

DEGRADATION IN SOILS

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Summary The persistence of many pesticides in soil can be predicted from the product of Availability and Degradability, two values assigned from arbitrary scales to a given chemical structure. Availability is defined in terms of the fraction of chemical in soil solution and can be found from simple adsorption measurements or from the octanol/water partition coefficient. Degradability of a given chemical depends on the relative rate of degradation of the most labile functional group in the molecule assessed on a 1-10 scale.

INTRODUCTION

Organic chemicals have been used in agriculture on a large scale for the last thirty years. Despite a large research effort, broad statements of principles concerning pesticide behaviour and persistence in soil have been slow to emerge. Recent publications, particularly from workers at Dow Chemicals (Goring and Hamaker 1972; Goring et al 1975), have drawn together results with a wide range of compounds. This paper is an attempt to take their approach further and suggest broad correlations between chemical structure, physical properties and persistence which can be used to predict persistence of new or unstudied chemicals.

Why are pesticides degraded in soils? Because they are there. A trivial answer but one with important philosophical implications. Does the soil respond to the chemical or does the chemical respond to the soil? If specific mechanisms have to be developed for the degradation of each new compound we have little chance of saying anything sensible about the relative degradability of different structures. But, if the soil is largely indifferent to the presence of the chemical and continues about its normal business, then degradation will depend upon the susceptibility of the chemical to enzymes and chemical species already present, and we can look for the reasons for persistence within the chemical itself. This is not to say that the soil cannot respond to the chemical, particularly if large amounts of a simple substrate are present; but in general the amount of pesticide present is very small and it seems reasonable to ignore adaptive phenomena and assume that, although most degradative processes are microbial, they are not specifically directed to the pesticide.

A very simple view of soil is that it is a mineral system coated with organic matter able to adsorb chemicals from the water phase. The water phase is crucial because it functions both as a reaction medium and as a transport medium through which the chemical moves from surface to surface whether these be organic, inorganic or microbial. The reacting species present, which may also act as adsorbing surfaces, are

- 1) transition metal oxides, dissolved oxygen plus metal ions, organic radicals and oxidative enzymes as oxidising agents.

2) organic, inorganic and enzymatic nucleophiles for hydrolysis and displacement reactions.

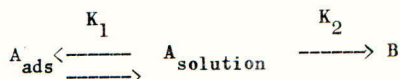
3) chemical and enzymatic reducing systems.

A chemical entering this system will be changed rapidly or slowly depending on how susceptible it is to the various mechanisms present and how available it is to those mechanisms. Highly stable chemicals will persist for appreciable times even if freely available; low availability will confer some stability on otherwise readily degraded chemicals; and the combination of stability with low availability will give a very persistent chemical indeed.

Figure 1 shows the distribution of 65 pesticides between four persistence groups given by Goring et al (1975) and five mobility classes given by Helling et al (1971). Availability in soil is a function of adsorption and thus high mobility is a consequence of high availability. Within this very varied group of pesticides the association of increased persistence with increasing adsorption is clear. Although the chemicals are varied they are far from a random collection: the immobile and highly persistent group are organochlorine insecticides; the large group with intermediate mobility and 6-26 week persistence are mainly pre-emergence herbicides developed because just these properties are desirable for good weed control.

There are many exceptions to the general trend and this reflects the importance of stability, the short-lived chemicals with low mobility containing reactive groups and the more persistent but mobile compounds having no easily-attacked groups.

In the simplest soil model an applied chemical is distributed between the adsorbed phase and the water phase where reaction or redistribution to the reaction site occurs. For a chemical A transformed to a product B we have:



where K_1 is the rate constant for adsorption, K_1^{-1} is the rate constant for desorption and K_2 is the rate constant for conversion of A to B.

Making some simplifying assumptions it can be shown that:

$$T_{\frac{1}{2}} \propto K_p / K_2$$

where K_p is the partition coefficient in favour of the adsorbed phase. The larger K_2 is, the more degradable is the chemical and the shorter is the half-life. As K_p increases then less chemical is available for reaction and half-life increases. ^P

Persistence, of which $T_{\frac{1}{2}}$ is a measure, varies with both soil and external factors such as climate. It cannot therefore be precisely defined. We can never know K_p and K_2 with any great precision in a variable material such as soil but this paper attempts to set ranges of K_p which define Availability (A) and ranges of K_2 which define Degradability (D) on arbitrary scales with the most available compounds and most easily degraded groups having small values and the least available compounds and most stable groups having large values. A measure of persistence can then be obtained from the product A x D and the bigger the product, the greater the persistence.

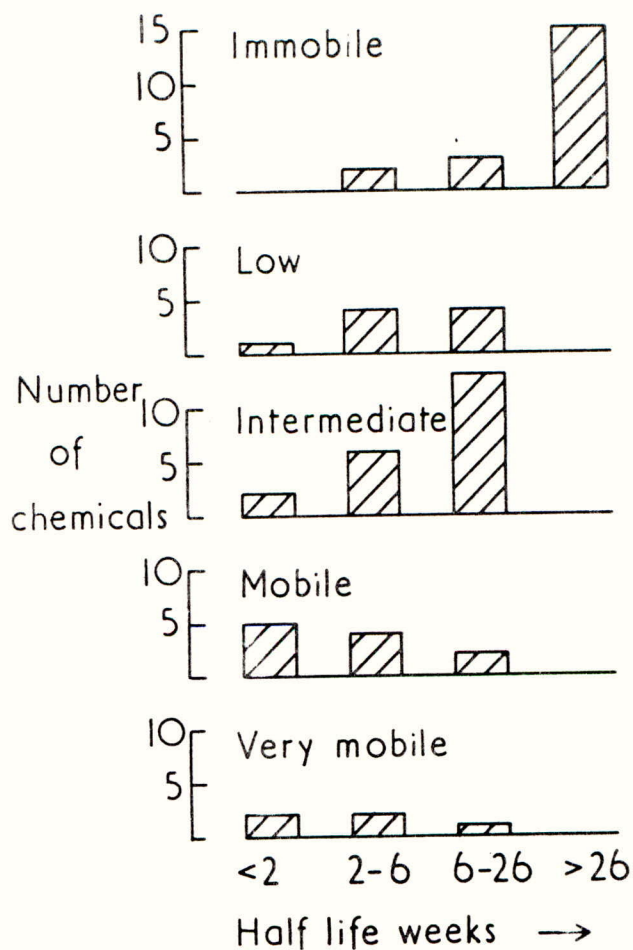


Fig.1. Distribution of 65 pesticides between persistence groups and mobility classes

AVAILABILITY

Can one assess quantitatively for complex molecules adsorption in soils by all the possible mechanisms suggested by Bailey and White (1964) when physical chemists are still arguing about the adsorption of short chain alcohols on pure iron oxides? Obviously not, but for practical purposes we need only concern ourselves with the adsorption onto organic matter of non-ionic compounds and the adsorption of organic cations.

From the soil/water distribution K the soil organic matter/water distribution, Q , is given by

$$Q = 100 K / \% \text{ organic matter}$$

and this is fairly constant from soil to soil for a given chemical. Q is related to the octanol/water distribution coefficient, P , of the chemical (Briggs 1973a) by:

$$\log Q = 0.52 \log P + 0.62$$

The fraction of chemical in soil solution can thus be assessed from K , P or Q .

Availability is defined in terms of the per cent of chemical in soil solution on a scale from 1 where more than 75% is in solution (high availability) up to 14 where less than 0.01 per cent is in solution (low availability). Table 1 gives the fraction in solution used to define availability and the corresponding values of K , Q and $\log P$ calculated for a soil containing 15 per cent moisture and 2 per cent organic matter.

Table 1. Definition of availability classes for chemicals in a soil containing 2 per cent organic matter and 15 per cent moisture

Chemical in soil solution (per cent)	Availability (A)	K	Q (100K/o.m.)	log P
> 75	1	< 0.05	< 2.5	< -0.42
75-50	2	0.05-0.15	2.5-7.5	-0.42-0.49
50-25	3	0.15-0.45	7.5-22.5	0.49-1.40
25-10	4	0.45-1.35	22.5-67.5	1.40-2.32
10-5	5	1.35-2.85	67.5-142	2.32-2.94
5-2.5	6	2.85-5.85	142-292	2.94-3.55
2.5-1	7	5.85-14.9	292-742	3.55-4.32
1-0.5	8	14.9-29.9	742-1492	4.32-4.91
0.5-0.25	9	29.9-59.9	1492-2992	4.91-5.49
0.25-0.1	10	59.9-150	2992-7500	5.49-6.25
0.1-0.05	11	150-300	7500-15,000	6.25-6.83
0.05-0.025	12	300-600	15,000-30,000	6.83-7.41
0.025-0.01	13	600-1500	30,000-75,000	7.41-8.18
< 0.01	14	> 1500	> 75,000	> 8.18

The influence of increasing organic matter content is shown in Table 2. The fraction of chemical in soil solution falls as organic matter increases and availability falls by two or more classes as organic matter increases from 1 to 10 per cent. Similar decreases in availability can be calculated for decreasing moisture contents. Availability assigned to chemicals in this paper assumes the soil conditions given in Table 1.

Table 2. Effect of organic matter content on chemical in soil solution

Soil organic matter per cent	Per cent chemical in solution at 15% moisture			
	Q = 10	Q = 50	Q = 200	Q = 1000
1	60	23	7	1.4
2	43	13	4	0.7
5	23	6	1.4	0.3
10	13	3	0.7	0.1

The mobility classes defined by Helling and Turner (1968) in terms of R_f on soil thin layer plates and expressed in terms of Q and $\log P$ by Briggs (1973a) cover roughly the same ranges at the freely available end of the scale but compress the highly lipophilic compounds into a single group. Very mobile compounds have availability 1-2, mobile 2-3, intermediate 4, low 5-6 and immobile 7-14.

Ionisation of acids or bases lowers $\log P$ by circa 4 and 3 respectively (Leo et al, 1971). Anions are weakly adsorbed in soil but organic cations are strongly adsorbed in their own right with K circa 100 for monocations (Austin and Briggs, 1976) and 10,000 for di-cations assessed from the adsorption of paraquat by soils (Knight and Tomlinson, 1967). Thus the availability of weak acids and bases in soils is strongly pH dependent.

This assessment of availability is based on results from short term adsorption measurements. It says nothing about desorption but assumes that relative ease of desorption will be the inverse of strength of adsorption and partially accounted for in the availability scale.

DEGRADABILITY

This is much more difficult to define in independent terms than availability and the suggestions made here are only preliminary. The aim was to define degradability of functional groups on a 1-10 scale, with easily metabolised groups (K_2 large) at the bottom of the scale and the stable groups at the top. Each step up the scale represents a 3-5 fold decrease in the reaction rate.

Four simple rules are used to define degradability of the whole molecule.

1. Each functional group in a molecule can be transformed in a characteristic manner.
2. The rate of transformation depends on the molecular environment.
3. The most labile group in a polyfunctional molecule will be transformed most rapidly.
4. Any metabolic step creates a new function group with a unique susceptibility to further change and influence on the rest of the molecule.

For example, parathion has six possible points for metabolism:

Reduction of the nitro group (fast); hydroxylation of the benzene ring (slow); hydrolysis of the aryl ester bond (moderately fast); conversion of $P = S$ to $P = O$ (slow); hydrolysis of the alkyl ester bonds (slow); and oxidation of the ethyl group (slow). The observed products are nitrophenol and aminoparathion (Lichtenstein and Schultz, 1964) but since aminoparathion is itself very labile the major pathway for degradation probably proceeds via this compound. Conversion of the electron-

withdrawing nitro group to the electron-donating amino group will slow hydrolysis but makes the ring more readily hydroxylated and the amino group itself can be attacked. In this case the degradability of the parent depends on the nitro group because it is the most readily transformed part of the molecule. With other substituents the aryl ester bond could define degradability.

The general approach to assessing how degradability varies with molecular environment is discussed below in detail for oxidation of amines and more briefly for a number of other oxidative and hydrolytic transformations.

Oxidative transformations

1. **Amines and phenols.** In biological oxidations the attacking species is electrophilic (Dagley 1975) and electron-withdrawing substituents generally slow oxidative degradation. The oxidation of aromatic amines in soil is a good example. The amino group is oxidised, probably by a free radical pathway, to an anilino radical. At high concentrations these radicals self-condense in a variety of ways to form dimeric and higher polymers in modest yield but at low concentrations they condense only with soil organic matter.

Table 3. Oxidative condensation of chloroanilines to azo benzenes

Chloro Substituent	Sum of Hammett constants ($\Sigma\sigma$)	Azo formation in soil	Azo formation by peroxidase	% in soil after 8 weeks
-	0	degraded	degraded	8
4	0.23	+	+	25
3	0.37	+	+	18
3,4	0.60	+	+	36
2	0.67	+	+	20
3,5	0.74	+	-	42
2,4	0.90	+	?	40
2,3	1.04	+(loss of Cl)	?	
2,5	1.04	-	-	49
2,4,5	1.27	-	-	
2,6	1.34	-	-	30
2,4,6	1.57	-	-	

The chloroanilines have been extensively examined, and Table 3 is an adaptation of work by Bartha *et al* (1968) and Thompson and Corke (1969) with the addition of the Hammett constant, a measure of electron-withdrawal by the chlorine substituents. A fairly clear picture emerges. Soils do rather better than peroxidase in forming azobenzenes but little is formed where the sum of the Hammett constants is greater than 0.9. Degradation in soil can involve ring hydroxylation as well as amino group oxidation and the effect of substituent position on the two pathways will differ. However, with the exception of 2-chloroaniline and 2,6-dichloroaniline, there is fair agreement between ease of azo formation, degradation rate and electron-withdrawal by the chlorine atoms. The high stability of pentachloroaniline is well known.

The half-lives of aniline, monochloroaniline and dichloroaniline are approximately in the ratio 1:4:16 and the general rule adopted for assessing the stability of benzene rings to oxidative attack is that each chlorine or equivalent electron-withdrawing group lowers degradability by at least one class.

There are many pesticides, such as picloram, asulam, chloramben, dichloran, dealkylated triazines and reduction or dealkylation products of the dinitroaniline group of herbicides, which contain amino groups but, like the polychloroanilines,

they all have strongly electron-withdrawing groups in the molecule reflected in their feeble basicity and slow oxidation of the amino group.

Increasing stability to electrophilic attack caused by increasing electron-withdrawal eventually leads to susceptibility to nucleophilic attack as in the ready hydrolysis of 2,4,6-trinitroaniline to picric acid. Such a mechanism may explain the conversion of pentachloroaniline to pentachlorothioanisole and benifen to 2,6-dinitro-4-trifluoromethylphenol (Kaufman, 1974).

The free-radical pathway for amine oxidation is also relevant to phenol oxidation in soils. The condensation of polyphenolic compounds has long been thought of as the route for formation of the stable humic fraction in soils. (Briggs 1973b) showed that p-cresol very rapidly dimerises in soil to form Pummerer's Ketone, the major product from the oxidation of p-cresol enzymatically or by many one-electron oxidants. As with the amines, this step is concentration dependent and radical coupling with soil organic matter is probably the major route for loss. Kazano *et al* (1972) have shown that 1-naphthol in soil is more than 70 per cent incorporated into soil organic matter. Any hydroxylations of aromatic rings are likely to be followed by substantial incorporation into the soil organic fraction. Again electron-withdrawing groups will slow both oxidation and hydroxylation, and pentachlorophenol is a persistent material.

2. S-, O-, and N-alkyl groups. Thioethers are rapidly oxidised to give sulfoxides which are then further oxidised but more slowly to sulphones. The alkyl group, if a short chain, is then stable because of strong electron-withdrawal. Demethylation of dialkyl ethers is rapid, and faster than that of aryl methyl ethers which varies with the electronic properties of substituents on the aromatic ring. Dealkylation of N-alkyl groups is similarly fast for aliphatic compounds but depends on other substituents in aromatic compounds. Thus triazines are dealkylated slowly, the heterocyclic ring being approximately equivalent in electron-withdrawal to a trinitrobenzene ring. The dealkylation of trifluoralin appears exceptional but here two bulky ortho-nitro groups force the N-alkyl groups out of the plane of the ring and this steric inhibition of resonance gives the dialkylamino group more alkyl character and higher basicity.

Oxidative demethylation of N-methyl carbamates and ureas is relatively slow because of the strong electron-withdrawal by the carbonyl group.

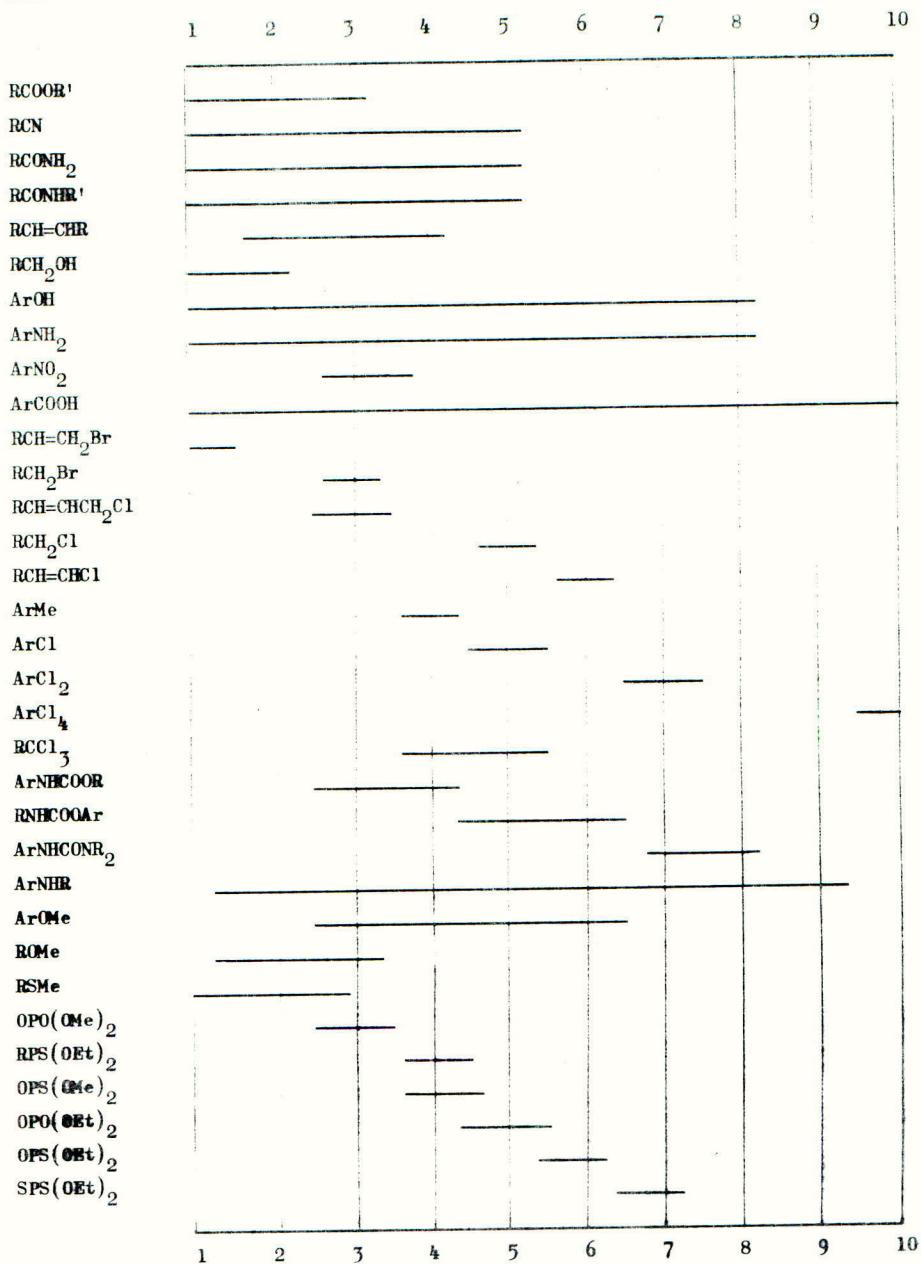
3. Alkenes. Microbial oxidation of alkenes usually proceeds via epoxides subsequently yielding products of ring opening of the epoxides. Epoxidation of aldrin and heptachlor is relatively rapid despite their highly lipophilic character. Again chlorine substitution on or near the double bond is likely to slow epoxidation.

Hydrolysis

1. Halides. Moje (1960) discusses the relative stability of alkyl halides in various environments. Hydrolysis rates are slower for Cl than Br, slower for saturated alkyl halides than for allylic halides and very slow for vinyl halides. Halogens on aromatic rings are very stable to hydrolysis as are the chlorotriazines.

2. Esters. Hydrolysis of simple, unhindered esters of phenoxyalkanoic acids (Smith 1976) or ioxynil (Collins 1973) is very rapid in soils. Chain branching in the acid decreases hydrolysis rates for phenoxyacetic acids (Smith 1976) and highly hindered esters such as chlorobenzilate have half-lives of several weeks in soil (Wheeler *et al* 1973). This probably explains the moderate soil persistence of benzoylprop ethyl (Beynon *et al* 1974) and the pyrethroid insecticide permethrin which is sufficiently stable to be effective as a seed dressing for the control of wheat bulb fly in winter wheat (Griffiths *et al* 1975). Sulphates and related esters are more stable than carboxylic acid esters.

Figure 2. Degradability of functional groups on a 1-10 scale.



----> Increasing stability in soil

3. Nitriles. Ioxynil and bromoxynil are readily hydrolysed to the corresponding amides and acids in soil (Collins 1975). Cyanazine has a hindered nitrile group and is hydrolysed less rapidly via the amide to the acid (Beynon *et al* 1972) while dichlobenil with a highly hindered nitrile group is hydrolysed only slowly to 2,6-dichlorobenzamide which is quite stable (Beynon and Wright 1972).

4. Anilides, carbamates and phosphates. Simple anilides such as propanil are rapidly hydrolysed to the parent anilines. The herbicidal carbamates (N-aryl O-alkyl carbamates) are much less persistent than the insecticide carbamates (N-alkyl O-aryl carbamates) as would be expected from Pullman's dipositive bond theory for enzymatic hydrolysis (Schnaare 1971). For both groups electron-withdrawing groups on the aromatic ring increase the hydrolysis rate.

Similar considerations are true for organophosphorus esters. Dimethyl esters are hydrolysed both chemically, and in soil, much faster than the corresponding diethyl esters, and the thiocompounds are yet more stable. Introduction of a P-C bond increases hydrolysis rates (Adamson and Inch, 1975).

Assignment of Degradability

In assessing degradability it is assumed that the most labile functional group will determine the rate of transformation of the molecule and the major metabolic pathway. Based on known pathways and known rates of chemical or enzymatic transformation, the estimated relative rates of transformation of a number of functional groups are shown in Figure 2.

For groups shown with variable degradability the value assigned in a particular case depends on the effects of the rest of the molecule (steric and electronic) on the transformation concerned as outlined in the earlier discussion.

Thus, if we consider esters, R COOR', unhindered esters are short-lived in soil and have degradability 1. Steric hindrance makes esters more stable to hydrolysis but even highly lipophilic and highly hindered esters only persist for a few weeks and degradability 5 is assigned to highly hindered esters.

For aromatic carboxylic acids, Ar COOH, persistence is highly dependent on the other substituents in the aromatic ring. Benzoic acid is metabolised in soil in a few hours (Briggs 1975b) but TBA (2,3,6-trichlorobenzoic acid) is very stable because of both the steric and electronic effects of the chlorine substituents. Degradability 1 is assigned to benzoic acid and 10 to TBA and values for other acids would depend on the position and electronic effects of the substituents if these substituents themselves are not more readily transformed.

PERSISTENCE

Using the simple model, the product of availability and degradability should give a measure of persistence. In general this holds well and the half lives corresponding to various values of $A \times D$ are:

1 - 15	< 1 week
15 - 25	1 - 4 weeks
25 - 35	4 - 12 weeks
35 - 50	12 - 36 weeks
> 50	> 36 weeks

This is illustrated in Table 4 using persistence data (Bro-Rasmussen *et al* 1970) for some organophosphorus insecticides.

Table 4. Persistence of organophosphorus insecticides in soil.

Compound	Availability	Degradability	A x D	Half-life (weeks)
Dichlofenthion	8	6	48	52
Trichloronate	9	4	36	20
Chlorfenvinphos	7	5	35	18
Bromophos	7	5	21	5
Diazinon	6	6	36	5
Mecarbam	4	5	12	2
Dimethoate	5	5	9	1

There is quite good agreement with prediction with the exception of diazinon which is degraded much faster than expected. The closely related pirimiphos-ethyl is comparable to chlorfenvinphos in persistence (Suett 1975).

A similar exercise with organochlorine insecticides is shown in Table 5 using data from Edwards (1975).

Table 5. Persistence of organochlorine insecticides in soil.

Compound	A	D	A x D	Half-life (weeks)
DDT	11	6	66	150
Dieldrin	10	6	60	150
Lindane	10	5	50	60
Chlordane	10	5	50	50
Heptachlor	11	4	44	40
Heptachlor epoxide	9	5	45	35
Isobenzan	9	4	36	20
Aldrin	12	5	56	15

In a degradative pathway both degradability and availability change at each step. Dieldrin is less lipophilic than aldrin but the epoxide is remarkably stable possible because of steric effects. For organophosphorus compounds, oxidation of thions (P = S) to oxons (P = O) would lower log P by about 1.8 and increase the hydrolysis rate 10-fold. A diethyl phosphorothionate with log P = 5.5 (A x D = 56) would be oxidised to a diethyl phosphate with log P = 1.7 (A x D = 20), and this would be further metabolised rapidly, even if it were formed, so that detection of significant amounts of the phosphate would be unlikely.

The effect of metabolic changes on aromatic rings can be seen in Figure 5 where the Hammett constant for para-substituents is plotted against the Hansch pi constant. The general trend is for lipophilicity to decrease (CH₃ → CH₂OH → CHO → COOH) with increasing electron-withdrawing power particularly in the sequence SMe → SMe → SO₂Me. The halogens are unique in that they are lipophilic, electron-withdrawing and stable.

Similar changes can be seen for aliphatic compounds. Oxidation of phorate and disulfoton to less lipophilic sulfoxides is rapid followed by a slower oxidation to the sulphones. Further oxidation of the side chains is expected to be slow, as is the hydrolysis of the phosphorothiolothionate ester group. Both sulphones are slowly leached in soil but are highly stable (Suett, 1975). Table 6 summarises prediction and Suett's results. Phorate sulphone is assessed to be more degradable than disulfoton sulphone because the strongly electron-withdrawing sulphone group is one carbon closer to the ester link.

Figure 3. Hammett sigma constants and Hansch pi constants for para-substituted benzene

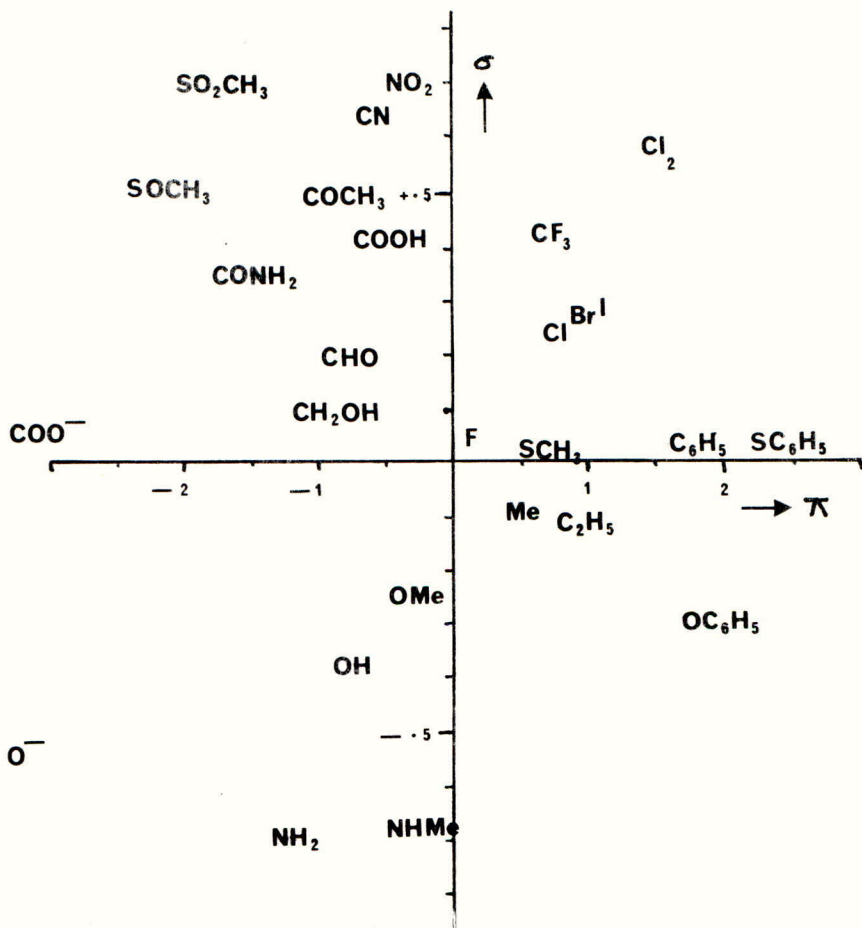


Table 6. Soil persistence of phorate and disulfoton

Compound	A	D	A x D	Half-life (weeks)
Phorate	7	1	7	1
Phorate sulphoxide	5	3	15	1-2
Phorate sulphone	5	6	30	8-12
Disulfoton	8	1	8	1
Disulfoton sulphoxide	6	3	18	2-3
Disulfoton sulphone	6	7	42	> 24

As a final illustration, the persistence predicted by this method for 43 pesticides is compared in Table 7 with the persistence suggested by Goring *et al* (1975). For acids such as TBA, highly stable but freely available because of ionisation, persistence is longer than predicted. Heterocyclic compounds too are generally more stable than the corresponding benenoid derivatives, with the exception again of diazinon. However, considering the assumptions involved, agreement is very good.

Table 7. Predicted and observed persistence of some pesticides

Pesticide group	Pesticide	A x D	Pesticide	A x D
Non-persistent DT ₅₀ < 2 weeks	Allyl alcohol	2	Dichloran	15
	Captan	10	Dimethoate	9
	Chloropicrin	4	DNOC	9
	2,4 D	4	Methyl bromide	9
	DD	12		
Slightly persistent DT ₅₀ 2-6 weeks	Aldicarb	15	Methyl parathion	15
	Amitrole	10	Nitrapyrin	24
	Chloramben	14	Parathion	21
	Chlorpropham	15	Sesone	12
	Diazinon	36	Swep	15
	Dicamba	12	Thionazin	24
Moderately persistent DT ₅₀ 6-26 weeks	Atrazine	36	Fonofos	32
	Bromacil	24	Ipazine	36
	Carbaryl	25	Linuror	42
	Carbofuran	25	Picloram	30
	Dichlobenil	36	Simazine	36
	Diphenamid	35	TBA	20
	Diuron	35	Terbacil	32
	EPTC	25	Trifluralin	27
	Fenuron	28		
Persistent DT ₅₀ > 26 weeks	DDT	66	Methoxychlor	45
	Chlordane	50	Toxaphene	> 50
	Heptachlor	44		

Conclusion

This simple approach ignores quite deliberately all the more complex aspects of pesticide behaviour in soil. From a rigorous point of view the kinetic assumptions are wrong, climate is not mentioned, the approach to adsorption is simplistic and the assessment of degradability is too intuitive for comfort. However, remembering the biochemist's truism 'Don't waste clean thoughts on dirty enzymes' I contend that in the highly variable soil environment generalisations are enlightening and minute detail confusing until placed in a broad context.

The approach outlined in this paper provides a fairly precise estimate of the persistence of most chemicals in soil and refinement should improve it further. Sufficient information is now available for us to say that we know how a chemical with given physical properties and molecular features will behave in soil, and it is ironical that some registration authorities require increasing amounts of environmental information when the real need for this is decreasing.

With the exception of the organochlorines, which are a class apart and should be regarded as such, pesticides properly used have negligible environmental impact.

Table 8. Predicted properties of some environmental pollutants

Compound	log P	A	D	A x D	Half-life (weeks)
Biphenyl	4.0	7	5	21	1-2
4-Cl	4.7	8	3	24	2
4,4'-di Cl	5.4	9	5	45	30
2,4-di-Cl	5.4	9	3	27	4-6
3,5',4,4'-tetra Cl	6.8	11	7	77	200
sym hexa-Cl	8.2	14	9	126	> 300
Sym octa-Cl	9.6	14	10	140	> 300
Terphenyl	5.9	10	3	30	6
2,4",5-tri-Cl	8.0	13	5	65	150
Pentabromotoluene	6.0	10	9	90	> 200
Napthalene	5.4	6	4	24	2
hexa-Cl "	7.6	13	10	130	> 300
DDT	6.6	11	6	66	150

Table 8 gives the properties calculated for a number of environmental pollutants. The predicted relative stabilities of the lower chlorinated biphenyls agree closely with those found by Tucker *et al* (1975) for activated sludge treatment. It is a sobering thought that, in comparison with some of the materials listed, DDT is likely to appear ephemeral.

Acknowledgement

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PERSISTENCE OF PESTICIDES IN PLANTS

R. J. Hemingway

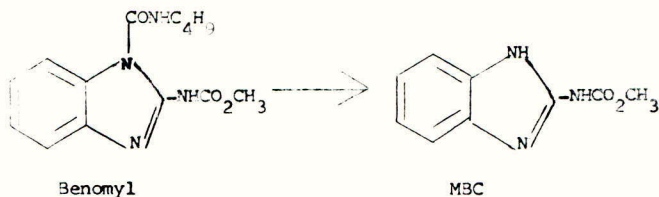
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Summary The various factors affecting the persistence of pesticides on plants are discussed. The importance of volatility, water solubility, chemical stability, formulation and method of application in relation to the biological effect of the pesticide are described. The implications of persistence to environmental and toxicological as well as agricultural effects are considered. It is concluded that a degree of persistence is essential and that it is important to recognise and utilise the persistence of individual pesticides in the most appropriate manner.

INTRODUCTION

In this review of the persistence of pesticides on plants, the implications of persistence to environmental, toxicological and agricultural aspects will be stressed. However before dealing with the implications of persistence, it is necessary to discuss the various factors which affect the persistence of pesticides both on the plant surface and also inside the plant.

It is also important to think about persistence in both chemical and biological terms. For instance, if a pesticide is itself chemically persistent on a plant, its effect will be reasonably long lasting. However, new growth of the plant may well not be protected unless the chemical is translocated to the new growth. Conversely, if a pesticide is not persistent chemically, its biological effect may also be of short duration. However, the effect may be prolonged if a transformation product of the chemical exerts a biological effect in its own right. An obvious example of this is benomyl which is chemically rather unstable. The fungicidal effect of benomyl is however prolonged by its transformation product methyl benzimidazole carbanate (MBC) which has fungicidal properties in its own right (Sims et al., 1969; Kilgore & White, 1970).



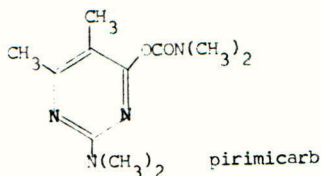
The biological effect may also be prolonged if the transient pesticide is able to break a disease cycle or to prevent the build up of an epidemic. An example of this is the dormant season spray technique which was discovered at Long Ashton and East Malling and is being developed by ICI. This treatment involves spraying apple trees with a suitable detergent to kill overwintering mildew and thus control primary and to some extent secondary mildew occurring much later in the year.

FACTORS WHICH AFFECT THE PERSISTENCE OF A PESTICIDE

1. Volatility

When compounds with a fairly high vapour pressure are applied to plants, a considerable and rapid loss of residue can be effected by volatilisation. The vapour pressure of the aphicide pirimicarb over a range of temperatures is shown in Table I.

Table I Vapour pressure of pirimicarb over a range of temperatures.



Temperature °C	Vapour pressure Torr.
25	15.8 x 10 ⁻⁶
30	30.0 x 10 ⁻⁶
35	44.8 x 10 ⁻⁶
45	170.8 x 10 ⁻⁶
55	550.8 x 10 ⁻⁶

Using 2-¹⁴C-pirimicarb, loss from the leaf surface has been shown to be rapid (Table II) and usually accounts for 50 - 75% of the applied sample (Hemingway and Davis, unpublished). The volatile material has been shown to be pirimicarb itself and not a metabolite (Leahey and Bewick, unpublished).

Table II Loss of 2-¹⁴C-pirimicarb from lettuce in bright sunny conditions

Temperature in open sunlight	Time (hours)	% of radioactivity remaining
30	0	93
40	1	54
36	3	37
39	5	42
32	24	26

Pirimicarb is a very rapidly acting aphicide and its volatile nature can clearly help to shroud plants in a blanket of vapour. In one experiment, the inside of a glass beaker was treated with 2-¹⁴C-pirimicarb and the beaker inverted over a broad bean plant (*Vicia faba*). Aphids on the plant were rapidly killed and an autoradiograph of the plant showed that radioactivity had transferred from the beaker to the plant (Bowker, unpublished).

Loss by volatilisation also helps to ensure that the compound is not persistent and that residues on treated crops are small.

Pirimicarb can thus be used close to harvest to "clean up" crops and yet still not leave chemical residues.

The insecticide pirimiphos-methyl, which has a vapour pressure of approximately 1×10^{-4} torr at 30°C , is another example of a pesticide which is rapidly lost from plants. When applied to the surface of citrus leaves and the plants maintained in the dark at a range of temperatures for 2 hours, pirimiphos-methyl was lost rapidly (Fig 1). Under these conditions photochemical breakdown will not occur. When applied to the leaves of various plants maintained in a greenhouse, loss of radioactivity was rapid (Fig 2). In this case loss of both pirimiphos-methyl and photodegradation products could have occurred (Bowker, unpublished). Clearly with such a rapid loss, the chemical will not have a persistent action and can be used on crops close to harvest as a general insecticide.

% loss after
2 hours

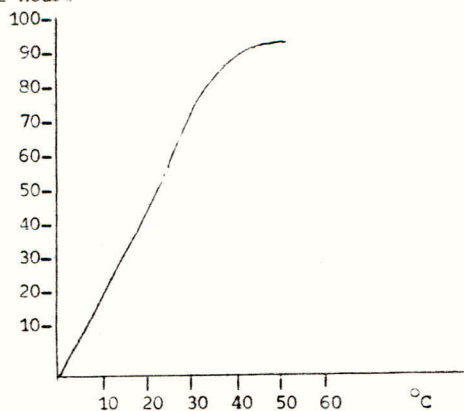


Fig 1. Vapourisation of pirimiphos-methyl (unformulated) from citrus leaves

% Applied radioactivity

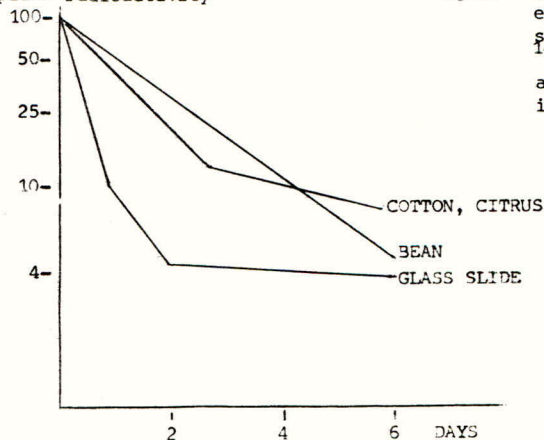


Fig 2. Total ^{14}C in hexane/acetone extracts of leaves and glass slides after application of ^{14}C -pirimiphos-methyl (as an E.C. with 750 ppm active ingredient)

2. Water solubility

Residues on a plant surface are exposed to weathering by natural rainfall and, in some cases, by overhead irrigation. Compounds which are water soluble will clearly be subject to washing off the surface under these conditions with a consequent reduction in residue and possible loss of biological activity. This is illustrated by the results in Table III where a combination of water solubility and physical washing off is involved. It also applies to a range of other water soluble pesticides.

3. Stability

Pesticides in or on plants may be degraded or metabolised by a variety of processes.

3.1 Photochemical degradation

Residues on the surface of a plant will be exposed to solar radiation. The sun has a broad range of energy emissions but the lowest wavelength light is about 290 nm (Luckiesh, 1930). Light in this higher energy region is responsible for the majority of pesticide photochemical breakdown. One example is the degradation of paraquat to N-methyl isonicotinic acid and methylamine hydrochloride. When plants, treated with paraquat, are maintained in the dark, breakdown of the herbicide has not been observed (Slade, 1966).

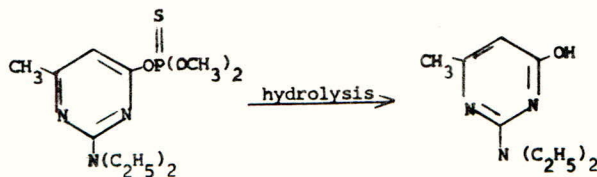


A large number of other pesticides are also degraded photochemically and this is an important way in which residues are reduced.

3.2 Hydrolysis

Many pesticides can be degraded by hydrolysis either on the surface of a plant or inside the plant. These degradations can be chemical or enzymic and are often catalysed by light. Hydrolysis is particularly important in removing the toxic group from a wide range of organophosphorus and carbamate insecticides.

Dramatic differences in rates can often be seen depending on the prevailing conditions. An example, which illustrates this well, is pirimiphos-methyl. In aqueous solution (approx 4 ppm) at 20° in daylight almost quantitative hydrolysis to the corresponding hydroxypyrimidine occurs within 3 days. In the dark, an equivalent solution is hydrolysed to the extent of only about 25% in this time. The same compound, when used as a treatment for stored grain with a moisture content in the region of 12%, is stable for several months (Bowker, unpublished) and can thus provide prolonged insecticidal protection.



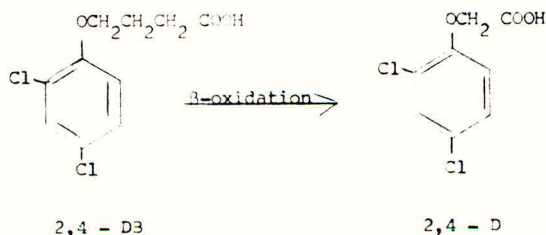
pirimiphos-methyl

Hydrolysis reactions similar to the one given are typical for most organophosphates and carbamates as well as a variety of other pesticides.

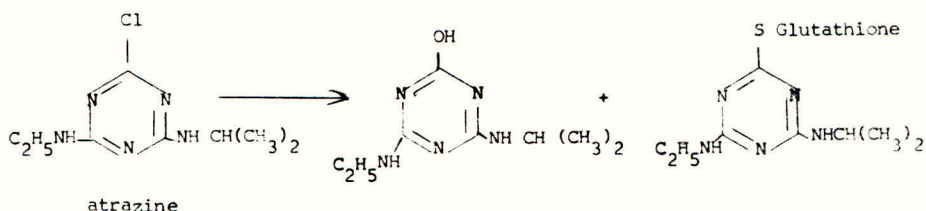
3.3 Metabolism by plants

Many pesticides, when applied to plants, can penetrate into the leaves or, after soil application, can enter the roots and be translocated inside the plant. Once inside the cells of the plant, the compounds can be subject to a wide variety of enzymatic changes.

2,4-dichlorophenoxybutyric acid (2,4-DB) is a classic example of a herbicide where differences in persistence in different plant species is used to obtain a selective herbicidal effect. The herbicide is used to control weeds in lucerne, grass and undersown cereals. In weed species, 2,4-DB is oxidised to the phytotoxic 2,4-dichlorophenoxyacetic acid (2,4-D). In crops, where this β -oxidase system is less well developed, the parent compound is persistent and hence the plants are not subjected to 2,4-D (Wain, 1964).

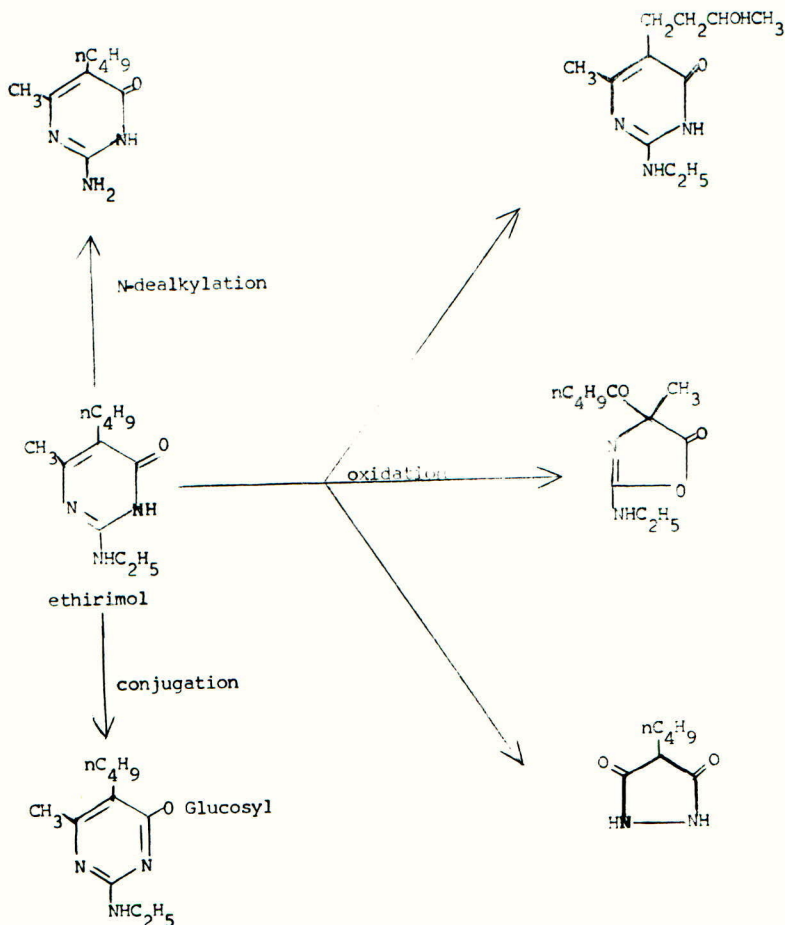


A similar effect is seen with the triazine herbicides. Atrazine is widely used for weed control in maize. The herbicide is detoxified in the crop by formation of the glutathione conjugate and by hydrolysis. Plants in which these reactions are slow are killed by the herbicide (Prear, 1972).



Similar detoxification of herbicides is seen with propanil in rice and bentazon in cereals. In our laboratories in recent years, we have studied the metabolism of ethirimol in cereal crops. In the foliage, the metabolic breakdown is very complex and a variety of novel products are formed (Cavell & Teal, unpublished; and Cavell et al., 1971). This variety of products illustrates both metabolic transformations as well as conjugation by glycoside formation - both ways in which many pesticides are detoxified.

Fig 4. Metabolism of ethirimol in cereal plants.



4. Formulation

By exploiting physical effects, formulation can also play a major role in modifying the persistence of a pesticide.

In general, the better the distribution of pesticide on a surface, the more effective it will be. This is illustrated with some results from a laboratory study evaluating the fungicide dimethirimol against cucumber powdery mildew (Table III).

Table III Differences in persistence of dimethirimol applied to cucumber plants as a dispersible powder (D.P.) and as a col.

Treatment	% active ingredient	% of leaf diseased with powdery mildew			
		Unwashed		Washed	
		9 day	30 day	9 day	30 day
Fine col	0.01	0	1.5	5.0	38.3
	0.04	0	0.9	0.	1.5
Course col	0.01	0	1.8	45.0	95.0
	0.04	0	0.7	3.5	53.3
D.P.	0.01	0	0.5	67.5	100
	0.04	0	0.5	42.5	62.5
Untreated		67.5	100	71.7	98.3

The three formulations are equally active when the leaves are not washed. In fact the D.P. maybe slightly more effective. After washing, the fine col formulation is spectacularly more effective showing that it adheres to the leaves much better than the larger particles.

However the increase in surface area brought about by better distribution may increase various types of breakdown and result in lowered persistence. An example of this is shown by the persistence of malathion applied as an ultra low volume (ULV) and as an emulsifiable concentrate (EC) formulation to cotton plants. The ULV formulation persisted longer than the water diluted EC formulation on leaves and glass slides. Faster evaporation took place from the EC formulation especially at 50° and, in addition, the EC formulation penetrated the leaves more quickly and, once inside the leaf, metabolism to the dicarboxylic acid metabolite was observed. These effects result since the EC spreads as a thin film over the entire leaf surface whereas the ULV formulation is present as discrete micro-droplets (Awad et al., 1967).

This observation is supported by data from the field where it has been shown that the ULV formulation is at least as persistent as and usually more persistent than the EC formulation (see Awad et al., 1967 for references).

Other ways in which formulation can have a dramatic effect on persistence are by encapsulation or the use of delayed release formulations. For example mirex has been used as an encapsulated oil bait for the control of fire ant (Solenopsis saevissima var. richteri). In this way it is more persistent and reliable than a granule formulation (Markin et al., 1975). In a similar way, Bacillus thuringiensis is sprayed in gelatin capsules for control of maize stem borer.

Delayed release preparations of methyl parathion, impregnated into a polyamide resin, are also used for the control of boll weevil on cotton and for weevils on alphas. It is claimed that this formulation persists up to 2½ times longer than the EC formulation.

5. Method of application

A compound of relatively short persistence can be made to have a prolonged biological effect if a continuous supply is made available to the plant. A good example of this is dimethirimol when used for the control of powdery mildew on cucumbers. Although the compound is metabolised rapidly in plants to a complex series of products (Cavell et al., 1971) metabolism in soil is slower. When a continuous supply is available in the form of a root drench, the foliage is protected against powdery mildew for about 6 weeks. A similar effect is observed when ethirimol is used as a seed dressing to control cereal powdery mildew for several weeks.

EFFECTS RESULTING FROM PERSISTENCE

1. Environmental and Toxicological Effects

The major environmental effects of pesticide residues on plants are perhaps best dealt with as toxicological effects, which can be classified as -

- 1.1 Effects on beneficial fauna and wildlife.
- 1.2 Problems of residues on food crops.
- 1.3 Transfer of residues from the diet of animals to meat and animal products.
- 1.4 Effect on agricultural workers.

1.1 Effects on beneficial fauna and wildlife

In general, commercially available pesticides do not cause major serious effects on beneficial fauna and wildlife. Studies are carried out to detect any such harmful effects during development of new products and observation of such an effect would lead to a change in the likely use of the pesticide or would lead to the product being abandoned. For instance, observation of bird deaths during trials of a foliar applied pesticide would require a change in the way in which the pesticide was applied. Also observation of bee kills would necessitate that the pesticide should not be applied when bees are foraging.

These however are major effects and more subtle effects may only be seen after the pesticide has been in use for some time. For instance, the wide spread use of persistent organochlorine insecticides on apples and cotton has resulted in red spider becoming a serious pest problem. The persistence of the pesticide has allowed a resistant strain of red spider to develop by killing the more susceptible insects for a long period. In addition, the natural predators have also been eliminated as a side effect of the persistent pesticide.

Also with the longer established organochlorine pesticides, which are both persistent and of low polarity, accumulation in body fat and bio-magnification along food chains are well known. Even though this accumulation may not be harmful to animals or man, it is a disturbing phenomenon and one which should be avoided whenever possible.

Effects such as those described above are looked for during the development of a pesticide using various model systems and evaluation is continued during the stages of limited commercial clearance.

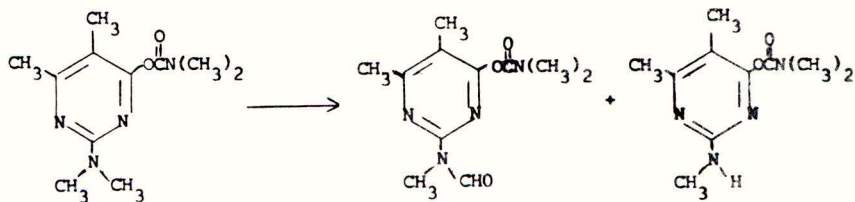
1.2 Problems of residues on food crops

The residues of pesticide on crops destined for human consumption are usually very small and there is little or no evidence that the levels found in practice pose a hazard to health (Abbott *et al.*, 1970; and Duggan and Duggan, 1973). Even with a chemically persistent compound, there is often sufficient reduction in residue levels by weathering or by growth of the crop to ensure that the levels found in practice are low. The amount ingested is usually well below the internationally agreed acceptable daily intake (ADI).

At present, all registration authorities lay stress on the importance of measuring residues on crops produced in controlled trials. Also with the great advances made in the field of analytical chemistry, it is now possible in many cases to detect subnanogram amounts of compound both relatively quickly and accurately. Thus, the measurement of residue levels down to 0.01 ppm is now normal practice.

In addition to residue analysis for the parent pesticide, an extensive metabolism study to follow the fate of the pesticide on a crop is normally carried out. The major metabolites of the pesticide are identified and studied in detail and the structures of minor metabolites are determined so far as present techniques allow. In most cases metabolites representing 5-10% of the parent compound or down to the 0.05 ppm level would be identified. These studies are usually very time consuming and expensive especially if several minor metabolites are present. The studies are carried out with radio-labelled pesticide, usually ^{14}C , and it sometimes becomes difficult to decide when a radiolabelled product is still a metabolite and not radioactivity naturally incorporated into the plant.

Previously residue analysis for the pesticide was discussed. In addition to this however residue determination of major metabolites of toxicological importance are usually made. Thus in the field of organophosphate and carbamate insecticides, analysis of one or more metabolites is common. Pirimicarb is a good example of this. As a result of metabolism studies, the formyl and desmethyl derivatives have been shown to be breakdown products on plants (Manley, unpublished).



pirimicarb

Since these products are carbamates with a toxicity similar to that of pirimicarb, a residue analysis method has been developed and their residues have been measured on a wide range of crops. The residue of the metabolites is normally less than that of the parent compound and is frequently below 0.05 ppm.

Another category of residue exists on plants, namely "bound residue", which cannot be extracted by the normally used solvents (non-polar or polar organic solvents or water). Bound residues are currently of interest and techniques are being looked at for their extraction and identification. Possible extraction solvents are DMSO or aqueous solutions of sodium chlorite, sodium hydroxide or hydrochloric acid. An alternative approach is to demonstrate the biological unavailability of such residues. For example, rice plants treated with propanil were extracted with chloroform and water and the radioactive residue remaining unextracted was fed to rats and dogs. Since most (80 - 90%) of the bound radioactivity was excreted in the faeces, the residue was largely biologically unavailable to the animals (Sutherland, 1975). Residues of this type are of doubtful toxicological significance and should not normally be of great concern.

As a result of the large amount of metabolic information and residue analytical data for the pesticide and its major metabolites, combined with an extensive dossier of information to establish the toxicological properties of the pesticide and its "no effect" level in animals, the safety of pesticide residues can be assessed. Usually the maximum allowable residue is at least 100 times less than the 'no-effect' level and the danger to health from pesticide residues is negligible.

My personal view is that sufficient studies are already carried out on pesticide residues in plants to ensure that they are of little or no toxicological significance. There is no absolute guarantee of safety for a pesticide residue but the likelihood of a residue being hazardous is extremely small. One already accepts a small element of risk by consuming crops which are known to contain toxic natural products, rhubarb, brassicae, tea, coffee etc (Hessayon, 1972).

1.3 Transfer of residues from the diet of animals to meat and animal products

Pesticides are sometimes used to treat crops which are subsequently fed to animals eg grass, cereal crops, lucerne, some brassicae. In some cases, the residue levels are greater than would be allowed for human use and it is important to study the transfer of any residue into the meat, milk or eggs.

With a residue which is chemically persistent on the feed, it is possible to design a meaningful experiment. Several such studies have been carried out with paraquat as a residue on grass (Calderbank et al., 1968, Hemingway et al., 1976, Edwards et al., unpublished). The results show that as little as 0.003% of a dose of paraquat is found in the milk of ruminants (Hemingway et al., 1976). This minute residue is also a mixture of products. In the case of organo-phosphorous compounds, often about 0.2% of the dose is found in the milk. (Dorough, 1971).

However, when a pesticide is degraded rapidly on a crop to a complex series of metabolites, it becomes difficult to design a realistic experiment. It may no longer be meaningful to dose an animal with parent compound and, because of the complexity of metabolites, it may be impractical to prepare a large dose of a metabolite mixture and impossible to analyse the milk and meat for the products of such a dosing. I suspect studies of this type are being considered by interested parties but there is no standardised way to carry out such a study at present.

When a pesticide is applied directly onto an animal to control a skin disease or attack by insects, a different situation applies. Residues can be transferred to the milk or meat by dermal absorption or by the animal licking off the applied pesticide. Usually one is dealing with the parent compound in these situations and meaningful experiments to study the transfers involved are not difficult to design.

1.4 Agricultural workers

An obvious risk to agricultural workers of both persistent and non-persistent chemicals is during spraying. However such risks are covered in the instructions for use of the pesticide. If there is a toxic hazard the use of various degrees of protective clothing is specified, or the product is not recommended for that application.

A less obvious risk is that of re-entry to the treated crop for harvesting or other purposes. This risk is greatest in hot climates where workers are only lightly clothed and where insecticides are frequently used. For example in California, workers are occasionally affected by toxic pesticides. In these cases, a minimum re-entry period for workers into some crops sprayed with insecticides is specified. Techniques are currently being investigated to measure leaf residues on citrus crops so that this problem can be evaluated in more detail (Gunther et al.,1973).

2. Agricultural

Throughout this talk I have introduced examples of the agricultural implications of the persistence or non-persistence of pesticides. I would like to conclude with some more examples. Clearly persistence of a pesticide is in itself neither a desirable or undesirable property. In general, very persistent pesticides such as DDT and dieldrin are currently out of favour. However some degree of persistence is usually necessary and it is important to recognise this and use it to its best advantage.

For example if one has a persistent biological effect one can use this to reduce the number of applications which are made and hence save in chemical and labour costs. An example of this is with some of the newer systemic fungicides which require far fewer sprays during the growing season than the traditional fungicides which they have to some extent replaced. A comparison of the persistence of the effect of bupirimate and dinocap is shown in Table IV (I.C.I. bupirimate technical data sheet; see also Finney et al.,1975).

Table IV Comparison of persistence of bupirimate and dinocap applied to apple to control powdery mildew.

Days after application	<u>% mildew cover on apple leaf.</u>					
	bupirimate EC			dinocap		
	ppm ai			ppm ai		
	20	10	5	20	10	5
1	0	0	0	2	7	21
4	0	2	22	29	33	95
7	0	33	75	68	100	100
10	46	88	91	100	100	100

Similarly a root drench with the systemic fungicide dimethirimol will protect a cucumber crop from powdery mildew more effectively than frequent spray application of other chemicals.

A similar effect is also seen where a chemical can break a disease cycle. I have referred previously to the use of dormant season sprays for apple mildew. Another example is with virus yellows disease on sugar beet. Here it is important to control the spread of aphids while the plants are young. Without this control virus yellows will spread and reduce the yield. However later in the season, spread of aphids is less important. Ideally one therefore requires an aphicide which will control aphids for the first few weeks of the life of the plant.

Persistence is also vitally important in the field of stored products. Benomyl for instance is used to control post harvest rots on oranges and other fruit and the persistence of malathion and pirimiphos-methyl is important to control insects in stored grain.

Persistence however does carry with it a number of hazards. A prolonged biological effect may have an adverse effect on actual predators or on a range of beneficial insects and other fauna. It may also give rise to unacceptably high residues. For these reasons, non-persistent insecticides also have a special place. They are useful to "clean up" crops prior to harvest or for use at critical times. Treatment of pollen beetle in rape, for instance, requires the use of insecticides with low bee toxicity coupled with short persistence eg. mevinphos.

Also, in general, non-persistent products can have a broader spectrum of biological activity without causing a serious harmful effect. If the biological effect is short lived, the danger of building up resistant species and of causing a permanent effect on predators is smaller. Also the danger of upsetting the balance of species is reduced.

In conclusion I hope that I have made it clear that

- (a) The degree of persistence on plants is a property to be recognised and used to good advantage.
- (b) That persistence is not a simple property, ie when the biological effect disappears a variety of chemical residues remain.
- (c) That persistence can often be modified by a changed pattern of use or by a change in formulation.

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