthermore, in all extracts it was possible to identify the metabolites desamino-MAT (3-methyl-6-phenyl-1,2,4-triazin-5(4H)-on) and oxadiazol (2-methyl-5-phenyl-1,3,4-oxadiazol).

Depending on the soil, MAT and its metabolites displayed differences in leaching behaviour. In the sandy soil, a maximum of 6.5, 4.3, and 1.3% of the applied radioactivity was found in the leachates after 0, 30, and 105 days of pre-incubation respectively. Differences between the two application rates thus appeared for the first time (Table 2). The corresponding maximum values for the clayey loess soil were 1.6, 0.7, and 0.4% without distinct differences between the applied quantities. MAT as well as the metabolites desamino-MAT and oxadiazol, already identified in the soil extracts, were detected in all leachate extracts examined. A maximum of 1.0, 0.4, and 0.1% MAT was found in the leachates from the sandy soil after 0, 30, and 105 days (Table 2), already demonstrating that aging and resulting degradation decreased the translocation of MAT and its metabolites considerably.

Table 2
Leaching behaviour of [phenyl-^{14}C]metamitron after aging in the sandy soil (BBA standard soil 2.1) and a clayey degraded loess soil. Application rate 7 kg a.i. ha^{-1} (3.5 kg a.i. ha^{-1}). Average of two replicates. Applied radioactivity = 100 %

	Sandy soil			Clayey loess soil		
Time of incubation [days]	0[1]	30	105	0	30[2]	105
Mineralized						
to $^{14}CO_2$	--	6.7	17.5	--	26.4	17.9
		(5.9)	16.4)		(22.2)	(18.8)
Soil column						
0 - 10 cm	17.8	46.5	53.8	29.4	65.9	60.4
10 - 20 cm	31.0	16.2	10.4	54.8	1.0	6.0
20 - 30 cm	39.4	14.7	3.3	4.3	0.3	0.2
Percolate						
fraction I	0.1	0.8	0.3	n.d.	<0.1	n.d.
	(0.2)	(0.5)	(0.2)	(n.d.)	(<0.1)	(n.d.)
fraction II	6.4	3.5	1.0	1.6	0.7	0.4
	(2.3)	(1.5)	(0.8)	(1.3)	(0.7)	(0.3)
Metamitron (MAT)	1.0	0.4	<0.1	<0.1	--	--
	(0.3)	(0.1)	(<0.1)	(<0.1)	--	--
Desamino-MAT	0.5	0.3	<0.1	0.1	--	--
	(0.2)	(0.1)	(<0.1)	(0.1)	--	--
Oxadiazol	1.1	0.4	n.d.	<0.1	--	--
	(0.2)	(0.1)	(<0.1)	(<0.1)	--	--
Recovery	94.7	88.4	86.3	90.1	94.3	84.9

n.d. = not detected
[1] only one replicate in case of the high application rate
[2] in case of the loess soil leaching after 30 days of aging had to be repeated due to problems during the percolation procedure

Thus after completing the leaching experiments in the sandy soil, 17.8, 46.5, and 53.8% of the applied radioactivity was retained and fixed in the upper 10 cm of the soil column after 0, 30, and 105 days of incubation, which is equivalent to 20, 60, and 80% of the radioactivity applied to the upper 4 cm of the soil columns. The corresponding values for the loess soil were 29.4, 65.9, and 60.4% or 33, 98, and 91% respectively. Due to its higher soil organic matter, clay, and silt contents the degraded loess soil probably adsorbed MAT and its metabolites more effectively than the sandy soil. According to investigations by Kerpen & Schleser (1980) and Schmidt et al. (1975), especially the organic C content exerts a decisive influence on the adsorption and hence on the solubility of MAT in the soil. The close connection between adsorption and translocation behaviour can also be seen from the laboratory experiments carried out by Jarczyk (1975) with soil columns and is furthermore confirmed in practical field experiments by Mittelstaedt & Führ (1981). However, the latter only observed a very small amount of 0.3% of the applied radioactivity washed out with the percolate during the experimental period of 17 months after the application of [3-^{14}C]MAT.

Leaching Experiments with Methabenzthiazuron (MBT)

Depending on the soil type used, only 0.5-1.0% of the applied radioactivity was mineralized to $^{14}CO_2$ during an incubation period of 105 days (Table 3). 55% of the applied radioactivity could be extracted from the loess soil and 73% from the sandy soil. Of this 95-98% was identified as unchanged MBT and 0.5-1.3% as amino-MBT (1-methyl-1-(2-benzthiazolyl)urea).

Table 3
Leaching behaviour of [benzene-U-^{14}C]methabenzthiazuron after aging in the sandy soil (BBA standard soil 2.1) and a clayey degraded loess soil. Application rate 2.8 kg a.i. ha^{-1} (1.4 kg a.i. ha^{-1}). Average of two replicates. Applied radioactivity = 100 %

	Sandy soil			**Clayey loess soil**		
Time of incubation [days]	0	30	105	0	30	105
Mineralized to $^{14}CO_2$	--	0.2	0.4	--	0.3	0.9
		(0.3)	(0.5)		(0.4)	(1.0)
Soil column						
0 - 10 cm	101.7	89.6	94.4	93.8	93.0	95.0
10 - 20 cm	0.1	0.4	0.3	0.1	0.2	0.3
20 - 30 cm	<0.1	0.2	0.2	n.d.	0.1	0.2
Percolate						
fraction I	n.d.	<0.1	<0.1	n.d.	n.d.	n.d.
	(n.d.)	(<0.1)	(<0.1)	(n.d.)	(n.d.)	(n.d.)
fraction II	<0.1	0.2	0.3	<0.1	0.1	0.1
	(0.1)	(0.2)	(0.3)	(<0.1)	(0.1)	(0.1)
Recovery	101.8	90.6	95.6	93.9	93.7	96.4

n.d. = not detected

After completing the leaching experiments, more than 99% of the radioactivity applied to the soil column remained in the upper 6 cm irrespective of incubation time or soil. In the sandy soil, 0.3% of the applied radioactivity was found in the leachate after preceeding aging for 105 days, which indicated a slight increase in mobility of MBT with increasing incubation time. In the clayey loess soil, on the other hand, only a maximum of 0.1% of the applied radioactivity was detected in the leachate irrespective of the leaching date (Table 3). These data are in agreement with data from Jarczyk (1972) and Kubiak (1986) who performed the leaching test without a preceeding aging of MBT in soil. These data suggest the conclusion that MBT and its metabolites should not be expected to appear in the groundwater.

Long-Term Lysimeter Experiments with MBT and MAT

The concentration of ^{14}C-activity in the leachate reached its peak with 470 Bq l^{-1} 18 months after post-emergence spray application of [carbonyl-^{14}C]MBT to winter wheat (Fig. 2). With increasing time the percolating radioactivity levels off to about 200-270 Bq l^{-1}. However in all percolate samples the ^{14}C-activity was still too low for further identification in spite of the fact that up to 110 MBq were applied to 0.5 m^2 surface area (Kubiak, 1986).

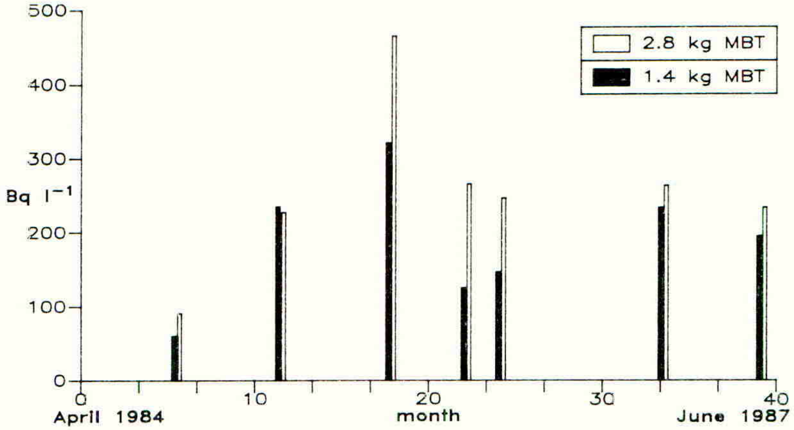


Fig. 2. Radioactivity detected in the percolates of outdoor lysimeters with 110 cm of an undisturbed agriculturally used soil profile (degraded loess soil) after post-emergence spray application of [carbonyl-^{14}C]MBT to winter wheat. Average values of always two 0.5 m^2 lysimeters.

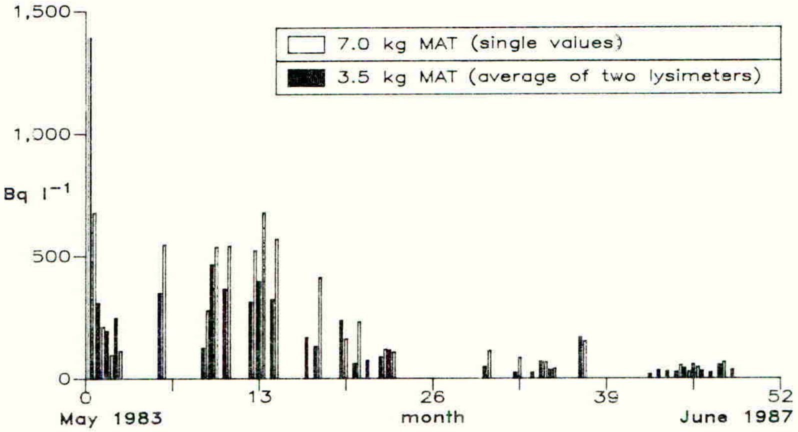


Fig. 3. Radioactivity detected in the percolates of outdoor lysimeters with 80 cm of an undisturbed agriculturally used soil profile (degraded loess soil) after pre-emergence spray application of [3-^{14}C]MAT to sugarbeets. Average values of one and two 0.5 m^2 lysimeters respectively.

Jarczyk (1987) studied the active ingredient residues washed out with the leachate during ten years using 1.5 m deep lysimeter monoliths under natural precipitation conditions after pesticide application in conformity with agricultural practice. He detected MBT residues in average concentrations of 0.7-14 ug l^{-1} under unfavourable fallow conditions in certain years. In the long term lysimeter experiment under cropping conditions however, the radioactivity detected in the percolates calculated as MBT equivalents on the basis of the specific ^{14}C-activity of the labelled herbicide applied results in maximum concentrations of 3.5 ug l^{-1} for the high and 1.2 ug l^{-1} for the low application rate.

Although MBT is rapidly bound in the soil, which is confirmed by the leaching experiments described above, MBT adsorption according to Böttger (1976) is a largely reversible process so that in the course of time most of the active ingredient is subjected to degradation, mineralization and translocation processes in the soil (Führ & Mittelstaedt, 1979). On the whole, however, the MBT degradation and mineralization processes take place at a slow rate, as shown by the results from laboratory (Cheng et al., 1978; Kubiak, 1986) and field lysimeter experiments carried out by Führ (1975), Führ & Mittelstaedt (1976), Kubiak (1986), Jarczyk (1987).

It may be concluded from the experimental results that a slow, but steady translocation in depth of the active ingredient takes place under field conditions, so that a contamination of the groundwater by small amounts of MBT residues cannot be excluded. This situation is precisely reflected by observations concerning the leaching behaviour of [carbonyl-^{14}C]MBT under real field conditions in long-term lysimeter experiments (Fig. 2), whereas this herbicidal active ingredient could be classified as environmentally safe in the light of the leaching tests (Table 3).

On the other hand, a comparison of the two experimental systems shows better agreement for the evaluation of the leaching behaviour of the herbicide MAT. The amount of ^{14}C-activity in the percolate washed out during the leaching tests rapidly decreased with increasing residence time of the [phenyl-UL-^{14}C]MAT in the loess soil (Table 2 and 4, Fig. 3).

Table 4
Radioactivity in the percolates of undisturbed soil profiles (80 and 100 cm respectively) after application of [3-^{14}C]metamitron to sugarbeets in April 1983 and [carbonyl-^{14}C]methabenzthiazuron to winter wheat in March 1984 respectively: Annual total amounts. Average of four 0.5 m^2 lysimeters. Applied radioactivity = 100 %

	METAMITRON		METHABENZTHIAZURON	
	percolate l m^{-2}	appl. ^{14}C %	percolate l m^{-2}	appl. ^{14}C %
1983	98	0.15		
1984	256	0.36	137	0.03
1985	104	0.04	241	0.18
1986	110	0.03	109	0.06
1987(June)	135	0.04	303	0.19
Total	703	0.62	790	0.46

The traces of MAT and desamino-MAT residues still identified in the percolate of the leaching test after 105 days of aging can be attributed to the fact that the degradation of the active ingredient is considerably delayed in the standardized degradation test for various reasons (Führ & Mittelstaedt, 1979, Kubiak, 1986) as compared to the field situation. MAT has proved to belong to the well degradable active ingredients, which was confirmed in field tests by Jarczyk (1976) and in the long-term lysimeter experiments started by Kubiak (1986) in which no residues of MAT and desamino-MAT were detected in the soil extracts already 100 and 110 days after application respectively. It can therefore be excluded for the long-term lysimeter experiments with [3-^{14}C]MAT, due to the rapid degradation of MAT in the soil, that the radioactivity measured in the percolate has its origin in active ingredient residues. It is rather likely to be ^{14}C-labelled carbonate and labelled carbon built into indigenous organic soil compounds after degradation of the [3-^{14}C]MAT applied. Even in the 10-year lysimeter investigations carried out by Jarczyk (1987) no MAT residues were ever detected in the leachate withdrawn every month.

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LATERAL MOVEMENT OF 2,4-D FROM GRASSY INCLINES

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ABSTRACT

Experiments were conducted under controlled environment growth room (indoor) and outdoor conditions to determine the quantity of 2,4-D recovered in water collected after lateral runoff from the surface of *Poa pratensis* sod. When runoff water was collected immediately after application of the herbicide at a dose of 1 kg a.e./ha to turfgrass grown under indoor and outdoor conditions, 91 and 71% of the applied 2,4-D was present in the effluent water, respectively. Within 1, 2, 6, and 10 days after application of the herbicide to turfgrass grown indoors, 65, 55, 50, and 32% of the 2,4-D dose was recovered in the runoff water, respectively. When compared to the quantity of 2,4-D recovered per flat at time 0, there was a 30, 55, and 65% decrease in the recovery 1, 6, and 10 days after treatment, respectively. Within 0.5, 1, 2, 7, and 11 days after application of the herbicide to turfgrass grown outdoors, 57, 48, 32, 25, and 12% of the 2,4-D dose was recovered in the runoff water, respectively. When compared to the quantity of herbicide recovered at time 0, there was a 20, 55, and 83% decrease 0.5, 2, and 11 days after treatment, respectively. Two weeks after treatment, approximately 10% of the applied 2,4-D was still present in the runoff water from sod grown outdoors.

INTRODUCTION

The herbicide 2,4-D [(2,4-dichlorophenoxy)acetic acid] is recommended for the control of broadleaved weeds in parks, golf courses, and lawns, as well as along roadsides in the heavily populated areas throughout southern Ontario (Thompson *et al.* 1984). In many use-situations this compound is applied to grassy inclines adjacent to drainage ditches, slews, and ponds. Because of the high levels of annual rainfall and use of irrigation waters on golf courses and home lawns there is a need to establish whether these herbicides will move laterally in runoff water. There is substantial evidence to indicate that the phenoxy alkanoic acid herbicides can be readily washed from agricultural soils, to eventually contaminate ground and surface waters (Barnett *et al.* 1967, Bovey *et al.* 1974, Frank & Sirons 1980, Merkle & Bovey 1974, Que Hee & Sutherland 1981, Trichell *et al.* 1968, Wauchope & Savage 1977). However, little information exists on the lateral movement of the phenoxy alkanoic acid herbicides from grassy inclines with surface water into drainage systems. This fact coupled with the current public concern about the health risks and impact on non-target sites (Thompson *et al.* 1984) of the phenoxy alkanoic acid herbicides made it imperative that studies be conducted to determine the environmental fate of these compounds in surface runoff water.

MATERIALS AND METHODS

Plant material

Turfgrass strips (88 cm length X 26 cm width X 2.5 cm depth) were cut from a two year old sward of Kentucky bluegrass (Poa pratensis) and placed in plastic flats (88 cm length X 26 cm depth X 6 cm depth) containing a peat:soil:vermiculite mixture (1:1:1). The turf was allowed to re-establish for 3 months in a controlled environment growth room maintained at 25/18 ^{o}C day/night period. The light source provided a photosynthetic electron flux of approximately 550 uE m^{-2} s^{-1}. Relative humidity was maintained at 65-70%. Trimming and subirrigation were performed as required. Fertiliser (20:20:20 N:P:K; 3 g/l) was used to subirrigate the turf once every week.

After 3 months, some of the flats containing turfgrass were moved outside and allowed to adjust to the environmental conditions for 3 weeks. The turfgrass was watered and fertilised as described above. The outdoor environment resembled typical summer conditions in southern Ontario, with an average day/night temperature of 28/20 ^{o}C, a 16 h photoperiod, and a relative humidity of 70- 80%. Prior to rainfall, the flats were covered with a clear sheet of plastic which was removed immediately after the rainfall ceased.

Herbicide application and collection of runoff water

A commercial formulation of 2,4-D amine (470 g a.e./l) was applied at a dose of 1 kg a.e./ha using a motorized hood sprayer equipped with a flat-fan nozzle (8002E) and calibrated to deliver 195 l/ha at 276 kPa.

Immediately following herbicide application, four replicated treated flats were randomly assigned sampling times of 0, 1, 2, 3, 5, 6, and 10 days after treatment for the indoor experiments. Outdoor experiments included sampling times of 0 h, 6 h, 12 h, 1, 2, 3, 7, 11, and 14 days after treatment. Herbicide residues were estimated by placing the flats in an apparatus designed to incline the turf at a 28^{o} angle from a horizontal plane. Exactly 5 l of distilled water was sprayed uniformily on the surface of the sod and the effluent that ran off the surface of the turf was collected in a stainless steel vessel.

Herbicide extraction

The runoff water was transferred to a glass bottle, shaken for one minute, and its total volume determined. A 500 ml aliquot of the effluent water was filtered through a glass fibre filter (11 cm diam; Whatmen 934-AH) and acidified with 2 ml of H_2SO_4 (37 N). The aqueous solution was extracted twice with 150 and 100 ml, respectively, of ethyl acetate. The ethyl acetate fractions were combined, dried by passing over anhydrous sodium sulphate, and collected in a boiling flask containing methanol (2 ml). Rotary evaporation was used to remove the ethyl acetate, and the methanolic concentrate was then transferred to a sample tube. The boiling flask was rinsed with methanol (2 X 5 ml) to ensure that all herbicide residue was removed.

Preparation of derivatives and sample clean-up

All sample extracts containing 2,4-D in methanol were converted to derivatives using a boron trifluoride/methanol reagent (140 mg/g; BDH Chemical, Toronto, Ontario). The reaction was performed with sample tubes tightly sealed and partially immersed in a water bath (90 °C) for 15 min. The efficiency of the methylating process was 95%.

Clean-up of the derivatised samples involved partitioning of the reaction products from distilled water (25 ml) into petroleum ether (3 X 5 ml). The ether fractions were combined, dried with anhydrous sodium sulphate, reduced to a volume of 6 ml under a stream of nitrogen gas at 50 °C, and brought to a final volume of 10 ml with iso-octane.

Chromatography

Quantification of the methyl ester of 2,4-D was performed using a gas-liquid chromatograph equipped with an electron-capture detector and a glass column (2 m length X 0.6 cm outside diam) packed with 5% OV-17 on a solid support of Gas Chrom Q (80-100 mesh). The conditions employed were: carrier gas, oxygen-free nitrogen at 43 ml/min; temperatures, injector 200 °C, column 180 °C, detector 300 °C. Chromatographic peak areas were integrated electronically and compared with reference standards to obtain the mass of the herbicide. Results were corrected for esterification and extraction efficiencies which previously had been determined in replicated tests using samples fortified with analytical standards.

Statistical analysis

All experiments were of a randomized design with four replicates per treatment. All experiments were conducted twice. Data from growth room and outdoor experiments were subjected to a one-way analysis of variance to determine the statistical significance of the reduction in herbicide residues over time. A protected LSD test was used to evaluate the differences between means.

RESULTS

When effluent water was collected immediately after the application of the herbicide, 91.3% of the applied 2,4-D was present in the runoff water collected from turfgrass grown under controlled environment conditions (see Table 1). This level is equivalent to 11.4 mg per flat, and represents a residue concentration of 3.23 mg per litre of runoff water. The total applied herbicide was a calculated number (12.5 mg) based on the spray that theoretically should have been intercepted by the surface of the turfgrass contained in a flat. Within 1 day after application, the total quantity of 2,4-D collected in the runoff water was reduced to 8.1 mg which is equivalent to 64.6% of the total dose applied to a flat. There were two further decreases to 6.3 and 4.0 mg per flat by day 6 and 10, respectively. These levels are equivalent to 50.0 and 31.9% of the total applied dose, respectively. When compared to the quantity of 2,4-D recovered per flat at time 0, there was a 30, 55, and 65% decrease in recovery 1, 6, and 10 days after treatment, respectively. Because of the difference in the total amount of runoff water collected at each time, the statistical trends were not exactly the same when a comparison was made between the data expressed on mg per litre and on a mg per flat basis. Within 1 day after herbicide application, 2.30 mg per litre of 2,4-D was recovered and decreased to 1.93

and 1.43 mg per litre, respectively, 5 and 10 days after this application. When compared to the concentration of 2,4-D collected at time 0, there was a 29, 43, and 55% decrease 1, 6, and 10 days after treatament, respectively.

TABLE 1

Residues of 2,4-D recovered in effluent water collected after runoff from the surface of Poa pratensis sod grown under controlled environment conditions[a].

Time after application	Residue recovered in runoff water		
(days)	mg/1[b]	total recovery (mg/flat)[c]	% of dose applied[d]
0	3.23 (0.29)a	11.4 (0.5)a	91.3 (3.9)a
1	2.30 (0.29)b	8.1 (1.0)b	64.6 (7.9)b
2	2.30 (0.39)b	6.9 (1.8)bc	54.9 (14.9)bc
3	2.05 (0.19)bc	5.6 (1.3)c	44.4 (10.6)c
5	1.93 (0.30)c	6.8 (1.4)bc	54.7 (11.1)bc
6	1.85 (0.25)c	6.3 (0.5)c	50.0 (4.0)c
10	1.45 (0.13)d	4.0 (1.1)d	31.9 (8.8)d
$LSD_{0.05}$	0.36	1.6	11.9

[a] Means in a column are followed by the standard deviation value in parenthesis. Means followed by the same letter(s) are not significantly different at the 5% value according to a protected LSD range test.
[b] 2,4-D recovery expressed as mg/l of surface runoff water.
[c] Quantity of 2,4-D present in the total volume of runoff water collected from a flat.
[d] Quantity of 2,4-D recovered in the runoff water when expressed as a percentage of the theoretical dose (12.5 mg) applied to each flat of turf.

In the outdoor experiments, there was a significant effect due to time, no matter how the data were expressed (see Table 2). At time 0, 70.9% of the applied 2,4-D was present in the runoff water. This level is equivalent to 8.7 mg per flat and represents a residue concentration of 2.33 mg per litre of runoff water collected. Within half a day after treatment, there was a significant decrease in recovery to 7.7 mg per flat which is equivalent to 57.2% of the total dose applied per flat. There were two further decreases to 3.9 and 2.0 mg per flat by day 2 and 11, respectively. These levels are equivalent to 31.5 and 12.2% of the total applied dose, respectively. When compared to the quantity of 2,4-D recovered per flat at time 0, there was a 20, 55, and 83% decrease 0.5, 2, and 11 days after treatment, respectively. Because of the difference in total amount of runoff water collected after each time interval, the statistical trends were not exactly the same when a comparison was made between the data expressed on a mg per litre and a mg per flat basis. Within half a day after herbicide application, 1.90 mg of 2,4-D per flat was recovered and this level decreased to 1.25, 0.90, and 0.50, respectively, 2, 7, and 11 days after application. When compared to the concentration of herbicide in the runoff water collected at time 0, there was a 19, 47, 62, and 79% decrease 0.5, 2, 7, and 11 days after treatment, respectively.

TABLE 2

Residues of 2,4-D recovered in effluent water collected after runoff from the surface of Poa pratensis sod grown under outdoor environmental conditions[a].

Time after application	Residue recovered in runoff water		
(days)	mg/l[b]	total recovery (mg/flat)[c]	% of dose applied[d]
0	2.33 (0.17)a	8.7 (1.6)a	70.9 (12.2)a
0.25	1.95 (0.24)b	7.7 (1.4)ab	61.7 (10.8)ab
0.5	1.90 (0.29)bc	7.2 (1.1)bc	57.2 (9.3)bc
1	1.68 (0.50)c	5.9 (0.1)c	47.5 (1.7)c
2	1.25 (0.17)d	3.9 (1.1)d	31.5 (9.1)d
3	1.05 (0.13)de	3.1 (0.3)de	24.9 (2.5)d
7	0.90 (0.08)e	3.1 (0.7)de	24.5 (5.9)d
11	0.50 (0.16)f	2.0 (0.6)ef	12.2 (8.5)e
14	0.38 (0.05)f	1.2 (0.3)f	9.8 (2.2)e
$LSD_{0.05}$	0.24	1.4	11.4

[a] Means in a column are followed by the standard deviation value in parenthesis. Means followed by the same letter(s) are not significantly different at the 5% value according to a protected LSD range test.
[b] 2,4-D recovery expressed as mg/l of surface runoff water.
[c] Quantity of 2,4-D present in the total volume of runoff water collected from a flat.
[d] Quantity of 2,4-D recovered in the runoff water when expressed as a percentage of the theoretical dose (12.5 mg) applied to each flat of turf.

DISCUSSION

When a comparison was made between the data from the indoor and outdoor experiments, there was a significant difference in the amount of 2,4-D present in the runoff water (see Tables 1 and 2). At time 0, significantly more 2,4-D was removed by the runoff water in the indoor than in the outdoor experiment. Furthermore, approximately 17, 23, and 20% more of the applied 2,4-D was recovered per flat under indoor conditions, 1, 2, and 3 days after application, respectively. Ten days after treatment, 32% of the applied herbicide was present in the runoff water obtained from flats grown under controlled environment conditions, whereas in the outdoor experiments only 12.2% of the applied dose was recovered in the runoff water 11 days after treatment. However, comparison between the data from the indoor and outdoor experiments indicates that the rate of decrease in the 2,4-D residues found in the runoff water was not different over the duration of either experiment.

In another experiment conducted under controlled environment conditions, the turfgrass was lightly misted with 1 l of water 72 h after application of 2,4-D. Runoff water was collected from the surface of the sod 24 h after misting (96 h after herbicide application). When the results from this experiment were compared with those results from previous indoor experiments, significantly less 2,4-D was recovered in the runoff water from turfgrass that received a mist treatment. For example, in the misting experiment 2.0 ± 0.7 mg of 2,4-D per flat was recovered 96 h after herbicide application, whereas when the turfgrass received no misting treatment 6.8 ± 1.4 mg of 2,4-D per flat was recovered 120 h after 2,4-D application. These results are equivalent to 0.68 ± 0.09 and 1.93 ± 0.29 mg of 2,4-D per litre of runoff water recovered from turfgrass which had and had not been misted, respectively. Thompson *et al.* (1984) found less than 0.01% of the applied 2,4-D was dislodgable by wiping the sod with cheese-cloth one day after application if the turf received 18 mm of rainfall 1 h after spraying. Conversely, it took 7 days for the herbicide to dissipate to the same level when the turf received no rain. Taken together our results and those of Thompson *et al.* indicate that a light irrigation to incorporate 2,4-D 2 to 3 days after herbicide application may reduce the amount of 2,4-D that may be removed in subsequent runoff events.

Under controlled environment conditions it has been shown that 8% of the applied 2.4-D could be removed by wiping the turf with cheese-cloth 9 days after treatment (Thompson *et al.* 1984). However, in the same study it was found that 55% of the applied 2,4-D was still present on the surface of turf leaves 9 days after treatment. These results may explain why we recoved approximately 32% of the applied 2,4-D in the runoff water collected from sod grown indoors.

In our outdoor experiments, considerably less 2.4-D was recovered in the runoff water than in runoff water from indoor experiments. Thompson *et al.* (1984) found a similar relationship between the ratio of disappearance of dislodgeble residues in outdoor versus indoor experiments. They postulated that the faster disappearance of 2,4-D in outdoor studies may have been due to greater rates of photodecomposition. However, recent outdoor studies with shaded versus unshaded field plots did not show a large difference in 2,4-D degradation.

In conclusion, these studies establish that runoff water can dislodge up to 10% of the 2,4-D two weeks after application to sod grown under outdoor conditions. Therefore, the magnitude of the 2,4-D residue potentially available in runoff water is a significant environmental concern for at least a few weeks after the herbicide is applied.

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ADVISORY PROBLEMS WITH RESIDUAL SOIL HERBICIDES

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ABSTRACT

The causes of herbicide damage are discussed with special reference to cases where herbicide persistence has affected subsequent crops, these are illustrated by examples taken from field crops. The results of field experiments to establish damaging residue levels are given for atrazine, chlortoluron, pendimethalin, and triallate. Damage symptoms together with those identical, from other causes are presented. Ways of reducing the damage risk are also discussed.

INTRODUCTION

Although the incidence of crop damage is very small compared to the total hectarage treated, when it occurs it can inflict serious financial losses to farmers and growers. In the South East of England we investigate about 350 crop damage cases annually. These probably represent a fraction of the total number that occur, with many not reported because they are slight or thought to be due to other causes.

Overdosing of herbicides can occur in a number of ways. A miscalculation of the rate can damage the entire crop, although more commonly it occurs in patches where the soil may be stoney or of a lighter texture. The most common cause of damage is due to uneven spraying produced by overlapping of spray booms causing strips of poor crop across the field and regular patches in the headland turning areas. Uneven pressure along spray booms, incorrect boom height and blocked nozzles can produce regular patterns of damage. Inefficient mixing, settling out of herbicide in the spray tank and the slipping of tractor wheels on a gradient all cause overdosing in parts of the field. Heavy rain soon after application can move the chemical into the root zone, especially in cloddy or unweathered seedbeds on light soils.

When examining suspected cases of herbicide damage it is most important that a pattern of damage is recognised together with an accurate assessment of symptoms, and the date when these are first observed. The rates and dates of the chemical spray together with rain and wind data at the time of and soon after spraying are often important. Chemical or biological methods of residue assessment should be conducted for confirmation.

Symptoms of damage may not show up until a certain rate of transpiration is reached, which may take several weeks. In cases of severe but sub-lethal damage the crop can recover to yield normally, eg. compensating by greater tiller development.

HERBICIDE PERSISTENCE

The breakdown of herbicides in soils is complex and does not always follow first order kinetics (Duseja 1980). Breakdown is mainly by chemical and microbiological processes. These are highly dependant on soil moisture, temperature, soil fertility and pH. Losses due to volatility are important for some herbicides, eg. dichlobenil and trifluralin, in the case of the latter photodegradation is also important. These processes are comprehensively reviewed by Kearney and Kaufman (1975) and Hance *et al* (1980).

The degradation of atrazine applied to maize crops in the Southern counties of the UK during April/May were monitored (Caverly, 1974-79) and varied from year to year with levels decreasing rapidly following the onset of autumn rains.

The simulation models developed by Walker (1973; 1974) have proved very useful in their assessment of herbicide breakdown although localised weather of the type occurring in the SE of the UK can be misleading and in these cases residue levels must be established by analysis.

CHEMICAL SELECTIVITY

Herbicide selectivity may be due to physiological differences between crop and weed where rates of uptake and/or degradation are sufficiently different. In many cases the selectivity is obtained by the relative positions of crop roots and herbicide placement, together with its subsequent movement. Well established crops like hops and top fruit, with well developed root systems can often tolerate higher than recommended rates which in some cases, eg. diuron, can lead to residual build-up.

Table 1 shows the main problem areas of damage to subsequent crops, the persistence values are those reported by Eagle (1979)

TABLE 1:
Persistence and Incidence of Crop Damage.

Persistence (weeks)	>50	30-50	15-30	<15
Incidence of damage 1976-79 SE Region	2	26	22	5
Hectares treated 1971-74	1,058	19,865	507,878	106,091

These figures show that most cases of damage confirmed are with those chemicals showing moderate - high persistence. In almost every case it was apparent that the recommendations had not been followed.

EXAMPLES OF DAMAGE CASES AND SYMPTOMS

Arable Crops

Most arable cropping receiving soil applied herbicides in the SE, is on medium to light textured land, grass in which problems seldom occur generally being grown on heavier soils. The climate is such that dry conditions can be interspersed with periods of heavy rainfall. Winter wheat was severely damaged by a spring application of isoproturon following a period of heavy rain.

Sample Depth (cm)	pH	OM %	TEXTURE	Isoproturon mg/kg
0 - 2.5	-	-	fine loamy sand	0.46
2.5 - 7.5	6.5	1.1	fine loamy sand	0.30
7.5 - 15.0	-	-	fine loamy sand	0.28

On heavier land where the crop was healthy the levels in the same horizons were 1.24, 0.21 and 0.03 mg/kg respectively.

Soil analysis following the grubbing of an orchard showed 2.1 mg/kg diuron in a general sample taken to a depth of 0-15 cm across the field. The grower was advised to abandon his thoughts of drilling cereal crops for at least two seasons. His first crop was linseed which has good tolerance to this herbicide. Although the crop failed in patches, the yield was satisfactory.

Results from samples (0-7.5cm) taken during summer were:

	Texture	pH	Organic matter %	Diuron mg/kg
Healthy crop	Silty loam	6.2	2.4	2.34
Damaged crop	Silty loam	6.4	2.6	3.55

Samples taken 12 months later from the same areas in the subsequent pea crop showed 0.38 and 0.63 mg/kg. The crop following this was winter wheat which was almost free of damage.

The following table shows results of an atrazine persistence study (Caverly 1976) after its application for annual weed control in maize.

TABLE 2

Sampling Depth cm	Organic Matter	Atrazine mg/kg
0 - 15.0	4.22	0.29
0 - 7.5	5.78	0.20
0 - 7.5	2.52	0.14
0 - 7.5	3.20	0.27
0 - 7.5	3.80	0.09

These field samples were taken in September after an April/May application. Most of these values are above the damage threshold. Examples of field damage cases to cereals are given in Table 3, the samples being taken 0 - 7.5 cm.

TABLE 3

	Atrazine mg/kg	
	Healthy	Damaged
Winter wheat	0.05	0.32
" "	-	0.30
" "	-	0.23
Spring barley	0.05	0.49
" "	0.05	0.33
" "	0.02	1.40

The barley problems were from crops receiving the rate for perennial weed control.

Methabenzthiazuron damaged winter wheat due to overdosing caused by settling out of the chemical in the tank, the pattern in the crop showing as a large dead strip: the details are given in Table 4.

TABLE 4

		Texture	pH	OM %	Methabenzthiazuron mg/kg
Good	0-2.5 cm				2.25
	2.5-7.5 cm	Very fine sandy loam	7.3	2.1	<0.05
Poor	0-2.5 cm				30.60
	2.5-7.5 cm	Very fine sandy loam	7.3	2.2	1.30

Symptoms showed as stunting and necrosis/chlorosis to older leaf tips leading to plant death.

Carry over of residues of trifluralin applied to carrots caused much damage to winter wheat: the results of our investigations are given in Table 5. Plants were stunted with thickened roots.

TABLE 5

		Texture	pH	OM %	Trifluralin mg/kg
poor	0- 7.5 cm	Sandy silt loam	7.0	1.6	0.38
poor	7.5-15.0 cm		-	-	0.05
ploughed	0- 7.5 cm	Sandy silt loam	6.7	1.7	0.05
ploughed	7.5-15.0 cm		-	-	0.03

These results confirm the work of Stoinev (1967) that herbicide degradation is more rapid in soils after ploughing.

Problems due to metribuzin have occured to a number of crops in cases where after potatoes the land has not been ploughed as recommended; residue levels of 0.47 and 0.08 mg/kg were found in soil from damaged and healthy wheat. In dry summers propyzamide has damaged winter cereals especially where ploughing to 15 cm has not been carried out.

A sugar beet crop in Kent was almost totally killed in an area where previously a weed control trial on winter wheat had plots treated with chlorsulfuron.

Vegetables

Careful preparation of seedbeds is essential in order to obtain good weed control without crop damage. As vegetable growers are reluctant to plough due to loss of moisture, shallow cultivations are practised. On lighter soils these can lead to compaction which increases, due to root restriction, the risk of herbicide damage.

Table 6 shows the degree of sensitivity of these crops to atrazine following application to maize or sweetcorn.

TABLE 6

	Atrazine mg/kg				
	Curly Kale	Swede	Beet	Garlic	Stick Beans
Healthy	0.05	0.05	0.04	0.02	-
Damaged	0.38	0.12	0.06	0.67	0.14

Damage to seeded broad-leaved crops often does not show until the first true leaves are forming. It develops as a marginal chlorosis/necrosis to cotyledons and true leaves, which may then progress to an interveinal effect in the true leaves (Eagle and Caverly, 1981). Spring cabbage was damaged mainly in headland areas by trietazine/simazine applied to the previous crop of peas. Soil analysis showed 0.19 and 0.95 mg/kg trietazine in healthy and damaged parts respectively and 0.01 and 0.13 mg/kg of simazine. Symptoms first showed as a chlorosis/necrosis to older leaves which then progressed to cause plant death. Damage to another seeded summer cabbage crop was caused by uneven application of lenacil to the previous strawberry crop. Soil analysis showed less than 0.05, 0.06 and 0.14 mg/kg lenacil in samples taken from healthy, slightly damaged and severely damaged plants. Leaf symptoms produced by this herbicide were of a vivid discrete veinal chlorosis leading to total collapse of tissue.

Potatoes were damaged by carry-over of isoproturon in headland areas from the previous barley crop, residues found were 0.29 and 0.70 mg/kg from good and poor crops. Symptoms showed, as plants developed, as a chlorosis/necrosis to leaves older and a general chlorosis to whole plants.

Failure to plough after a potato crop that had received monolinuron caused damage to spring greens. Residues were 0.17 and 0.26 mg/kg from good and poor areas respectively. Symptoms showed as stunting, and death of cotyledons which progressed to affect true leaves. Two fields of cabbages were severely damaged by residues of TCA. The leaves of affected plants were brighter in colour than normal, due to loss of cuticle wax, and puckered.

TABLE 7

	cv January King	cv Primo
	TCA (mg/kg)	
Slightly affected	0.3	3.6
Moderately affected	14.1	7.2
Severely affected	35.0	13.4

Fruit and Hops

Most damage problems to this group of crops are caused by spray overlaps in plant rows often compounded by compaction restricting root systems. Strawberries are very sensitive to residues of the substituted urea herbicides and carry-over of diuron from top fruit produces some serious problems. Bromacil can leach through the profile and has caused a number of problems in raspberries. Symptoms snow as a discrete yellow veinal chlorosis before progressing, causing collapse to the interveinal tissue.

Glasshouse Crops and Nursery Stock

Problems often arise as a result of allowing the soil beds to become dry leading to persistence of residues. Propyzamide applied to lettuce damaged a subsequent tomato crop, symptoms showed as stunted growth; the level of propyzamide was 1.0 mg/kg. Peppers were damaged in soil containing 0.60 mg/kg lenacil. Symptoms showed as a vivid yellow chlorosis which led to total leaf collapse. The glasshouse had been constructed on land previously growing strawberries which had received this herbicide.

Problems to field nursery stock are similar to other row crops, mostly being caused by spray overlap in the rows. Those grown in containers standing on sand or gravel bases often with roots developed outside of the container can readily take up herbicides applied to the beds. This is well illustrated in Table 8 showing the results of an investigation following damage to the ornamental plant caryptales. The container compost was sectioned as indicated:-

TABLE 8

	Simazine mg/kg	
Sample depth	young plant	mature plant
0 - 5.0 cm	0.35	0.38
5 - 12.5 cm	0.20	0.19
12.5 - 15.0 cm	13.45	3.31

ESTABLISHMENT OF CROP DAMAGE LEVELS IN SOILS

A knowledge of threshold levels is vital when advising on crop damage problems for future cropping in soils containing residues. These may be established from 'ad hoc' problems or experiments designed to produce symptoms of crop damage. Information has been collated by Eagle (1979).The effect in a sandy soil of residues of dichlobenil on 6 different crops was studied by Williams and Eagle (1979). The granular formulation was applied to the soil surface with and without incorporation at 2 rates. Barley, cabbage, carrots, lettuce, radish and sugar beet were sown each year for 4 years following application, and soil residues were monitored analytically. Carrots were found to be the most sensitive crop and most treatments showed damage even after 4 years: soil residues at that time were in the range 0.05 - 0.20 mg/kg. Lettuce were also sensitive with cabbage and radish the most tolerant.

In field experiments by Caverly (1978) lenacil, linuron and trifluralin were applied at nine levels to give a maximum application rate of 10 kg/ha and thoroughly incorporated to 15 cm. Sixteen crops were sown during the season and soil residues monitored analytically. Of the crops studied potatoes and linseed were the most tolerant being generally unaffected by soil levels of 1.0 mg/kg. Cereals and rape were most sensitive and were damaged by levels as low as 0.1 mg/kg although the latter crop showed a marked tolerance to trifluralin. Similar experiments were conducted in 1979 with atrazine and chlortoluron on a clay loam; pH 8.0; OM 5.6%. Fertilisers were applied to raise the statusto 46-70 mg/l (P); 121-240 mg/l (K), the magnesium content being 51-175 mg/l. An assessment of crop damage was made approximately 6 weeks after drilling (Table 9) when soil samples were taken for residue analysis. Table 10 shows results of similar experiments with pendimethalin and triallate on a silty loam pH 7.4 and OM 3.8.

TABLE 9

Crop Damage Levels of Atrazine and Chlortoluron

Treatment mg/kg	Atrazine mg/kg	Onset of crop damage
Nil	<0.02	
0.05	0.04	
0.10	0.08	
0.15	0.11	Barley, beans(dwarf),beet(red), oats, swede, wheat.
0.20	0.20	Lettuce, lucerne, carrots, oilseed rape, onions, parsnip, turnip, ryegrass, sugar beet.
0.30	0.25	Brussels sprouts, cabbage, cauliflower, linseed potato.
0.50	0.30	Peas
1.00	0.60	
2.00	1.42	

Treatment mg/kg	Chlorotoluron mg/kg	Onset of crop damage
Nil	<0.02	
0.05	0.04	
0.10	0.09	
0.15	0.12	
0.20	0.15	Beans(dwarf), peas.
0.30	0.27	Brussels sprouts, cabbage, lettuce.
0.50	0.39	Barley, lucerne, oats, potato, sugar beet, swede, wheat.
1.00	0.78	Beet(red), carrot, linseed, oil seed rape, parsnip, ryegrass, turnips.
2.00	1.57	Linseed, onions.

These herbicides were soil incorporated in April and crops drilled 2 weeks later.

TABLE 10

Crop Damage Levels of Pendimethalin and Triallate (mg/kg)

	Barley	Beans (dwarf)	Cabbage	Carrots	Lettuce
Pendimethalin	0.20	1.94	1.94	1.94	1.94
Triallate	0.25	1.07	0.44	1.07	>2.97

	Linseed	Lucerne	Oats	Peas	Potatoes
Pendimethalin	1.94	0.60	0.18	1.94	>2.45
Triallate	>2.97	0.44	0.18	1.07	0.25

	Ryegrass	Sugar beet	Swede	Wheat
Pendimethalin	0.18	0.60	0.60	0.20
Triallate	0.25	1.07	1.07	0.44

These levels were obtained from residue data taken at the time of spring drilling from an autumn application of herbicides (maximum rate 5 kg/ha).

THE CAUSES OF CONFUSION IN SYMPTOM RECOGNITION

In cereal crops the die-back of older leaves showing first as a chlorosis/necrosis to leaf tips can be caused by residues of the triazines, subsituted ureas and uracil herbicides although frost or potassium deficiency can cause similar symptoms. Leaf distortion produced by the hormone group of phenoxy and benzoic acids to tomatoes can also look very similar to some virus disorders. The damage symptoms to broad-leaved crops from the substituted ureas and uracil groups show a veinal chlorosis. As these involve a large number of chemicals soil analysis is essential in order to confirm the reason for damage. Damage to cereals showing a stunting and thickening of coleoptile due to excessive carbetamide, pendimethlin, propyzamide and trifluralin, can be confused with the over-application of a mercury seed-dressing or by contamination of seed by the growth suppressant chlorpropham.

The amount of herbicide available to the crop and its stage of growth can influence the damage symptoms that occur. This is well illustrated in raspberry and strawberry crops where bromacil or lenacil have been applied. Leaf symptoms usually show as a discrete yellow veinal chlorosis but in the presence of high levels of residues or rapid plant growth they can manifest as an interveinal necrosis leading to total leaf collapse: Similar symptoms are produced by magnesium deficiency. The veinal chlorosis produced by the presence of chlorate residues could easily be confused with those caused by certain viruses eg. pepper yellow vein virus reported by Fletcher (1987). Plants showing damage as a bleached leaf chlorosis can be caused by residues of aminotriazole but drift of contact spays eg, glyphosate can produce very similar symptoms and these can even be confused with those of iron deficiency. Aminotriazole often causes a pink coloration as well.

In cases where crops have received herbicides and have failed due to adverse weather or other causes the question of redrilling often presents a difficult decision. The work reported by Cochet et al (1972) on the degree of risk in ploughed and non-ploughed situations has been particularly helpful.

MEASURES TO REDUCE SOIL RESIDUE ACTIVITY

Eagle(1979) showed the effect of ploughing down residues on cereal crops. He reported that the damaging effects of propyzamide, trifluralin and ethofumesate were markedly reduced after ploughing. (Hance et al., 1978) have shown that residues of atrazine and propyzamide were less damaging to barley and turnips after ploughing, and tine cultivation and rotovations were not effective in decreasing crop damage.

A case of severe crop damage following application of manure contaminated with 2,3, 6-TBA occurred to a tomato crop. There was no significant decrease in soil residues during the life of the crop from an initial level of 0.01 mg/kg. During the winter months, after high rates of irrigation, residues fell to below 0.001 mg/kg and a subsequent tomato crop was almost without damage.

Stimulation of aerobic microbiological activity increases the rate of residue degradation and this can be assisted by tillage or subsoiling to improve drainage. In this respect application of organic manures is useful but their contribution to the true organic matter status is long term.

Reduction in herbicide activity by the use of activated carbon was first reported by Lucas and Hamner (1947). It is now common practice to dip the roots of strawberry plants in carbon where residues are present. In Kent several acres of strawberries died after being planted into soil containing 0.16 mg/kg linuron that had persisted from previous vegetable crops, where this herbicide had not been applied plants were healthy and residues zero. This illustrates the sensitivity of transplanted bare-rooted plants to the presence of soil residues. Exceptionally good growth was observed in replants after carbon treatment. Short term protection was observed by the treatment of pelletised seed with carbon (Croxford, 1975) and band or overall applications although effective, caused some reduction in weed control in subsequent crops (Ogg, 1978).

CONCLUSIONS

Most damage problems are caused by poor application of herbicides. Very few cases have led to any major changes in label recommendations. A complete diagnosis of damage problems is often not easy and relies on a number of parameters but rainfall, soil organic matter and texture are the most important. The final assessment requires the support of analytical residue data together with damaging threshold levels. More work needs to be done to establish damage thresholds in differing soil types for those herbicides where little data exists and this should be in conjunction with residue analysis.

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EFFECTS OF SOIL AND WEATHER CONDITIONS ON HERBICIDE SAFETY

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ABSTRACT

Occasionally, serious damage is caused by well established normally safe, soil acting herbicides applied according to label recommendations. The soil and weather conditions which can give rise to damage are discussed.

INTRODUCTION

The main factors which determine whether a soil acting herbicide is safe to a crop are: (i) the dose, which may be dependent on the soil type, (ii) the relative selectivity of the herbicide for the crop and (iii) the position of the herbicide in relation to the seed and root system of the crop. Obviously, the greater the selectivity the less important is this separation and, conversely, if there is little selectivity the separation is extremely important.

The objective of this paper is to consider the soil and weather conditions which occasionally lead to crop damage from normally safe and well tried herbicides. The examples given are for cereal crops but examples of similar types of injury to other crops caused by other herbicides could be quoted for most of the problems described.

PHOTOSYNTHESIS INHIBITING HERBICIDES APPLIED TO WINTER CEREALS

In most years, no damage is seen from herbicides in this group when applied in the autumn, even in spray overlaps which are double dosed, because crop growth and herbicide uptake are slow. Damage has occurred occasionally, however, from pre-emergence applications in abnormally warm, sunny autumn conditions when there was adequate moisture leading to rapid emergence, rapid early growth, above average transpiration and optimum herbicide availability. Under these conditions, excessive amounts of herbicide are taken up. In 1977, damage to winter barley occurred on light sandy soils in East Anglia. The herbicides involved were isoproturon, methabenzthiazuron and terbutryne; damage was favoured by shallow drilling of the first two herbicides which would tend to increase root uptake, and by deep drilling of terbutryne which is active through the emerging shoot. In 1983, similar and more widespread damage occurred in early sown winter barley from the same herbicides and also from linuron. Winter wheat was similarly affected by isoproturon, chlortoluron and linuron. The factors inducing herbicide damage in 1977 were also evident in 1983 and, in addition, early drilling when day length was greater also encouraged rapid growth and increased transpiration.

In 1983, the majority of damage from chlortoluron and isoproturon followed post-emergence applications raising the possibility that foliage uptake might have been important, particularly as analyses (Butchart, 1984) showed that in some damaged crops the herbicide had not moved down to the root zone. In a field experiment at Cambridge in autumn 1984, however, it was shown that application of activated charcoal to the soil to preclude uptake from the soil before a post emergence application of isoproturon prevented damage to winter barley in spray overlaps. Where uptake from the soil was prevented there was no damage but analyses showed in this case also that the herbicide was above the roots. Uptake therefore could hardly have been by the roots. An alternative explanation is that uptake from the soil, which caused damage where no charcoal was applied, may have been by absorption through the coleoptile. Shone and Wood (1976) showed that the related herbicide diuron can be absorbed through the hypocotyl of radish seedlings suggesting that absorption via the coleoptile must be considered a possibility. In the conditions described the coleoptile would be in contact with a high concentration of herbicide.

Winter and early spring applications of chlortoluron and isoproturon are usually totally safe to cereal crops because a significant part of the root system is normally at that time below the depth to which the herbicide penetrates. This spatial separation can break down, however, if the soil is compacted below drilling depth and enough rain follows the herbicide application to leach it down to the compacted layer. Roots will not penetrate wet, compacted soil. In these circumstances, damage can occur when rapid growth starts in the spring because most of the root system is in the herbicide layer and this leads to enhanced uptake. The risk of this type of damage is increased by a sudden change from winter to very warm conditions leading to rapid growth and a greatly increased demand for moisture from a surface root system. Such conditions occurred, for example, in April 1987.

A rare combination of circumstances led to instances of damage from chlortoluron and isoproturon in the spring of 1986. The main factor causing the injury was the extremely cold weather throughout February which caused frost lift injury to the deeper roots so that most active roots were near the surface. Crops had not fully recovered from the winter injury when rapid growth followed in late April after heavy rain had leached herbicide into the root zone. Crops had been drilled in dry weather, often resulting in loose seedbeds, and damage was invariably worst where the soil was least consolidated and frost lift was most severe.

Symptoms of chlortoluron damage to wheat, induced by residues of another herbicide which had stunted the root system, were seen in 1987. The symptoms occurred after rapid growth during very warm April weather in a crop grown after peas treated with pendimethalin in the previous spring. The roots in many parts of the field were stunted and swollen from pendimethalin damage so that growth below the chlortoluron layer was restricted and chlortoluron uptake consequently enhanced.

DINITROANILINE HERBICIDES APPLIED TO WINTER CEREALS

This group includes pendimethalin applied alone, and trifluralin in mixtures with one or more photosynthesis inhibiting herbicides such as linuron. Because both pendimethalin and trifluralin are very toxic to cereals, their safe use as herbicides in cereal crops depends on efficient separation between herbicide and seed/roots. Normally, this is easy to achieve because both herbicides have a very low solubility and are strongly adsorbed by the soil, provided the drilling is not shallow. Therefore damage usually does not occur. The separation between herbicide and seed can break down however when the seedbed is coarse and heavy rain falls immediately after pre-emergence applications. Unstable soils such as sandy clay loams and silt loams collapse when wet and under these conditions herbicide treated soil can move into spaces within the seedbed close to the seed and stunt growth. The interval between sowing, herbicide application and rainfall can be critical with this type of problem. In 1986, a trifluralin mixture was applied on 19 November to two adjacent fields on the same soil type drilled on 8 and 12 November in cloddy soil conditions. Heavy rain followed on 20 November. The later drilled field was severely damaged but the earlier drilled field was only moderately affected, presumably because some roots had penetrated below the depth to which the herbicide moved.

DIFLUFENICAN DAMAGE TO LATE SOWN WINTER WHEAT

Although not used commercially for very long, experience with diflufenican applied pre- or early post-emergence has generally been very satisfactory. In ADAS experiments on wheat, some transitory damage was seen at one site where the drilling was deep, but yield was not affected. In 1987, severe damage from diflufenican plus isoproturon was seen in a field of January sown winter wheat. The damage symptoms of leaf yellowing and mauve colorations on the leaf sheath indicated injury from diflufenican rather than from isoproturon.

The conditions which gave rise to the damage were; (i) deep sowing to 5-6 cm which, under good growing conditions, would be expected to cause no more than transitory leaf yellowing; (ii) early January drilling and pre-emergence application followed by prolonged very cold weather; (iii) the sandy clay loam soil was capped at the surface. These conditions would have caused very slow emergence so that the shoot would have been in contact with the surface herbicide concentration for very much longer than in more favourable growing conditions. Diflufenican uptake would consequently be much greater than normal.

CONCLUSIONS

The experiences described in the paper illustrate the near impossibility of devising label recommendations for soil acting herbicides which are safe to the crop under all circumstances. With hindsight it would usually be possible to stipulate practices which would have avoided crop damage. However, the infrequency with which the extreme soil and weather conditions occur makes it impractical to take account on the label of all eventualities. It must be accepted that even the safest and best tried herbicides are likely to occasionally cause crop damage.

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SESSION 7B

WEED CONTROL IN VEGETABLES AND FRUIT

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PROBLEMS OF HERBICIDE USE ON FIELD GROWN VEGETABLES UNDER LOW LEVEL PLASTICS

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ABSTRACT

There were about 6000 ha of low level plastics used with outdoor vegetables in 1986/87. This area is large enough to make a significant impact on the market with several crops and influence the economic viability of many growers. The techniques of mulching and film covering have limiting factors, one of the most important being weed control. What is advantageous for a crop is often even better for the weeds. The paper sets out to summarise experimental results to date, to define the problems and suggests guidelines for overcoming some of them. Many problems occur because of the lack of experimental data, due in part to the rapid uptake of the techniques of using low level plastics, which has overtaken experimental studies.

INTRODUCTION

Investigations into mulching and film covers (or crop covers) were commenced by ADAS in 1978. It was not until 1982 that the vegetable industry began to recognise the potential of the techniques and uptake since then has been rapid. The objectives ten years ago were primarily to give a longer cropping season on early frost free sites and better continuity. However more recently other benefits such as improved quality and yield, pest control, better overwintering, improved seedling emergence and a shorter growing season have seen the use of plastics taken up in many growing areas and earliness is not always the main objective. Over the seasons many types of cover and mulch have been trialled but the industry until recently has mainly used clear polythene that may or may not be perforated with slits or holes or is sometimes photodegradable. Nonwoven covers have become more prominent over the past three seasons and now account for about 15% of the area.

Crops

The main crops covered with clear polythene are early potatoes and carrots (approx. 1000 ha of each). Clear polythene mulch (much of it photodegradable) on sweet corn accounts for 350 ha - 400 ha: the use of covers on outdoor lettuce has risen to a similar area with nonwoven materials accounting for 50% of covered lettuce. Other crops with significant areas are courgettes, runner beans, calabrese, celery, and cabbage. Some twelve other, more minor crops are also grown using the techniques ranging from outdoor tomatoes, early swedes, radish and herbs. Covering of outdoor seed beds to improve germination and emergence is also becoming more widespread.

Herbicide use

There has never been any approval or recommendations for the use of any herbicides on any crop when using low level plastics. Even though the soil and crop is covered, often for several months, the industry has regarded the practice of using mulches and covers as part of the outdoor field vegetable situation. This has inevitably led to problems ranging from herbicides having no effect, to affecting the crop and not the weeds. At other times weed control has been enhanced by the use of covers. In many crops the lack of suitable herbicides for whatever reason remains one of the most serious limiting factors in the use of mulches and covers.

ADAS trials

Weed control has been a particular limiting factor in the crops of lettuce, courgettes and runner beans under mulches and covers. There have also been problems of weed in carrots under covers. Over the past three seasons trials on selected crops have been conducted by Experimental Horticultural Stations at Rosewarne, Arthur Rickwood and Efford. In the last year trials have commenced at Luddington on weed control in early summer cauliflower and leeks.

1. Weed control in lettuce under nonwoven film cover. Efford 1986.
The variety Saladin was sown on 28 February into 43 mm peat blocks. The dazomet treatment was applied on 6 March, the trial being planted on 14 April. The post planting herbicides were applied before the cover was laid on 16 April. Cover removal was on 1 June. (See Table 1).

2. Weed control in courgettes. Efford and Rosewarne 1986
Light inhibiting mulches have been compared with herbicides both at Efford and Rosewarne. Similar core treatments and planting techniques were used at both sites. After planting and herbicide application covers were laid the same day because of the danger of frost. (See Table 2).

The trials at Efford EHS also indicated that low rates of dazomet have potential in giving good weed control in lettuce as well as courgettes. Crop was transplanted on 28 April. Dazomet was applied on 11 March at 19 g/m². (See Table 3).

3. Runner beans. Efford 1986
Trials at Efford on runner beans have also compared mulches and herbicides. The variety Enorma was sown in mid-April. Trifluralin was incorporated and the light inhibiting mulch laid prior to sowing, the seed being sown through. Other treatments include pre emergence herbicides applied on the 18 April and clear mulches for warming the soil laid the following day. (See Table 4).

4. Overwintering carrots under film covers. Arthur Rickwood 1985/86
The variety Tancar was drilled on 12 October. The film cover of clear polythene (200 holes/m²) was laid the same day. The cover was removed on 23 April. The harvest date was 31 May. (See Table 5).

Treatments: 1. Predrilling (incorporated into seed bed)
- a. Nil
- b. trifluralin at 0.76 kg/ha as Treflan at 1.5 l/ha.
- c. trifluralin at 1.1 kg/ha a.i. (2.3 l/ha.c.p.)
- d. trifluralin at 2.2 kg/ha a.i. (4.6 l/ha.c.p.).

2. Post drilling (before covering) applied as log-dose strips in 300 l/ha water.
- a. 0.131 to 2.0 kg/ha a.i. linuron as 0.875 to 14 l/ha Linuron 15 (15% e.c.)
- b. 0.137 to 2.0 kg/ha a.i. chlorbromuron as 0.275 to 4.4 kg/ha Maloran (50% wp).
- c. 0.187 to 3.0 kg/ha a.i. fluorochloridone as 0.75 to 12 l/ha Racer (25% e.c.).

The log-dose strips were divided into sectors as follows.

Herbicide	Log dose			
	High	High/Medium	Medium/Low	Low
linuron l/ha	14 to 7	7 to 3.5	3.5 to 1.75	1.75 to 0.875
chlorbromuron kg/ha	4.4 to 2.2	2.2 to 1.1	1.1 to 0.55	0.55 to 0.275
fluorochloridone l/ha	12 to 6	6 to 3	3 to 1.5	1.5 to 0.75

RESULTS

TABLE 1

Iceberg lettuce under nonwoven cover (Growtect)

	Weed assessment	Marketable heads	
	Cover (%)	Cl.I & II (%)	Mean wt(g)
Bare soil			
propyzamide (as Kerb 50W) at 2.8 kg/ha	5.5	63	592
propachlor (as Ramrod flowable) at 4 l/ha	17.5	51	574
propyzamide at 1.4 kg/ha plus propachlor at 4 l/ha	5.8	51	580
dazomet (as Basamid) at 19g/m²	5.8	56	653
control no herbicide	23.7	59	552
SED±			
Nonwoven cover			
propyzamide at 2.8 kg/ha	11.7	75	486
propachlor at 4 l/ha	33.8	68	470
propyzamide at 1.4 kg/ha plus propachlor at 4 l/ha	9.2	72	491
dazomet at 19 g/m²	6.2	93	546
control no herbicide	47.5	59	473
SED ±			20.0

The nonwoven cover advanced the crop by 14 days. Bare soil records were therefore taken 14 days later than the nonwoven material. The weed cover was greater under the crop cover from all treatments. This difference was least apparent on the dazomet plots. Propachlor on its own did not give good weed control, especially under cover. The percentage marketable was greater from the cover compared to bare soil but head weight was less. Dazomet gave a significant increase in head weight from both bare soil and covered plants. Other differences were generally small but the control and propachlor alone gave the smallest heads reflecting the extent of weed competition. Weather conditions were moist and showery when the post planting herbicides were applied giving them every chance to work properly and propyzamide gave a good result.

TABLE 2

Results at Efford and Rosewarne 1986. Early Courgettes

	Weed Assessment 0-9 (0 = no weed)			Marketable yield (t/ha)		
	Black Mulch	Enide + Dacthal*	Control	Black Mulch	Enide + Dacthal*	Control
Efford	1	3	7	22	5	14
Rosewarne	0	3	5	22	20	12

All treatments were covered with perforated polythene 200 x 10mm holes/m²

*diphenamid (as Enide 50W) at 9 kg/ha plus chlorthal-dimethyl (as Dacthal) at 9 kg/ha.

Much of the data between the two stations is remarkably similar, the exception is the yield from the diphenamid plus chlorthal-dimethyl treatment. At Efford considerable damage was caused. The explanation for this is not clear and further studies are required to find out under what circumstances damage occurs.

TABLE 3

Early Courgettes. Weed Control. Efford 1986

	Growth Assessment 2 June (1 = poor 5 = good)	Weed Assessment 28 June (1 = no weed 9 = >60% cover)	Early Yield to 5 July (t/ha) Marketable
no herbicide bare soil	1.0	8	0.46
no herbicide clear mulch	4.0	7	4.25
dazomet with clear mulch	4.8	2	7.76
SED ±	-	-	0.461

Clear mulch without weed control gave a considerably better early yield than bare soil, and the plants in the early stages were able to outgrow the weeds. However the areas treated with dazomet gave the best growth, successful weed control and a high early yield.

TABLE 4

Runner Bean Trial. Efford 1986

Treatments as rates of commercial products	Weed assessment	Vigour (5 = good)	Marketable Yield (t/ha)
	Cover (%)		
Bare soil			
pre emergence			
diphenamid at 12 kg/ha plus chlorthal-dimethyl at 12 kg/ha	3	3.0	21
pendimethalin at 6 l/ha	8	2.3	18
pre sowing			
trifluralin at 1.7 l/ha	19	2.0	18
black polythene alone	3	3.8	26
no herbicide - control	73	1.3	10
Under clear polythene mulch			
pre emergence			
diphenamid at 12 kg/ha plus chlorthal-dimethyl at 12 kg/ha	14	5.0	28
pendimethalin at 6 l/ha	14	2.5	23
pre sowing			
trifluralin at 1.7 l/ha	48	4.0	25
no herbicide - control	90	2.7	22
SED ±		-	-

Weed control from the herbicides was not so effective under clear mulches.

However the high rate of diphenamid + chlorthal-dimethyl was impressive (but expensive), showing no phytotoxicity and giving the best yield. The black polythene also gave a good result. Although giving good weed control pendimethalin reduced crop vigour and yield; in the early stages leaves showed some puckering. Trifluralin on its own did not give a good enough control.

TABLE 5

Overwintering carrots under film cover. Arthur Rickwood EHS 1985/86
Crop yield (t/ha including fanged) on 31 May

trifluralin (l/ha)	Post drilling	high	high/medium	medium/low	low	mean
SED			(±0.91)			(±0.578)
nil	linuron	5.2	6.3	4.3	3.3	4.8
1.6		7.7	5.5	6.6	4.5	6.1
2.3		5.7	6.1	6.7	4.5	5.8
4.6		4.8	4.1	5.1	5.3	4.8
Mean (±0.43)		5.9	5.5	5.7	4.4	
nil	chlorbromuron	4.9	3.8	3.7	3.2	3.9
1.6		6.2	7.9	6.8	5.5	6.6
2.3		7.4	5.7	5.3	4.7	5.8
4.6		4.5	3.2	3.7	5.0	4.1
Mean (±0.43)		5.8	5.2	4.9	4.6	
nil	flucrochloridone	4.9	6.5	5.6	5.4	5.6
1.6		3.9	5.5	4.6	4.9	4.7
2.3		6.7	7.4	6.0	6.1	6.6
4.6		5.2	5.3	6.1	6.1	5.7
Mean (±0.43)		5.2	6.2	5.6	5.7	

SE per plot (24 df) = ±0.72 t/ha or 13.4% of GM

Yields tended to increase with the improved weed control at the high dose rates. The highest rate of fluorochloridone was the only treatment to give any indication of yield reduction due to herbicidal effects on the crop. Trifluralin at 1.6 or 2.3 kg/ha in combination with medium to high rates of linuron, chlorbromuron and fluorochloridone give the best regimes for adequate weed control without severely reducing crop vigour and leading to the highest yields.

DISCUSSION

All the trials at the three Experimental Horticultural Stations have shown that weed control can be successful when using low level plastics. When considering the results the soil types should be taken into account and that in the main there has only been one full year of trials. The first indications are that 1987 results will show a similar pattern.

Environment under mulches and covers

Before many of the problems of herbide use can be tackled a proper understanding of the environment under mulches and covers is required. To be able to monitor this is a problem in itself and it is only recently with modern data logging equipment that it has been possible to begin to ascertain the microclimate that is created. It is not until the industry appreciates the effect covering has, will the full benefits of using low level plastics be realised.

Because of the rise in soil temperature under cover some weeds germinate quicker and earlier in the season eg Solanum nigrum L., this could mean that they will escape normal timings of herbicide application, especially post emergence/planting treatments. By the time removal takes place they may be too big for control by herbicides. There are certain other species that grow particularly well under mulches or covers eg. Trifolium sps.

On bed systems when machine laying is used burying the edges of the plastics disturbs the soil and sometimes negates the herbicide application. If the plastic is to be in place for a long time applying a band of herbicide down the wheelings and over the edges may be appropriate.

Perforated clear polythene with 200 or 500 holes will always give uneven distribution of rain or irrigation. This can cause problems where herbicides are applied before covering especially if the cover was put on too soon. The chemical can also be prematurely leached if the water always runs to the same spot during a particularly wet spell.

Using clear polythene to advantage

The heat generated under solid clear polythene can be turned to advantage, especially during June and early July when used as a mulch. Crops with wide row spacings etc. sweet corn, runner beans, courgettes, normally have 650-750 mm between rows. The crop is best sown in small grooves, or shallow furrows to the sides of a domed shaped bed. Rainfall or irrigation is directed into these grooves leaving the space in between the row completely dry - especially the top 70-100 mm. The soil between the rows is either too dry for weed to germinate or if annual weed growth does occur a hot spell of weather in June will normally burn the weed off.

Effects of covering

Some of the important criteria have been identified by experience in conjunction with trials. After late March the soil surface becomes dry almost immediately after covering, especially in sunny conditions. Consequently any herbicide applied to the surface immediately prior to covering will also dry out and become inactive. Covering a few days later this can be turned to advantage.

Leaching is prevented under clear polythene or restricted under nonwoven materials. Studies made at Efford EHS and IHR Wellesbourne (H.A. Roberts and W. Bond) showed that herbicide residues were held for longer periods near the surface. The study at Efford EHS in 1985/86 was carried out using metribuzin (as Sencorex WG). 1.1 kg/ha was applied to a prepared seed bed in late October. Four days later seed beds were covered with solid clear polythene. Soil samples (0-50 mm) were analysed on the first week of February and on the sowing date in mid-March for test crops of lettuce, cabbage and onions. Although seedlings began to emerge in early April the phytotoxicity from the residues eventually killed the seedlings. The residues remaining in the surface in early February were equal to 0.2 kg/ha of metribuzin and only marginally lower at the sowing date. In an open ground situation the chemical would have dispersed by late January or earlier.

The ability of clear covers to prevent quick dispersal of the