Herbicide residues in the soil: some aspects of their behaviour and agricultural significance

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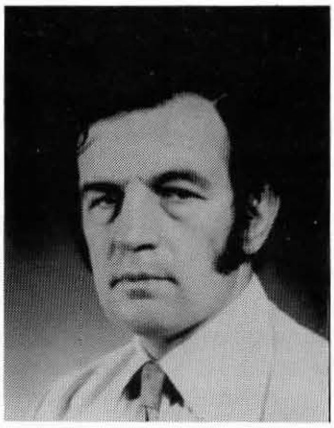

Introduction

A soil-acting herbicide must have a residual life which is adequate to maintain an effective concentration for the period during which weed control is required, but it must not persist sufficiently to pose a hazard to a succeeding crop. This is perhaps an oversimplification, since many would regard a compound which persisted significantly beyond the life of the crop it was applied to protect as being undesirable even if the following crop was tolerant. My use of the word 'significantly' raises the question of how to judge the importance of a residue. For most compounds it is possible to detect, and often measure quite accurately, quantities of a herbicide which are without any biological consequences as far as we are aware. The length of time required to establish with some confidence that there are no effects is, however, uncertain and may require toxicological information which is currently inadequate. This problem is difficult enough when confined to the agricultural context since even the basic criterion of crop yield may be misleading with respect to long-term effects. It is much worse if we consider the total environment because of the number of biological systems that must be taken into account.

In practice, therefore, there are some differences of emphasis in the evaluation of the significance of the persistence of residues between the agricultural and environmental view points. The farmer needs precise information, preferably on a field by field basis, whereas those concerned with the assessment of environmental impact can only hope to achieve a general impression. In both cases, however, the strategy is similar in that information is needed both to provide an understanding of the processes involved so as to be able to predict (and possibly manipulate) the behaviour of a pesticide and to interpret residue data.

Prediction of residue levels

No matter how detailed is the available information, accurate prediction in the field is impossible because of the variability that occurs from point to point. This arises both from variability in the initial application and variations in the ability of the soil to degrade the herbicide (Walker, 1980). Coefficients of variation of residues measured in samples from replicate plots commonly can be as high as 80%. Few would argue with the estimate of Taylor *et al.* (1971) that it is not practical to reduce this figure below 20% even by combining individual cores into bulk samples (Figure 1). It is against this background that we must judge efforts to predict persistence.

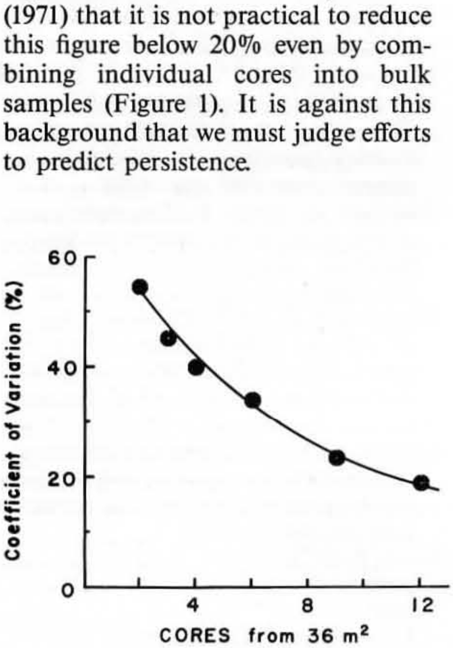

Figure 1 Predicted changes in the coefficient of variation of dieldrin content of bulk samples containing differing numbers of individual cores drawn from a 36 m^2 sampling area (Taylor *et al.*, 1971).

One approach to prediction is to fit regression equations to residue measurements obtained from many sites. Whilst this may be useful in specific circumstances, a large body of data is required and such a purely statistical approach does not contribute to an understanding of the processes involved. Thus we must look for procedures with some theoretical justification if we hope to make progress.

Briggs (1976) has devised perhaps the simplest scheme. He treats the soil almost as a chemical reagent in that he assumes that it is indifferent to the presence of a chemical so that the degradability of that chemical is a function of its own structure. Thus he excludes from consideration those compounds which induce adaptive changes in the soil microbiota. Given these simplifications, pesticide loss would be controlled by the availability of a chemical for degradative processes (A) and its inherent degradability (D). The next assumption is that breakdown only occurs in the soil water phase so that A is a function of the extent to which the molecule is adsorbed by the soil colloids. An assessment of adsorption of a molecule can be made from its octanol–water partition coefficient, its water solubility (Kenaga and Goring, 1980; Briggs, 1981) or from its parachor (Hance, 1969; Briggs, 1981). Numerical values for A are obtained by placing the chemical into one of 15 classes from a calculation of the proportion that would be in solution in contact with a model soil at a standard water content (Class 1 = low adsorption, 15 = high adsorption). Degradability is quantified by classifying functional groups on a 1 to 10 scale with the easily metabolisable groups given low numbers. This assumes that each functional group has a characteristic stability in any given molecular environment and that the most labile group in a polyfunctional molecule will be transformed most readily. The product $A \times D$ gives the measure of persistence. Some typical values are given in Table 1.

This method clearly cannot be useful on the farm scale but as a method for roughly classifying new compounds it has great potential, particularly as no further experimental work is needed, and, used in conjunction with toxicological information, it should also

Table 1 Predicted and observed persistence of some pesticides (Briggs, 1976)

Pesticide group		$A \times D$		$A \times D$
Non-persistent	allyl alcohol	2	dichloran	15
DT_{50}[1]2 weeks	captan	10	dimethoate	9
	chloropicrin	4	DNOC	9
	2,4-D	4	methyl bromide	9
	DD	12		
Slightly persistent	aldicarb	15	methyl parathion	15
DT_{50} 2 to 6 weeks	amitrole	10	nitrapyrin	24
	chloramben	14	parathion	21
	chlorpropham	15	sesone	12
	diazinon	36	swep	15
	dicamba	12	thionazin	24
Moderately persistent	atrazine	36	fonofos	32
DT_{50} 6 to 26 weeks	bromacil	24	ipazine	36
	carbaryl	25	linuron	42
	carbofuran	25	picloram	30
	dichlobenil	36	simazine	36
	diphenamid	35	TBA	20
	diuron	35	terbacil	32
	EPTC	25	trifluralin	27
	fenuron	28		
Persistent	DDT	66	methoxychlor	45
$DT_{50} >$ 26 weeks	chlordane	50	toxaphene	50

[1] DT_{50} = time to 50% disappearance

allow the identification of materials likely to provide environmental hazards.

Although the Briggs procedure is useful, it is in no sense ideal since it deliberately ignores many processes that are known to be involved. In particular the treatment of soil as a chemical reagent rather than as something akin to a biological tissue, although pragmatic, is not intellectually satisfying. Soulas (1982) has gone to the other extreme and attempted to derive a model which takes account of just about all the known factors. He divides the system into a liquid phase, which contains the soluble substrates and all the biomass, and a solid phase which contains constituents that can adsorb solutes. He assumes adsorption follows a linear isotherm and is totally reversible and instantaneous so that he ignores the possibility of hysteresis and the kinetics of sorption. Thus far the model is essentially the same as that of Briggs but here the similarity ends. First, in order to assess available energy sources for micro-organisms, a term is introduced to express mineralizable carbon in the soil as a function of total carbon and soil water content assuming that carbon solubilization is a first-order reaction. Then he considers the behaviour of soil microbial populations which he divides into two groups. The first contains organisms capable of degrading the pesticide, and is subdivided on the basis of whether the process is metabolic, that is the organisms derive energy from the process, or co-metabolic, where no energy is recovered. He acknowledges that this division is arbitrary as metabolic and co-metabolic processes are probably the extremes of a continuum but he introduces this simplification to make the mathematics easier. The other group contains organisms which do not degrade the pesticide and these are divided into those to which the pesticide is toxic and those which are tolerant. The overall scheme is described diagramatically in Figure 2. Mathematical models can then be developed from relations developed from studies of microbial growth and activity in batch or continuous cultures. This is possible because of his assumption that microbial activity is confined to the soil water phase, together with the additional assumption that the only available substrates are the pesticides and the mineralizable carbon fraction.

At the moment, there is insufficient experimental data available to test the validity of this model. Simulated calculations, however, do give disappearance curves whose shape conforms with observation. Figure 3 shows a simulation of the breakdown of a compound such as 2,4-D which induces adaptation by soil micro-organisms and a lag-phase is clearly present. Figure 4 shows a curve calculated on the basis of the soil population values existing at day 200 in Figure 3. In this case the adaptation stage is complete and the result is no lag-phase and a high rate of pesticide degradation.

This model provides an interesting basis for further research. Complicated though it is, it contains simplifying assumptions about the kinetics of the various physical and enzymatic processes involved and also introduces the very difficult experimental problem of how to distinguish and measure organisms which degrade pesticides by metabolic and co-metabolic activity.

Frehse and Anderson (1982) have proposed a similar if simpler method. They consider degradation is controlled by

a) the availability of the pesticide,
b) the quantity of organisms capable of degrading the pesticide, and
c) the activity of these organisms,

and that the driving forces are temperature, soil moisture, nutrient availability and the presence of other xenobiotic chemicals. Pesticide availability they assume to be a function of its concentration in soil water and the quantity and activity of micro-organisms they estimate from biomass and respiration measurements. Thus it should be easier to test this concept experimentally than that of Soulas.

These models, however, must still be considered as research tools and, like that of Briggs, cannot be used to help the farmer. For this purpose, the best procedure we have at the moment is that first proposed by Walker (1973) and subsequently refined, most recently by Walker and Barnes (1981). It is a semi-empirical simulation model which uses information obtained under controlled conditions in the laboratory to predict what will happen in the field. There are three basic assumptions: that degradation can be described by the first-order rate equation

$$dC/dt = kC$$

where C is pesticide concentration and k is the rate constant; that the rate varies with temperature according to the Arrhenius equation

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

where k_1 and k_2 are the rate constants at the absolute temperature T_1 and T_2; R is the gas constant and E is the energy of activation of the reaction; that the rate varies with soil moisture according to the empirical relation

$$\frac{ln^{2}}{k} = AM^{-B}$$

where M is soil moisture content and A and B are constants. Values of E, A and B are determined in laboratory

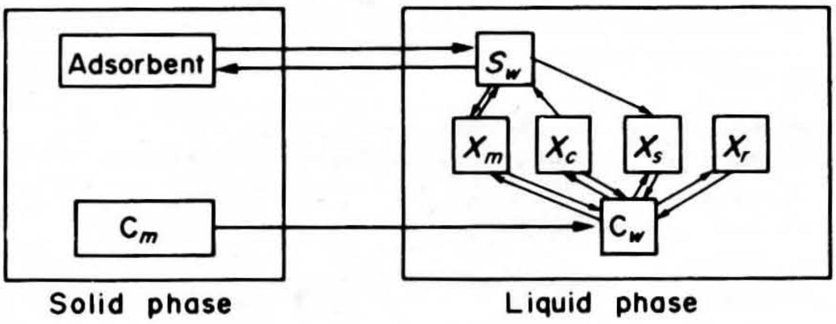

Figure 2 Flow diagram of exchanges taking place in the soil (Soulas, 1982). C_m mineralizable carbon; C_w carbon in solution; S_w pesticide in solution; X_m metabolizing micro-organisms; X_c co-metabolizing micro-organisms; X_s sensitive micro-organisms; X_r non-sensitive micro-organisms.

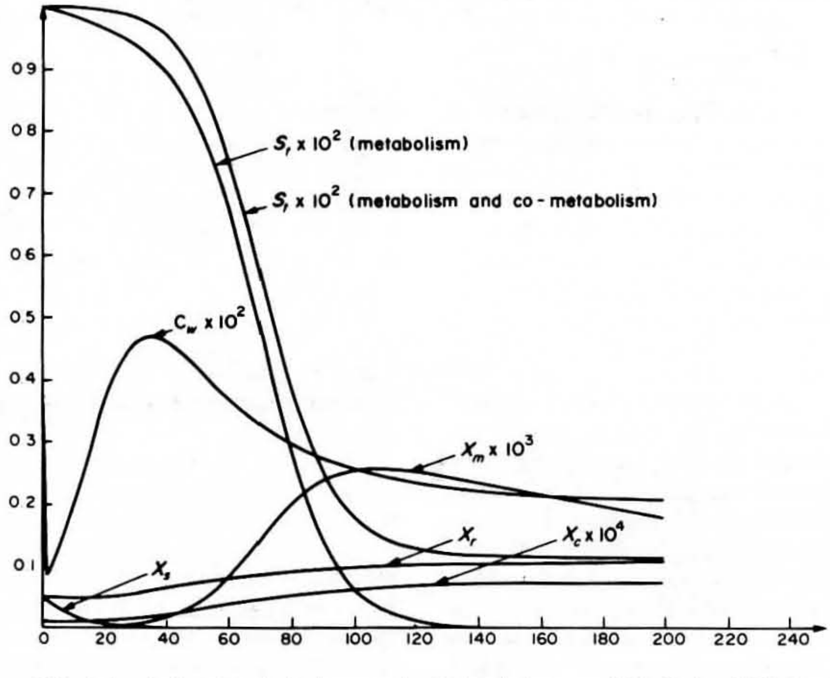

Figure 3 Simulation of adaptation of soil micro-organisms to break down a pesticide (Soulas, 1982). Meaning of letters as for Figure 2; S_t pesticide concentration in entire soil (solid + liquid phases).

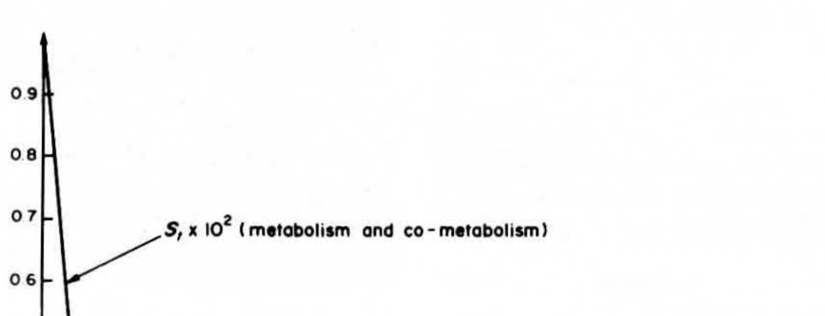

Figure 4 Simulation of pesticide breakdown by an adapted microbial population (Soulas, 1982). Meaning of letters as for Figure 2 and Figure 3.

studies in which decomposition rates are measured at different temperatures and soil moisture contents. These values are combined with soil conditions in the field, calculated empirically from meteorological data, to predict field persistence. In general the concordance between observed and predicted values is good. Figure 5 shows a typical example. Usually the model overestimates the field residue to some extent but rarely is the error large in relation to the point-to-point variability of residues mentioned earlier.

Its great disadvantage is that a substantial amount of laboratory work is required for each combination of herbicide and soil. This difficulty might be overcome if sufficient data could be generated from a range of soil and climatic conditions to enable regression equations to be derived to relate soil type with degradation characteristics. A step in this direction has been taken by the Herbicide–Soil Working Group of the European Weed Research Society, who have organized a world-wide programme in which 18 collaborators provided field and laboratory data from 27 sites using simazine as the test compound. The results (Walker *et al.*, in press) confirmed that the predictions are usually reasonable but a little high (Figure 6), and that it is valid to assume that the effect of temperature can be described by the Arrhenius relationship (Table 2) since activation energies were similar.

Breakdown rates in the laboratory were correlated negatively with the clay content of the soil but the inclusion of other soil properties in the regression gave no significant improvement. However, the relationships between breakdown rates and soil water content did not behave as expected, as in some soils water content had virtually no effect at all as shown by the lowest value of *B* in Table 2. This may be because the relatively low solubility of simazine ($\sim 5\ \mu g\ L^{-1}$) means that in soils of low water holding capacity there could be insufficient water to dissolve all the simazine so not all of the herbicide was available for degradation. Work is planned with a wider range of compounds to resolve this point.

The assumption that first order kinetics apply was confirmed in the sense that the laboratory data fitted the rate equation statistically (98% or better correlation), but close examination suggested that a higher order of reaction would have been more appropriate. This is perhaps the place to digress in order to consider the question of the kinetics of degradation processes in the soil since it is of some heoretical and experimental significance.

Kinetics of degradation

It has been known for many years that some compounds including 2,4-D, MCPA, chlorpropham, endothal, TCA, 2,2-DPA and chloridazon can induce adaptive changes in the soil microbial population so that after an initial 'lag-phase' when little breakdown occurs they are then decomposed rapidly (Torstensson, 1980). There is recent evidence (Obrigawitch *et al.*, 1982) that EPTC also comes into this category, and Kaufman and Edwards (1982) have reported that in some regions of the U.S.A. soil organisms have become adapted to degrade carbamates, thiocarbamates, acylanilides and acetamides so efficiently that these compounds can scarcely be used effectively. There must be some concern that this phenomenon could become more common in areas where pesticide use is intensive. However, at the moment in many situations soil organisms have not undergone adaptation so there is no measurable lag-phase and the degradation rate is roughly proportional to concentration, that is it follows first-order kinetics. As Burschel and Freed (1959) observed, the quantity of herbicide in the soil is very small compared with most of the other components so we might expect herbicide concentration to be rate limiting. Arguably this is an oversimplification since the soil is not a simple homogeneous fluid medium. In particular if we regard soil as a biological tissue the Michaelis–Menten rate law of enzyme kinetics might be more appropriate. This can be written

$$(C_o - C)/t = V_m - K_m \, ln(C_o/C)/t$$

where C_o and C are initial and final concentrations, V_m is the maximum velocity and K_m is the Michaelis constant. At high concentrations this law approaches zero-order (rate is independent of concentration) and at low concentration first-order. Meikle *et al.* (1973) found that the decomposition of picloram could be reasonably described in this way. However, Hance and McKone (1971) found that the degradation of atrazine, linuron and picloram in the laboratory did not conform well either to this equation or to the zero, half-order and first-order equations (Table 3).

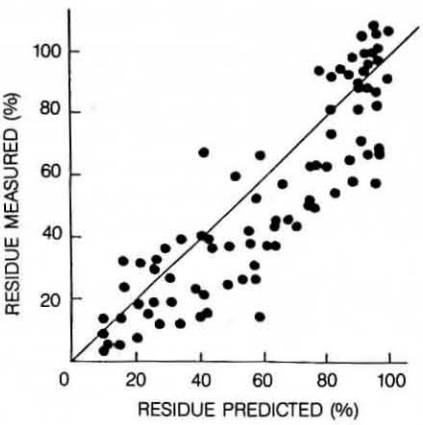

Figure 6 Comparison between observed and predicted simazine residues in different field experiments (Walker *et al.*, in press).

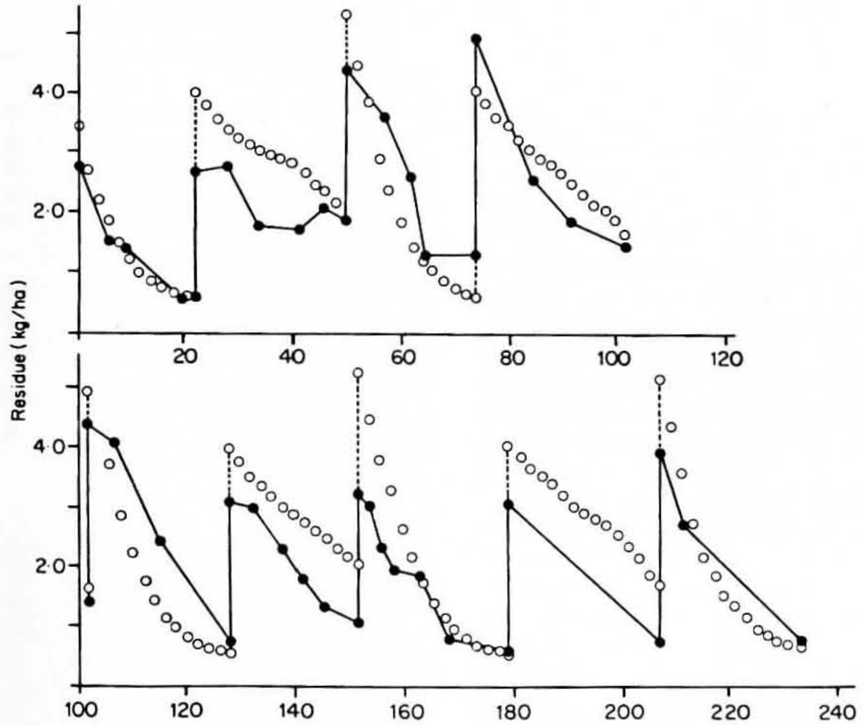

Figure 5 Simulation of simazine persistence in long-term experiments. ● observed; ○ simulated (Walker, 1980).

Table 2 Activation energy and moisture dependence of simazine degradation (Walker *et al.*, in press)

Site	Location	Activation energy (kJ mol⁻¹)	Moisture dependence[1]	
			A	*B*
1	Warwick	50.3	330	0.696
2	Saskatchewan	45.0	8171	1.191
3	Florence	55.9	73.4	0.199
4	Uppsala	39.4	280	0.346
5	Braunschweig	58.2	125	0.263
6	Alberta	56.0	2132	0.992
7	Oxford	27.2	1331	1.276
8	Ontario I	50.9	69.8	0.037
9	Ontario II	45.4	69.8	0.040
10	Wageningen	35.0	85.8	0.181
11	Maarn	34.4	291	0.152
12	British Columbia	69.0	123	0.508
13	Harpenden	83.6	379	0.698
14	Taipei	34.5	123.6	0.205
15	Taichung	45.0	83.6	0.131
16	Manila	62.4	–	–

[1] from the relationship $\frac{ln^2}{k} = AM^{-B}$

Hamaker (1972) attempted an empirical curve-fitting approach using the power–rate equation

$$C = [C_o^{(1-n)} + (n-1)kt]^{\frac{1}{(1-n)}}$$

where n is the apparent order of reaction and k the rate constant. In a survey of the literature he noted that many results seemed to conform to apparent orders higher than 1. Kempson-Jones and Hance (1979) also used this equation in studies of the kinetics of linuron and metribuzin decomposition. In 30 out of 40 cases the value of n was greater than 1 and in 8 cases it was more than 4. On the basis of orthodox theories of reaction kinetics reaction orders higher than 3 are unlikely. Therefore their occurrence suggests that they may be the result of an artefact of the experimental system. This was confirmed to some extent in further experiments with linuron and metribuzin which compared breakdown rates in soil incubated in polyethylene bags, in complete soil cores and in a perfusion apparatus (Hance and Haynes, 1981). The apparent order of reaction varied from 0.45 – 2.90 (Table 4) but there was no pattern that could be related either to the compounds or to the incubation methods.

Table 3 Test of the validity of three rate equations for describing the degradation of atrazine, linuron and picloram (Hance and McKone, 1971, recalculated)

Herbicide (soil)	C_o **mg kg^{-1}**	$\frac{C_o - C}{t}$ **(zero-order) Mean^2**	$\frac{(C_o)^{½} - (C)^{½}}{t}$ **(half-order) Mean^2**	$\frac{\log \frac{C_o}{C}}{t}$ **(first-order) Mean^2**
atrazine	20	4.7	0.63	0.15
(silt loam)	5	1.3	0.33	0.17
	1.25	0.32	0.12	0.17
	0.67	0.18	0.13	0.18
		R[1] = 26	R = 4.8	R = 1.2
atrazine	20	3.9	0.51	0.12
(calcareous	5	1.12	0.30	0.14
silt loam)	1.25	0.37	0.19	0.21
	0.67	0.18	0.14	0.19
		R = 22	R = 3.6	R = 1.7
linuron	20	3.8	0.47	0.10
(silt loam)	5	1.3	0.33	0.15
	1.25	0.36	0.19	0.18
	0.67	0.19	0.14	0.18
		R = 20	R = 3.2	R = 1.8
linuron	20	3.7	0.51	0.11
(calcareous	5	1.9	0.54	0.29
silt loam)	1.25	0.59	0.38	0.47
	0.67	0.38	0.32	0.51
		R = 9.7	R = 1.6	R = 4.5
picloram	20	3.7	0.39	0.08
(silt loam)	5	0.78	0.19	0.08
	1.25	0.25	0.12	0.11
	0.67	0.17	0.12	0.15
		R = 22	R = 3.2	R = 1.9
picloram	20	2.23	0.27	0.06
(calcareous	5	0.81	0.20	0.09
silt loam)	1.25	0.24	0.12	0.10
	0.67	0.15	0.11	0.14
		R = 15	R = 2.4	R = 2.3

[1] R = ratio of highest mean value to the lowest mean value

[2] Mean of figures calculated after 1, 2, 3 and 4 months

Table 4 Calculated values of n and k in the expression

$C = [C_o^{(1-n)} + (n-1)kt]^{\frac{1}{(1-n)}}$

correlation coefficients (r) for the regression of $1n\ C$ on t and first-order rate constants (k') (Hance and Haynes, 1981, recalculated)

Incubation method	n		k**(day^{-1}) (× 100)**	
Linuron				
polyethylene bags				
(i) fresh soil	2.90	(0.72)	0.22	(0.14)
(ii) air-dry soil	2.61	(0.76)	0.31	(0.17)
undisturbed cores	1.51	(0.19)	0.22	(0.07)
perfusion	0.45	(0.38)	3.8	(0.90)
Metribuzin				
polyethylene bags				
(i) fresh soil	1.26	(0.60)	4.3	(0.59)
(ii) air-dry soil	1.34	(0.66)	3.2	(0.43)
undisturbed cores	0.51	(0.25)	7.2	(1.3)
perfusion	2.58	(0.66)	0.21	(0.15)

Standard deviations in parenthesis

Apparent reaction orders higher than 1 suggest that diffusion controlled processes may operate, but this cannot be the only factor or there would have been consistency between the incubation methods irrespective of the compound. A slow adsorption or some other process that reduces the availability of the herbicide is another possibility, and Hamaker and Goring (1976) showed that a two compartment model based on this concept could describe the degradation kinetics of a number of soil-applied pesticides.

A further complication is that the biological activity of a soil changes during the course of a laboratory incubation and that its initial activity is greatly affected by the manipulation or storage it has received during the preparative stages. Even the action of taking a subsample for analysis may affect its activity and certainly stirring the soil during the course of an incubation stimulates CO_2 production (Guth, 1980).

The relationships between various measures of the biological activity of soil and the rate of degradation of a herbicide are by no means clear. For example Anderson (1981) found di-allate and tri-allate degradation were related to biomass, but Walker and Brown (1981) reported that although metamitron degradation was broadly correlated with a soil biomass measurement and atrazine degradation was related to soil respiration, propyzamide degradation could be related to neither. A similar type of inconsistency was noted by Hürle and Lang (1981) who found that the addition of 0.1% or 1% glucose to soil increased napropamide degradation but 2% glucose or a yeast extract treatment reduced it, whereas DNOC decomposition was enhanced by each of the four treatments. A final example in this litany of unexpected results is the influence of the rhizosphere. Microbial activity is much higher in this region than in root-free soil yet Seibert *et al.* (1981) with atrazine and maize, and Mudd *et al.* (in press) with isoproturon and wheat found rates of degradation in pot experiments were unaffected by the presence of plants. Seibert *et al.* (1981) also followed atrazine degradation after harvesting the maize plants and found breakdown was accelerated by the presence of *decomposing* roots. Given the confusion of observations it seems that even the complicated model of Soulas discussed earlier is a gross oversimplification. The suggestion of Senior *et al.* (1976) that a community of micro-organisms is more effective at degrading xenobiotics than single species should perhaps be incorporated into the thinking of model builders.

At the moment then we can only predict persistence in the most general terms. The Briggs approach can be used to estimate the broad persistence category that is appropriate for a new compound. The Walker model, because it takes account of the climate, can give an indication of whether we should expect unusually long or short persistence in a particular season and whether it is necessary to take soil samples for analysis. It is currently in use for this purpose in the U.K.

Physical and chemical processes

In passing, it should be noted that I have made no reference to the physical processes of loss, leaching and volatilization nor to chemical and photochemical decomposition. In most situations net water movement during the growing season is upwards rather than downwards because evapotranspiration exceeds precipitation, so leaching can usually be ignored. Volatile compounds are usually formulated so as to minimize evaporative losses or, alternatively, are incorporated into the soil immediately after application. Nonetheless such losses can be substantial and allowance should be made for them when considering compounds with high air–water partition ratios and low adsorption. Unfortunately there is only limited experimental data available (Hance, 1980). Chemical and photochemical degradation are certainly possible and relevant information is required by most pesticide registration authorities but it is difficult to assess their significance in the field. Consequently they tend to be ignored by the modellers, and this may be at least part of the reason that Walker's model so consistently overestimates field residues.

Interpretation of residue data

Whether a residue level is estimated by guesswork based on a model or is measured analytically, problems of interpretation may arise if it falls in the intermediate category between levels that can undoubtedly be ignored and those that will certainly cause crop damage. A good residue extraction method will, by definition, remove all the herbicide present in the soil that is not classified as 'bound' but there is no easy way of knowing how much of the solvent extractable residue is available to plants. At the moment the advisory practice is to classify the risk of damage based on past experience of field observations of damage. Table 5 shows an example of U.K. practice (Eagle, 1978).

Table 5 Approximate minimum herbicide residue levels that can damage winter wheat (Eagle, 1978)

Herbicide	**Soil type**	**Minimum damaging residue (mg kg^{-1})**
atrazine or simazine	sands and very light soils	0.05
	light soils	0.1
	medium soils	0.15
	heavy soils	0.2
metribuzin	mineral soils	0.08
propyzamide	mineral soils	0.1
terbacil	mineral soils	0.1
dichlobenil	mineral soils	0.1
linuron	mineral soils	0.2
lenacil	mineral soils	0.15
trifluralin	mineral soils	0.2

This information may be supplemented by experiments in which crops are sown in plots containing known residue levels, so that they are basically dose-response assessments. Caverly (1978) examined the effect of lenacil, linuron and trifluralin on 16 crops in this way. Some of his observations are presented in Table 6.

Table 6 Minimum residues causing visible symptoms of phytoxicity to various crops (mean of three sites, recalculated from Caverley, 1978)

Crop	**Herbicide residue (mg kg^{-1} in 0 to 15cm)** Lenacil	Linuron	Trifluralin
turnip	0.04	0.25	0.43
lettuce	0.07^{2}	0.28	1.06^{2}
wheat	0.09^{2}	0.24^{2}	0.19
barley	0.10^{1}	0.39^{2}	0.14
oat	0.10^{1}	0.33^{2}	0.11^{2}
rape	0.11	0.24	0.95^{2}
pea	0.13^{2}	0.91	0.82
ryegrass	0.18^{2}	0.49	0.10
onion	0.18^{2}	0.77^{2}	0.66
maize	0.18^{1}	0.41^{1}	0.12
carrot	0.18	0.91	2.45
parsnip	0.18	0.91	2.45
potato	0.21	0.67	0.82
dwarf bean	0.23	0.38	0.82
red beet	0.83	0.49	0.10
linseed	0.94	1.00	1.72

^{1} data from one site only
^{2} data from two sites

Schemes such as these, however, must include some sort of factor to take account of the effect of soil-type on the bioavailability of residues. In order to avoid this issue, Stalder and Pestemer (1980) suggested that the prediction of residue toxicity could be based on the quantity that can be extracted with water. They showed that there was a relationship between water extractable residues and the response of plants growing in the soil for nine herbicides and this seemed to be regardless of the age of the residue. Pestemer *et al.* (1980) then went on to establish in greenhouse water-culture experiments the maximum concentrations of a number of herbicides that could be tolerated by a variety of vegetable crops. Using this information together with levels of water soluble residues they were able to decide which crops could be grown safely. This method has an in-built safety margin since the prediction is based on phytotoxicity in water culture where herbicide activity is likely to be at a maximum. Whether it can be used generally is not yet known and in order to obtain a wide range of experience the European Weed Research Society is in the process of trying to organize a collaborative programme among workers from many countries.

Whilst the use of water extraction, if successful, will overcome uncertainties about the availability of residues, any interpretation must still take account of the effect of climate on the response of plants to herbicides. It is well established that moisture is needed if soil applied herbicides are to be active but temperature, humidity and light also affect plant responses (see for example Muzik, 1976). The magnitude of these effects can easily override soil availability factors. For example, Hance *et al.* (1968) measured the phytotoxicities of lenacil, linuron, prometryne and simazine to turnip and Italian ryegrass in 16 soils in field and greenhouse experiments. Although greenhouse activity was sometimes correlated with adsorption characteristics it was not correlated with activity in field experiments carried out on two occasions (Table 7).

The same point is made in a different way in an experiment in which lenacil

Table 7 Correlation of herbicide activity in field and greenhouse experiments

Factors	Lenacil Turnip	Lenacil Ryegrass	Simazine Turnip	Simazine Ryegrass	Linuron Turnip	Linuron Ryegrass	Prometryne Turnip	Prometryne Ryegrass	Mean coefficient
glasshouse ED_{50} with % adsorption	0.57	0.77[2]	0.61[1]	0.81[2]	0.89[2]	0.50	0.76	0.80[2]	0.71
autumn field ED_{50} with % adsorption	0.80[1]	0.99[2]	0.55	0.66	0.55	0.18	0.88[2]	0.68	0.66
spring field ED_{50} with % adsorption	0.67	0.87[1]	0.37	0.63	0.66	0.57	−0.04	−0.20	0.44
autumn field ED_{50} with glasshouse ED_{50}	0.69[1]	–	0.41	–	0.51	–	0.48	–	0.52
spring field ED_{50} with glasshouse ED_{50}	0.23	–	0.72	–	0.61	–	0.02	–	0.39
autumn field ED_{50} with spring field ED_{50}	0.68	−0.02	0.16	0.78	0.44	−0.37	0.44	0.43	0.32

ED_{50} concentration producing a 50% reduction in fresh weight (greenhouse) or in vigour score (field).
[1] significant at 5% level
[2] significant at 1% level

or linuron were applied to adjacent plots sown with turnip and perennial ryegrass on five different occasions from April to September (Hance, 1982). The selection of results given in Table 8 shows the variety of plant responses that occurred.

Both activity and selectivity varied. The effect of both compounds on turnip ranged from none at all to a reduction to little more than 12% of the control weight. Ryegrass was completely killed on one occasion by linuron and twice by lenacil but reductions of as little as 19% with lenacil and 38% with linuron also occurred at other times. At the April sowing date both compounds were more toxic to turnip than to ryegrass whereas in July the position was reversed.

Thus the prognosis of the likely effect of any particular residue level is fraught with uncertainty.

Residue problems in practice

Having considered some of the theoretical and technical problems associated with persistence and residues, perhaps a few examples of the practical agricultural problems created by residues in Europe is now in order. As Table 9 shows, European arable agriculture is dominated by small grain cereals, mostly wheat and barley with substantial areas of maize grown in France and Italy. However, the minor crops, potatoes, sugar beet and vegetables, although occupying a smaller area are generally of high value and so are of considerable economic significance.

Much of the cereal crop is autumn sown. Figure 7 shows how the trend towards autumn cereals has progressed in the U.K. Autumn drilling is an obvious situation in which damage from persistent herbicide residues might be expected. In the U.K. such damage usually arises from excessive or uneven applications or failure to plough, in combination with a dry period in late summer and autumn which slows dissipation. Propyzamide following application to rape and metribuzin following application to potatoes are two compounds that sometimes give problems in autumn-sown cereals. Rape is sometimes damaged by residues of the substituted ureas used in cereals. Trifluralin damage to cereals following brassica crops is not unknown even though it is a component of at least one proprietary cereal herbicide mixture. Problems arising from residues of atrazine applied to maize are not uncommon, although this is more important in France and Italy as would be expected from the crop areas set out in Table 9. However, it is difficult to identify any particular product as being responsible for an abnormal number of problems.

In the U.K. failure of autumn-sown cereals on such a scale that a rescue crop is sown in the spring is unusual so that problems to spring-sown crops from autumn applied herbicides are uncommon. In continental Europe, however, this seems to be a relatively common occurrence and much work has been done to identify crops that may be sown safely in soil containing residues (van Himme *et al.*, 1981; Jan and Duhaubois, 1981). It is worth mentioning that whatever the residue and crop the risk of damage is always reduced by ploughing. Conversely superficial cultivation may make things worse.

Control of persistence

Unfortunately it does not seem to be practicable deliberately to accelerate decomposition of embarrassing residues by artificial means although, as mentioned earlier, induction of organisms may lead to breakdown which is unintentionally too rapid. It is possible in the laboratory to change degradation rates to some extent by adding nutrients and adjusting the pH (Hürle and Walker, 1980) but the effect of such manipulations is uncertain and not usually very large. In theory, at least, the prospects for increasing persistence are better because of possibilities for formulating materials in such a way that their rate of release into the soil can be controlled. At present only the simplest type of control is found among commercially available herbicides, in the form of granules. The commonest type is made from attapulgite which is made into a paste, then hardened by firing, after which a solution of the active ingredient is absorbed into the granules. A detailed discussion of this and other types of granules is given by Hartley and Graham-Bryce (1980). More elaborate controlled release formulations have been developed for flowing water and for the release of insect pheromones into the air but these are required to operate for a shorter period than a soil-applied

Table 8 Variation of phytotoxicity with sowing date (Hance, 1982)

	Control weight (g plot^{-1})		Dry weight as percentage of control: Lenacil (0.5 kg ha^{-1})		Linuron (0.5 kg ha^{-1})	
Sowing date	Turnip	Ryegrass	Turnip	Ryegrass	Turnip	Ryegrass
27 April	6.57	1.00	12.2	29.3	12.1	61.7
24 May	22.0	0.29	100	0	87.0	62.0
23 June	18.6	0.02	92.0	–	77.0	–
19 July	31.2	1.60	100	0	100	0
5 September	13.3	2.08	86.0	81.0	74.0	61.0

Table 9 Crop areas in Europe 1979 (in 1000 hectares)

	Wheat	Barley	Maize	Potatoes	Sugar beet	Permanent grassland	Vegetables
total	10876	9612	2989	1172	1783	41560(e)	990(e)
F.R. Germany	1610	1982	110	277	389	5155[1]	55[1]
France	4063	2815	2003	275	547	12904	274
Italy	3335	278	870	139	283	5162	398
Netherlands	141	63	<1	166	124	1172	58
Belgium	191	158	5	37	117	684[1]	26[1]
Luxembourg	8	20	–	1	–	71	–
U.K.	1371	2347	<1	203	213	11436	160
Eire	49	324	–	41	35	4712[3]	9[2]
Denmark	110	1624	–	32	77	264	10[1]

(e) estimates

[1] 1978

[2] 1976

[3] 1975

Source: EEC Eurostats – Land Use and Harvested Areas and Production 1980

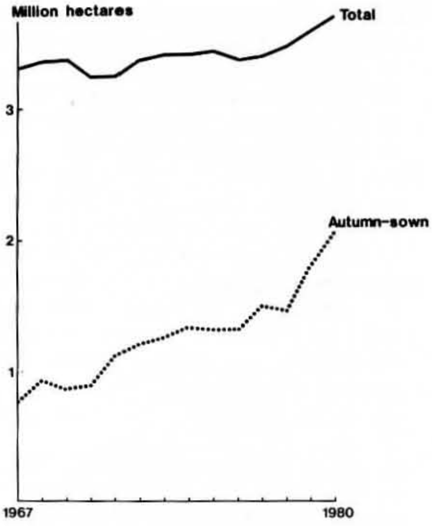

Figure 7 Recent changes in the total and autumn-sown areas of wheat and barley in the U.K.

herbicide. A variety of physical and chemical mechanisms for achieving controlled or delayed release are theoretically possible and many have been demonstrated experimentally (see Hartley and Graham-Bryce, 1980; Cardarelli, 1979; Beynon, 1976) but the chemical industry does not seem to have been able to exploit them as yet. The possibility of including microbial inhibitors, particularly with reference to soils with an enhanced ability to degrade thiocarbamates, is now under active consideration and has in fact been tried commercially in the U.S.A.

Conclusions

The weight given to the various topics touched on in this paper gives an indication of my assessment of their relative importance. The rather short section devoted to field problems will be seen by the cynic as simply a manifestation of bias on the part of someone with a laboratory background. There may be some truth in this, but really in western Europe there are no dramatic large-scale problems caused by herbicide residues which require a solution demanding major research and development. Indeed, recent American experience suggests that in future it is likely that we may have to deal with problems which result from too rapid metabolism of herbicides. There are, however, some years which produce a greater number of cases of damage than others and different crop sequences may carry different risks. These are issues of great importance to the individual farmer or even to quite large regions so thay cannot be ignored. Our future ability to handle such specific situations will rest, at least in part, on our gaining a better understanding of the various mechanisms involved in controlling the persistence of a herbicide, the availability of residues to plants and the response of plants that have taken up residues. Thus by and large soil-acting herbicides work reasonably effectively and safely but there remain sufficient uncertainties that it would be unwise to become complacent just yet.

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