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FACTORS AFFECTING THE CONTROL OF PERSISTENCE

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Summary

This paper describes some of the ways pesticide persistence can be controlled by formulation. Slow release and encapsulation processes are given particular attention and a detailed consideration of the diffusion processes involved is presented. The difficulties of controlling pest/chemical encounter, in both time and space at an appropriate concentration of the chemical, are discussed.

Several examples of formulations with particular mass transfer characteristics are included to indicate the care required when deciding what particular combination of properties will be appropriate to match a particular objective. Thus particle sizes, diffusion constants, concentrations, release times, distribution patterns, and lethal affects to a pest infestation are all considered in combination with the decay of the chemical in the environment.

INTRODUCTION

A great deal of control is exercised during the research, development, manufacture and storage of pesticides. Again, at times subsequent to their action, control is prominent as residues of eventual breakdown products, environmental and social factors are all subject to legislation.

However the detailed control of the chemical between the time of application and the end of pesticidal action is as yet not possible. Quite often in fact the controlling factors are not clearly understood.

Within this period two features relating to the active matter are of particular interest, persistence and its control.

What is persistence? Persistence is often related to the time for which biological response is perceived in the area under study. This is not really satisfactory as a chemical may cease to be effective in an area because it is no longer available to the pest*, although the chemical still exists. Thus persistence will be used here in relation to the period from application to the degradation of the original active molecule to an insignificant level. What an insignificant level is will depend upon the chemical, as well as on the use and placement of the chemical; thus inflexible rules are not recommended. As a guide for calculation purposes however a numerical assignment is convenient and this will be taken as 10^{-6} of the amount applied. Thus if 1 kg ha^{-1} is applied and 1 mg ha^{-1} is left, this is insignificant. This may be disputed as 1 mg is a lot of chemical, if considered in one particular space. However if it remains on one hectare of soil to a depth of say 10 cm then the concentration is less than about 1 part in 10^{12} on a mass basis.

*Pest will be used in the wider sense to cover insects and weeds

Any obscuring of the chemical by say physical processes, such as adsorption on soil, gives rise to a persistent chemical on this definition, as does the removal of the chemical via the atmosphere, if degradation does not occur. In both cases positive pesticidal persistence would have ceased in the area under study (Hartley, 1966).

On this basis the control of persistence is the control of breakdown of the chemical. However, more is required in terms of positive pesticidal action, and persistence control should be related to the area of application and target pests. Thus not only is the control of persistence required if improved performance is to be the result, but also the chemical needs to be matched to the pest infestation and life cycle in space and time, as depicted in Fig. 1. In this the ordinates are arbitrary scales. The control of chemical-pest encounter with precision is as yet unobtainable.

Generally in the current use situation a chemical pesticide is applied in the expectation of encounter with sufficient of the pest to ensure biological control. In this the time sequence of encounter between chemical and pest as well as the dose acquired are, by and large, random. Thus the chemical's route to pursue its objective is at the mercy of the elements and the biomass in general.

From the users viewpoint optimising effectiveness involves such things as convenience and short-term economics; thus an individual may not use the most effective chemical for crop protection as a first priority. Improving effectiveness by controlling persistence under such conditions may not influence the user extensively. Also improved effectiveness is not necessarily a consequence of controlled persistence. Thus material can be encapsulated so that persistence is increased but the activity, within a particular time period is decreased (Phillips, 1974). However if the biological effectiveness of the chemical can be matched with the infestation, as shown in Fig. 1, then the best use is made of controlled persistence. This assumes that a considerable amount of information relating to infestation is available and such is seldom the case. Because of this it can happen that the control of the chemical rather than the control of the pest becomes the objective. Few practical advances have been made in controlling persistence as well as pest-chemical interaction to such an extent that an overall improvement in pest control becomes obvious. While the pest-chemical interaction remains a random event in both time and space experimentation in the insect attractant area encourages the view that a 'seek and destroy' capability is possible. Coupling this with persistence control should greatly increase the effectiveness of pest control agents.

The emphasis in this introduction has been to indicate the necessity for control of a pesticide in both time and space. If this is accepted then the ways of achieving such a match require attention. It will be some time however before sufficient information is available, for example about the infestation profiles, to allow exploitation of this concept. Certainly the environmental conditions, climate particularly, are involved in the timing and placement of some infestations and it is conceivable that the chemical release could be controlled by these same environmental conditions. It must be remembered however that, once released, the chemical is subjected to all of the constraints of a conventional application.

One consequence of success in this area is the need to examine the biological activity resulting from a changed chemical intake pattern by the pest, and the relative merits of different sequences of sub-lethal doses on a variety of time scales require more investigation. This is critical if full use is to be made of the various possible distribution patterns of the chemical.

The relative importance of persistence and placement will, of course, vary with the objective and it is difficult to say which predominates even between, say, soil and foliage applications for insect control. All of this indicates how much information is required if full value is to be obtained from being able to control

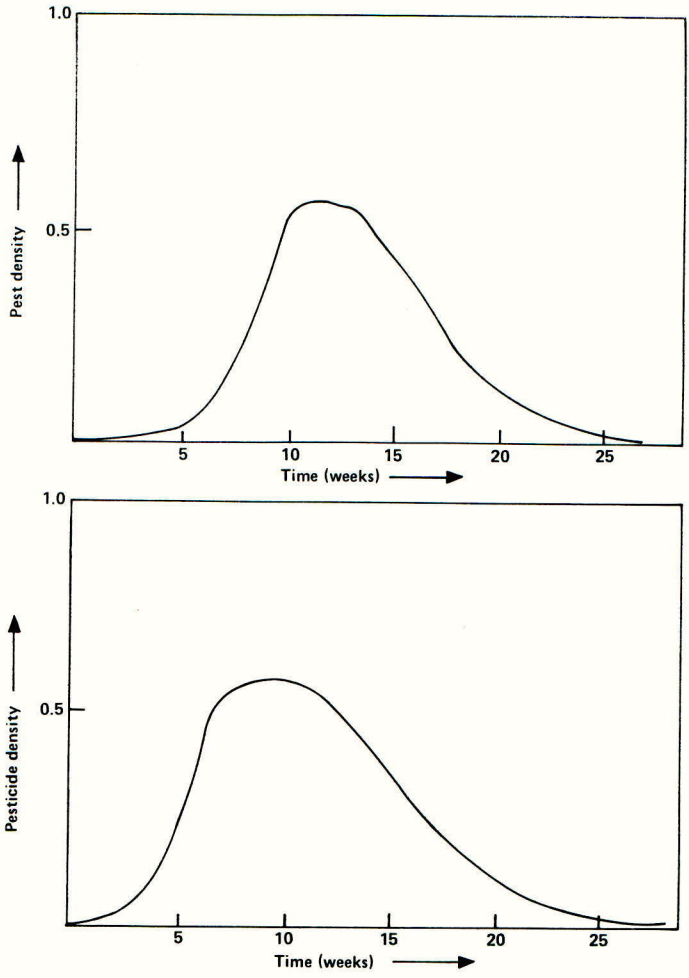

Fig 1 Chemical release, persistence and placement related to infestation

The release should occur into the space where pest-chemical encounter is optimal

persistence.

Some Factors Involved in the Control of Persistence

Having outlined some general views on persistence and control in relation to effectiveness it is necessary to consider those factors which control persistence in relation to pesticidal effectiveness and those factors which control absolute persistence of the chemical.

In recent years a considerable amount of work has been reported concerned with controlled release, as exemplified by the Controlled Release Pesticide Symposium (1974).

The lifetime of the environmentally exposed pesticide is dependent upon the rate of release from a source and the rate of destruction by possibly several mechanisms. Throughout this the transport and energetic characteristics of the system are the controlling features. Some factors which have affected the persistence of chemicals in an uncontrolled way in the past are now being deliberately used, with appropriate mechanisms, to control persistence. Thus hydrolysis, solubility, volatility etc are positively employed. While some of these processes are involved in controlled release mechanisms diffusion remains one of the major factors.

Following release the chemical is exposed to the normal range of physical, chemical and biological losses as depicted in Table 1, and a more formal presentation of this is given in Fig. 2. To obtain the overall picture from such a system would require extensive mathematical modelling, however some features can be examined here with a view to establishing which factors exercise control of the system.

As we are primarily concerned with the control of persistence the time period for activity needs to be defined as well as the time period for the presence of the material. Thus a chemical may be required to be effective for a particular period of say 5 weeks; however, it may be applied 5 weeks prior to this period and for social reasons it may be necessary to have it reduced to a low concentration in say 25 weeks. Such a scheme demands a concentration/time profile of the type shown in Fig. 1.

The major patterns of chemical release, shown in Fig. 3, were discussed by Osgerby (1972). These are related to a lethal dose of pesticide, C_L, and the time for which control is desired, T. In Osgerby's analysis this gives rise to a single point, and the patterns of release are constructed to pass through this point. It is now physically possible to obtain some of these profiles and they may be manipulated to give particular desired characteristics.

The major release mechanisms that can be employed are:

(i) A degradable matrix containing a uniform dispersion of the chemical which gives a continuous release profile. The time scale will depend upon the degradation rate and the chemical may be physically dispersed in the matrix or bound by particular chemical or physical bonds as described by Allan et al (1971).

(ii) A stable 'closed' matrix which has the chemical dispersed within it. The chemical is released by diffusion.

(iii) A stable 'open' matrix which allows material to enter and aid in the extraction of the chemical. Thus leaching by water is a possible mechanism.

(iv) An encapsulation process which relies upon diffusion only for release, or which allows leaching to occur and/or involves degradation of the retaining wall (Vandegaer, 1974).

Table 1

Source Sink Relationship for Persistence

Source	Release Chemical	Primary Loss Processes	Secondary Loss Processes	Pest Interaction
A protected region for the chemical. Diffusion and binding of the first type.	A susceptible region for the chemical. Transport via bulk flow and diffusion of the second type. A secondary source may be set up by binding to an environmental substrate creating a 'buffer region'.	Physical Vapour losses Irreversible binding Water transport (leaching) Chemical Hydrolysis Biological Microbial	Physical Removal on particulate matter. Chemical Oxidation Photolytic Thermal Biological Material removed chemically and physically by biomass without bio-response of the type required.	Encounter and Pick Up Physical interaction, rate of accumulation. Chemical interaction, storage, metabolism and positive action in the pest.

Subsequent to pest control a clean-up additive to ensure destruction of the chemical may be appropriate for a particularly persistent material.

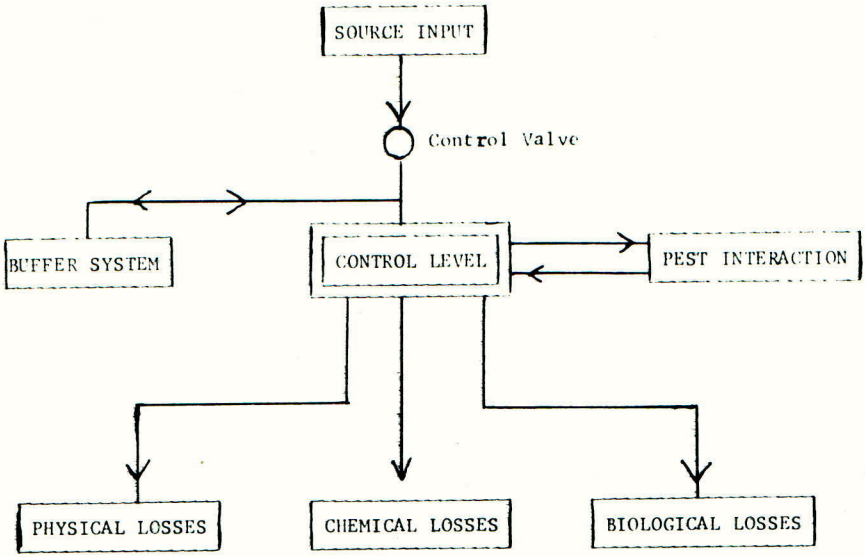

Fig. 2

Pesticide Input and Losses

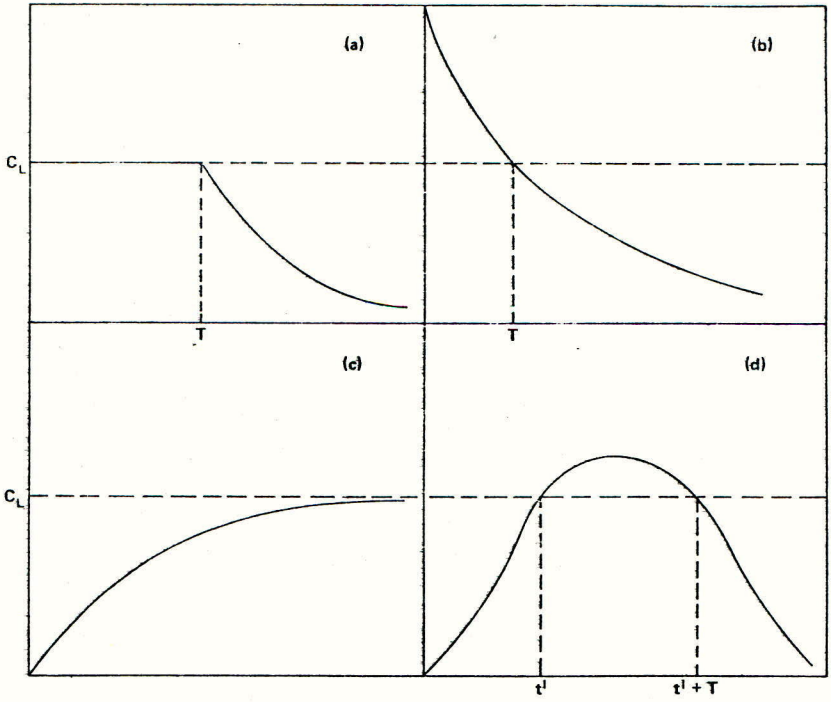

Fig 3 Toxicant release possibilities (Osgerby, 1972)

(v) A layered 'sandwich' system of chemical and support which relies upon diffusion or degradation for release.

In each of these there may be physical or chemical bonding which can further alter the release profile. Also the pattern of dispersion of the chemical in the support will affect the release, and a smooth or a 'pulsed' pattern could be created. Obviously the geometry and loading will be variable while a mixture of several types gives a further range of possible release characteristics (Fanger, 1974).

If this is coupled to the possibilities of different placement in the area to be protected with a range of mechanisms to 'trigger' release then the options are considerable.

These formulations, in original form, may interact with the pest effectively or may be ineffective in themselves but provide persistence control for the chemical. If the latter applies then the released chemical is at the molecular level and the pest will not encounter bulk chemical; thus the intake pattern will be critical. In this the approach becomes similar to pharmacodynamics for which many such chemical patterns have been examined (Ariens, 1968). The modelling of pesticidal behaviour in a similar manner is less well developed, although some models exist, for example that of Bridges and Farrington (1974).

The factors described above together with the loss processes listed in Table 1 determine the persistence pattern. Some of these will be considered in more detail. The problem arises, however, that while many systems have been examined practically for biological effectiveness this has, in the past, seldom been related to the physical chemistry of the system. The frame work for such an examination should emerge from some of the details presented below. These are often taken from well defined systems unrelated to biology and as such are often simplified for convenience.

Recently much better cover has been given to relating the biological activity with physical and chemical processes, as exemplified by the work of Collins et al (1973). Such efforts will add considerably to understanding and thus promote the development of more effective control measures.

Theory

The investigation of release characteristics from the array of options given earlier could involve considerable wasted experimentation. By examining some of the possibilities theoretically the major areas of interest can be highlighted or, at least, the unrewarding areas can be avoided. Consider first the diffusion characteristics in isolation, examining spherical monodispersed systems as a simple case. The mathematics for much of this is available in texts by Barrer (1951), Crank (1975) and Jost (1960).

The equation for radial diffusion in a sphere is given by Ficks second law.

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \qquad \ldots\ldots (1)$$

This implies that the medium through which diffusion occurs is isotropic and no specific interaction occurs between the diffusing molecules and the molecules constituting the diffusion medium. In equation (1) C is the solute (pesticide) concentration at time t and radius r from the source while D is the diffusion constant. Our interest is in solving this for a variety of conditions.

First when the diffusion species is uniformly confined within a sphere of radius a. At zero time ($t = 0$) then the concentration in the sphere ($r < a$) will be C_o and the surrounding medium ($r > a$) will be free of pesticide.

Let C_1 be the concentration of solute in the sphere at time t and C_2 be the concentration of pesticide in the surrounding medium at time t.

In the sphere we have

$$\frac{\partial C_1}{\partial t} = D_1 \left[\frac{\partial^2 C_1}{\partial r^2} + \frac{2}{r} \frac{\partial C_1}{\partial r} \right] \qquad \ldots\ldots (2)$$

and in the surrounding medium the concentration changes with time and distance are given by

$$\frac{\partial C_2}{\partial t} = D_2 \left[\frac{\partial^2 C_2}{\partial r^2} + \frac{2}{r} \frac{\partial C_2}{\partial r} \right] \qquad \ldots\ldots (3)$$

In equations 2 and 3 D_1 and D_2 are the diffusion constants of the pesticide in the sphere and surrounding medium respectively.

Typical boundary conditions are

$$\text{At } t = 0,\ r < a,\ C_1 = C_o$$

$$t = 0,\ r > a,\ C_2 = 0$$

$$t > 0,\ r = a,\ C_1 = KC_2$$

Thus micro-reversibility is maintained at the interface with K as the distribution (or partition) coefficient between the sphere and surroundings and continuity of flow across the interface is maintained without any interfacial resistance.

$$t > 0,\ r = a,\ D_1 \frac{\partial C_1}{\partial r} = D_2 \frac{\partial C_2}{\partial r}$$

Solution of the equation is simplified when the concentration in the surrounding medium can be considered zero at all times. This situation will be approximated if the diffusion constant in the sphere is much less than the diffusion constant in the surrounding medium. For a particle in soil or on foliage, exposed to air, such a situation exists. Thus diffusion in air is high ($D \approx 0.01$ cm^2 s^{-1}) while in soil $D \approx 10^{-7}$ to 10^{-8} cm^2 s^{-1} (Graham-Bryce, 1969; Scott and Phillips, 1972). Also convection will contribute to transport outside the sphere in both cases.

For the usual type of solid medium containing the pesticide the diffusion constant D, will be less than 10^{-10} cm^2 s^{-1}; thus the pesticide will be removed from the outer surface of the sphere at a rate greater than its approach to the inner surface. Such a system can be regarded as approximating to the desired boundary condition.

The pesticide mass which has left the sphere at time t (M_t) is expressed as a fraction of the corresponding quantity at infinite time (M_∞). This quantity (M_∞) is taken as the total amount of pesticide for this simple case. However, it may be some fixed value less than the total pesticide amount, according to the partition coefficient and other boundary conditions.

The ratio $\frac{M_t}{M_\infty}$ is given by Crank as

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha\,)\alpha + 1)\ \exp\ (-Dq_n^{\ 2}\ ta^{-2})}{9 + 9\alpha + q_n^{\ 2}\ \alpha^2} \qquad \ldots\ldots (4)$$

where the q_n's are the non-zero roots of

$$\tan\ q_n = \frac{3q_n}{3 + \alpha q_n^{\ 2}} \qquad \ldots\ldots (5)$$

and $$a = \frac{3V}{4\pi\alpha^3 K} \qquad \ldots\ldots (6)$$

where V is the volume of the immediate surroundings influenced by the chemical, that is, the value assigned to each sphere.

Thus α is the phase volume ratio taking into account the partition coefficient K. The parameter α is expressed in terms of the final fractional loss from the sphere as

$$\frac{3M_\infty}{4\pi a^3 C_o} = \frac{1}{1 + 1/\alpha} \qquad \ldots\ldots (7)$$

Solution to equation (4) can be considered for large values of α, which is the usual case for pesticides, and have been derived by Crank for a range of D, t and a. Thus the curve given in Fig. 4 can be readily employed to examine the release at any particular fractional loss. In this work the 50% release figure is chosen. Thus reading the value of $\left(\frac{Dt}{a^2}\right)^{\frac{1}{2}}$ as 0.18 when $\frac{M_t}{M_\infty} = 0.5$, and giving D and a particular values, allows t to be found for 50% release as shown in Table 2, providing the assumptions remain valid. It should be remembered that this relates to a mono-dispersed system.

This assumes the integrity of the sphere is retained, and no leaching or thermal effects or chemical changes occur.

As many spheres give equivalent release times for 50% depletion the number and size required to optimise upon distribution can be evaluated. Also the original loading of chemical into the spheres can be varied.

If 37 days is a convenient time for 0.5 kg release then materials given in Table 3 would be appropriate. Alternatively, mixtures could be used which would give the same time to release 50% but a different overall pattern.

Equation (4) can be closely approximated by the empirical equation (8) (Crooks, J.E. and Pedley, J.B. private communication).

$$\frac{M_t}{M_\infty} = 1 - \exp\left[-3.97\ \left(1 + \frac{0.7}{\alpha}\right)\left(\frac{Dt}{a^2}\right)^{\frac{1}{2}}\right] \qquad \ldots\ldots (8)$$

Before considering the details of this it is worth clarifying the condition at the sphere's outer wall. Say the concentration, 1×10^{-4} cm within the wall, is 1 mole l^{-1} at a particular instant. If this is considered as a steady state

Flux out of sphere = Flux away from sphere

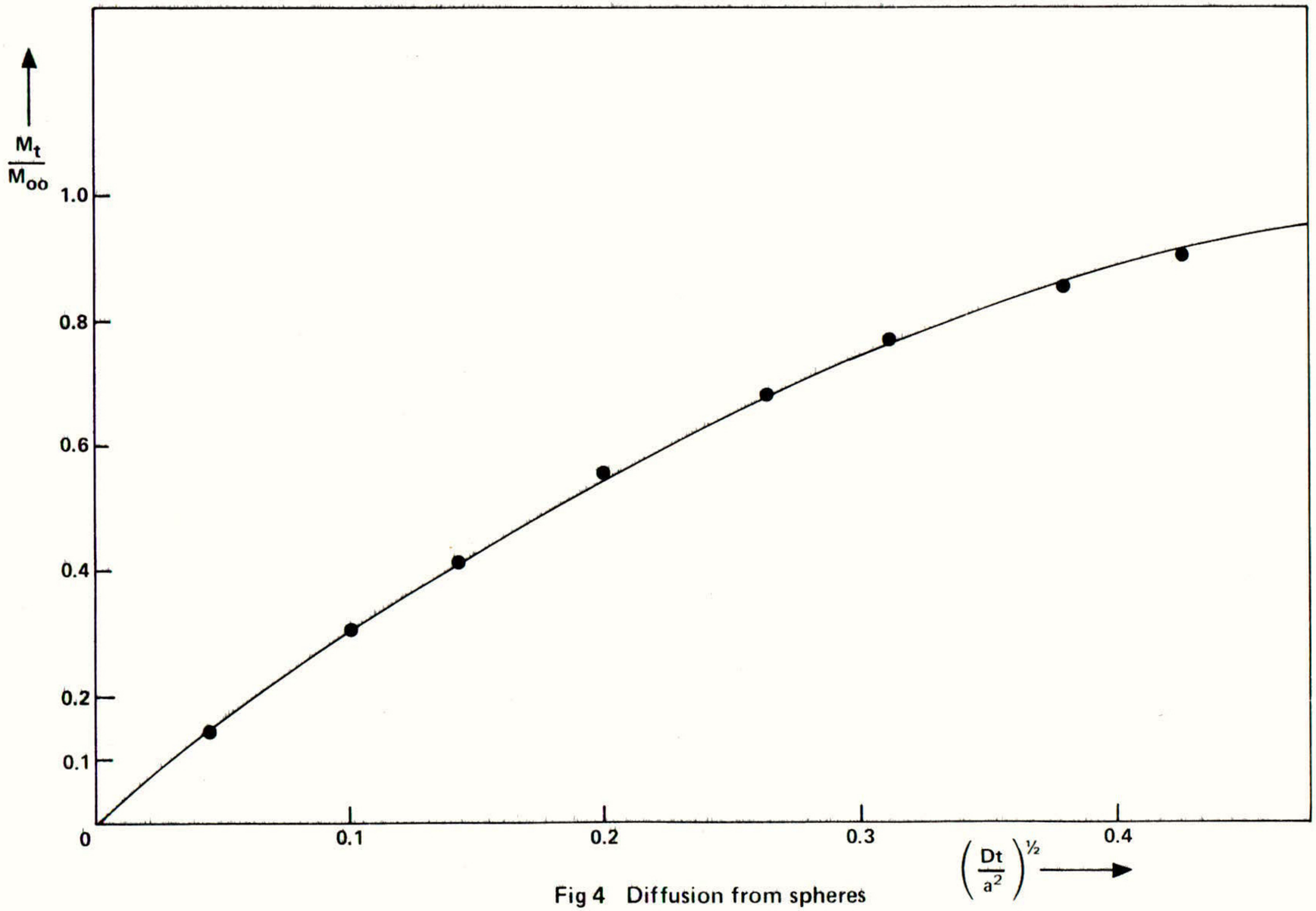

Fig 4 Diffusion from spheres

Table 2

Times for 50% Depletion of Spheres Under Particular Conditions

D cm^2 s^{-1}	a cm	$\left(\frac{D}{a^2}\right)^{\frac{1}{2}}$	At $\frac{M_t}{M_\infty}$ equal to 0.5		Time to release 50%; s	50% release time
			$\left(\frac{Dt}{a^2}\right)^{\frac{1}{2}}$	$t^{\frac{1}{2}}$		
10^{-10}	10^{-4}	10^{-1}	0.18	1.8	3.24	
	10^{-3}	10^{-2}	0.18	1.8×10^{1}	3.24×10^{2}	
	10^{-2}	10^{-3}	0.18	1.8×10^{2}	3.24×10^{4}	9 h
	10^{-1}	10^{-4}	0.18	1.8×10^{3}	3.24×10^{6}	37 day
10^{-12}	10^{-4}	10^{-2}	0.18	1.8×10^{1}	3.24×10^{2}	
	10^{-3}	10^{-3}	0.18	1.8×10^{2}	3.24×10^{4}	
	10^{-2}	10^{-4}	0.18	1.8×10^{3}	3.24×10^{6}	
	10^{-1}	10^{-5}	0.18	1.8×10^{4}	3.24×10^{8}	3700 day
10^{-14}	10^{-4}	10^{-3}	0.18	1.8×10^{2}	3.24×10^{4}	
	10^{-3}	10^{-4}	0.18	1.8×10^{3}	3.24×10^{6}	
	10^{-2}	10^{-5}	0.18	1.8×10^{4}	3.24×10^{8}	
	10^{-1}	10^{-6}	0.18	1.8×10^{5}	3.24×10^{10}	3.7×10^{5} day
10^{-16}	10^{-4}	10^{-4}	0.18	1.8×10^{3}	3.24×10^{6}	
	10^{-3}	10^{-5}	0.18	1.8×10^{4}	3.24×10^{8}	
	10^{-2}	10^{-6}	0.18	1.8×10^{5}	3.24×10^{10}	
	10^{-1}	10^{-7}	0.18	1.8×10^{6}	3.24×10^{12}	3.7×10^{7} day

Here the diffusion constant in the sphere will be taken as 10^{-12} cm^2 s^{-1} while in soil it is 10^{-8} cm^2 s^{-1}. In the soil 1 cm is considered sufficient for the concentration to drop to almost zero. Thus only for short periods of time under particularly favourable conditions, or at very high sphere densities, will the concentration in the external phase build up.

As the 'extraction process' from the surface will be via water or air rather than solids the partition coefficients are unlikely to aid in a concentration build-up as pesticides usually have low water solubilities and low vapour pressures.

Table 3

The Variation in Distribution Density to Achieve 50% Mass Release in 37 Days for Spheres Under Particular Conditions

D $cm^2\ s^{-1}$	Radius a cm	Loading of Spheres	No. of spheres for 1 kg active matter	Density of spheres cm^{-2} at 1 kg ha^{-1}
10^{-10}	1×10^{-1}	1%	2.5×10^{7}	2.5×10^{-1}
		5%	5×10^{6}	5×10^{-2}
		10%	2.5×10^{6}	2.5×10^{-2}
10^{-12}	1×10^{-2}	1%	2.5×10^{10}	2.5×10^{2}
		5%	5×10^{9}	5.0×10^{1}
		10%	2.5×10^{9}	2.5×10^{1}
10^{-14}	1×10^{-3}	1%	2.5×10^{13}	2.5×10^{5}
		5%	5×10^{12}	5×10^{4}
		10%	2.5×10^{12}	2.5×10^{4}
10^{-16}	1×10^{-4}	1%	2.5×10^{16}	2.5×10^{8}
		5%	5×10^{15}	5×10^{7}
		10%	2.5×10^{15}	2.5×10^{7}

From this it is apparent that the systems $D = 10^{-14}\ cm^2\ s^{-1}$, $a = 1 \times 10^{-3}$ cm, 1% loading and $D = 10^{-16}\ cm^2\ s^{-1}$, $a = 1 \times 10^{-4}$ cm, 10% loading, give similar cover density to that of the conventional emulsifiable concentrate.

Protracted release from such systems implies low concentrations in the surrounding medium, thus a lethal dose may require extensive 'harvesting' by the pest. As the pest will often destroy the pesticide at a high rate the accumulation of a lethal dose requires a reasonable intake rate. On the usual concentration/time basis (CT) CT will need to increase at very low times or very low exposures as depicted in Fig. 5. The crop may still be protected however owing to a deterrent (insects) or a growth retardation (weeds) effect.

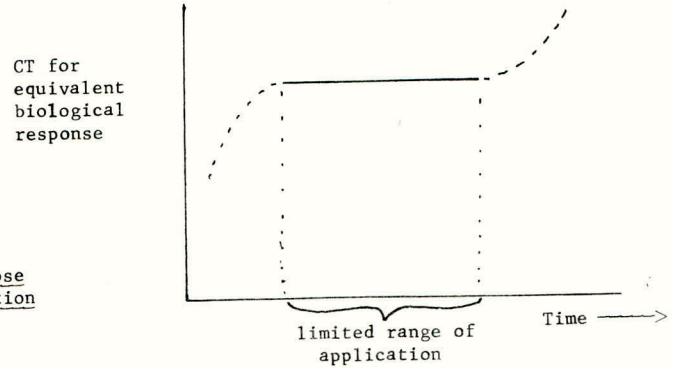

Fig. 5

Lethal Dose Accumulation

If a solid matrix is to release chemical to match the infestation as a population and the individual pest with a lethal dose then considerable dexterity is required in the control of persistence and placement. The complexity of considering populations rather than individuals is avoided here, for example only monodispersed systems are considered, but it is recognised that the inclusion of statistical reasoning would be a refinement.

Diffusion constants in the range 10^{-10} - 10^{-14} cm^2 s^{-1} are reasonable for polymeric materials and some other common carriers (Neogi, 1970). While the manipulation of the diffusion constants by use of additives, such as plasticisers, is a possibility, the mass that can be loaded into the sphere may be low if a 'solution' is to be obtained and thus a uniform concentration achieved. This is a necessary condition if diffusion alone is to control transport. Should the chemical be very soluble in the substrate then it implies a binding energy and thus partition and other energy terms must be invoked.

When binding energy is low the chemical and substrate must be mixed by mechanical means to produce a fine dispersion in the substrate which may approximate to a solution. Binding energy between molecules of the chemical itself may now need to be considered for part of the process as they must separate from one another to allow diffusion to occur.

What is the affect of binding energy in such a system?

Consider a chemical that gives a partition coefficient between the support substrate and a particular soil system. If we assume that the crude approximation of the ratios of the solubilities can be taken,

then $K_p' = \frac{\text{Solubility in substrate}}{\text{Solubility in soil}}$ based on the bulk soil water system and expressed in mass units, molal concentrations.

Assuming thermodynamics can be applied to such a system then the ΔG's emerge as shown.

a) $K_p' = 0.1$ $\Delta G = +1.29$ kcal $mole^{-1}$

b) $K_p' = 1$ $\Delta G = 0$

c) $K_p' = 10$ $\Delta G = -1.29$ " "

d) $K_p' = 100$ $\Delta G = -2.58$ " " at 283 K

If the entropy change upon being released to the surroundings is small and positive, say $\Delta S = 10$ cal $mole^{-1}$ K^{-1}. Then ΔH can be calculated using

$$\Delta G = \Delta H - T\Delta S \qquad \ldots\ldots (9)$$

For the cases a) to d) the ΔH's for partition are respectively 4.12 to 0.25 kcal $mole^{-1}$. Thus the heat of adsorption of the pesticide to soil and the heat of solution of the pesticide in the formulation matrix are similar under these conditions. If the chemical does bind to the matrix with a significant heat change then one of several types of system could be formed.

Considering the pesticide as a non-electrolyte the possibilities are; (i) an ordinary solution without specific binding sites, thus definite complexes are not formed; (ii) define binding sites with molecular complexes formed but not formal covalent bonds; or (iii) formal covalent bonding. This gives a classification of the energetics as

	kcal mole^{-1}
Very poor interaction	0 - 2
Ordinary solutions	2 - 6
Specific binding/complexes	6 - 15
Covalent bonds	35 - 100

To find out how a pesticide would be released from a solid solution the theory presented by Jost (1960) can be examined. In this the solid solution is considered as a simple molecular lattice containing vacancies. Molecules are free to move to a neighbouring unoccupied site if they have sufficient energy, U, to surmount the activation barrier separating the new site from the residence site. If n_v is the number of vacancies per unit volume and Z the nearest neighbour of a vacancy then the number of molecules per unit volume free to move will be

$$n_f = n_v Z e^{-U/RT} .$$

To create the number of vacancies n_v per unit volume we have to supply energy. Thus

$$n_v \approx n e^{-E/RT} \qquad \ldots\ldots (10)$$

where E is the energy necessary for the formation of 1 mole of vacancies, and n is the number of molecules per unit volume. Thus the number of molecules free to move and with sufficient energy is

$$n_f = nZe^{\frac{-(E + U)}{RT}} \qquad \ldots\ldots (11)$$

For a simple cubic lattice Z = 6 but the probability that a molecule next to a hole and with an energy U has a velocity component towards the hole will be approximately 1/Z. Thus by considering the probability for a molecule to be free to move

$$\text{Probability} = \frac{n_f}{n} = e^{\frac{-(E + U)}{RT}} \qquad \ldots\ldots (12)$$

Consider now the elementary equation for a gaseous diffusion constant, (Moelwyn-Hughes, 1947)

$$D \quad \frac{\lambda v}{3}$$

where λ is the mean free path and v is the mean velocity. If λ is replaced by d, the distance between nearest neighbours in the solid lattice, and putting P = E + U we obtain

$$D \quad \frac{dv}{3} \quad e^{\frac{-P}{RT}} \qquad \ldots\ldots (13)$$

At ordinary temperatures we may take v as 3×10^4 cm s^{-1} and d = 3×10^{-8} cm.

Thus $$D \quad 3 \times 10^{-4} \quad e^{\frac{-P}{RT}} \qquad \ldots\ldots (14)$$

P now represents the 'structural barrier' (E) as well as the thermal energy term (U). As the temperature rises P will decrease until, at the melting point when E = 0, it will relate only to the thermal motion. Thus when the solid melts the system returns to Fickian Diffusion.

How the diffusion constant varies with P can be seen from Table 4.

Table 4

Variations of Diffusion Constant with Energy Barrier at 283°K

P, kcal mole^{-1}	Diffusion constant cm^2 s^{-1}
2	8.45×10^{-6}
4	2.38×10^{-7}
8	1.89×10^{-10}
12	1.50×10^{-13}
16	1.19×10^{-16}

It will be noted that for an 'activation energy' corresponding to thermal energy, 2 kcal mole^{-1}, the diffusion constant is what would be expected for a liquid.

If the absolute solubility of the pesticide in the support matrix, x_s, is determined and the melting point of the pesticide is known, T_m, then the differential heat of solution ΔH_s can be calculated for a particular temperature T from

$$\ln x_s = \frac{\Delta H_s}{R} \left(\frac{1}{Tm} - \frac{1}{T} \right) \qquad \ldots\ldots (15)$$

The ΔH_s will relate to the energy term, U, while the term E will relate to the melting point of the pure matrix. Thus a correlation can be attempted for a range of materials even though the diffusion constants for some of them have not been measured directly.

Knowing P of equation (14) some idea of the diffusion constant to expect is determined and the appropriate size and loading to produce a given effect can be calculated.

Turning now to non-uniform spheres of the encapsulation type a different diffusion system is appropriate. Thus according to Crank (1975) the equation for the flow through a spherical wall is given by

$$\frac{Q_t}{4\pi ab(b-a)C_1} = \frac{Dt}{(b-a)^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp -\left[\frac{Dn^2\pi^2 t}{(b-a)^2} \right] \qquad \ldots\ldots (16)$$

This equation relates to the spherical system shown in Fig 6

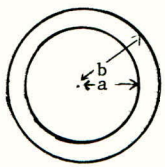

Fig. 6

Encapsulation System

In equation (16) Q_t is the amount escaping from the outer surface when the concentrations in the wall and outside the capsule are initially zero. Outside the capsule the concentration remains zero and the concentration in the capsule wall at the chemical-wall interface is C_1, the solubility in the wall. This will remain constant as long as the entire inner wall remains 'wetted'.

It will be noted that as t becomes large the equation approaches a steady state represented by

$$\frac{Q_t}{4\pi ab(b-a)C_1} = \frac{Dt}{(b-a)^2} - \frac{1}{6} \qquad \ldots\ldots (17)$$

Equation (16) has been worked out and plotted by Crank, Fig 7, so that for particular values of a, b, C_1 and D the relationship between Q_t and t can be established as well as the time to the steady state, that is when

$$\frac{Dt}{(b-a)^2} = \frac{1}{6} \qquad \ldots\ldots (18)$$

It must be remembered that the linear portion may continue for some time, involving considerable extrapolation; however, eventually the pesticide must become depleted and the graph will curve to meet the abscissa again as Q_t approaches Q_∞. This is comparable to case (d) of Fig 3.

Some values are presented in Table 5 for a compound of molecular weight 250 and density unity. Thus if the core contains pure pesticide the concentration is 4 mole l^{-1}. Considerable benefit could be obtained from such a system by matching the release profile to that demanded by the infestation as indicated in Fig 1. Mixtures of different capsules would allow a variety of systems to be matched.

The influence of a range of partition coefficients for the pesticide between the pure material and the wall, defined by

$$K_p = \frac{\text{Solubility of the chemical in the wall}}{\text{Solubility of the chemical in itself}}$$

$$= \frac{\text{Solubility of the chemical in the wall}}{\text{Concentration of pure material}}$$

both expressed in the same units, can be seen from Fig 8.

For low fluxes of pesticide K_p should be low, that is low solubility in the wall, all other factors being the same.

In Fig 8 the diagrams progress across the rows. Three possible partition constant values are depicted. While it may be difficult to achieve a partition constant greater than unity when pure paterial is in the core, it is feasible when the core contains a solution.

Using equations (17) and (18), in conjunction with Fig 7, the Table 5 can be constructed. This is achieved by (i) giving the core radius (a), wall radius (b), diffusion constant, and solubility of chemical in the wall C_1, particular values; (ii) calculating the amount contained in such a core volume in grams; (iii) deciding what amount of this to consider released, thus giving Q_t a value. The ordinate may now be calculated as a number and the corresponding abscissa value read from the graph. Knowing D, b and a, the time, t, to give this quantity released is calculated.

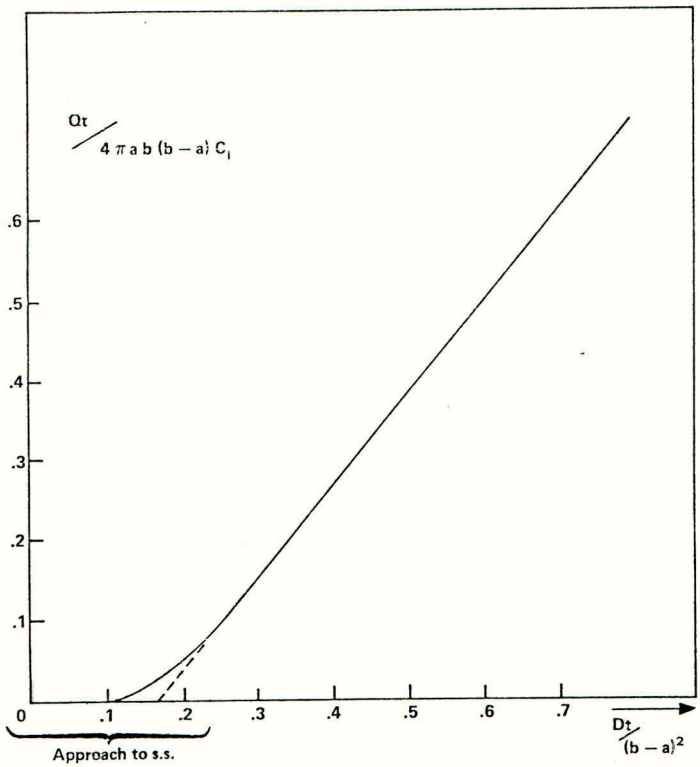

Fig 7 Quantity flowing through a Spherical Wall (Crank, 1975)

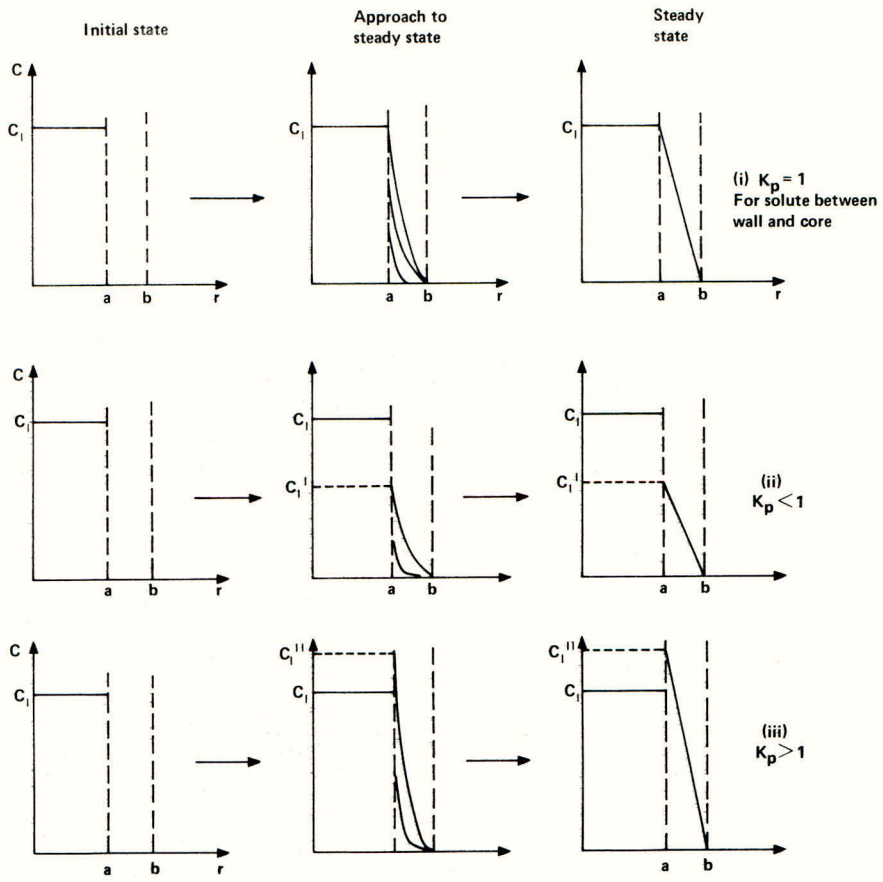

Fig 8 Flow through a Spherical Wall approach to steady state for a variety of partition values

Table 5

Theoretical Release Data for Encapsulated Chemical

Core radius cm	Wall thickness cm	Diffusion constant $cm^2\ s^{-1}$	Solubility in the wall $g\ cm^{-3}$	Time to release 50% s	Time to release 50% day	Time to Steady State s	Time to Steady State day	K_p
1×10^{-4}	1×10^{-4}	10^{-10}	1×10^{-4}	8.3×10^{4}	0.96	1.7×10^{1}		1×10^{-4}
		10^{-12}		8.3×10^{6}	9.6×10^{1}	1.7×10^{3}		1×10^{-4}
		10^{-14}		8.3×10^{8}	9.6×10^{3}	1.7×10^{5}	1.9	1×10^{-4}
		10^{-10}	1×10^{-2}	8.3×10^{2}		1.7×10^{1}		1×10^{-2}
		10^{-12}		8.3×10^{4}	0.96	1.7×10^{3}		1×10^{-2}
		10^{-14}		8.3×10^{6}	9.6×10^{1}	1.7×10^{5}	1.9	1×10^{-2}
		10^{-10}	1×10^{-1}	1×10^{2}		1.7×10^{1}		1×10^{-1}
		10^{-12}		1×10^{4}	0.12	1.7×10^{3}		1×10^{-1}
		10^{-14}		1×10^{6}	1.2×10^{1}	1.7×10^{5}	1.9	1×10^{-1}
5×10^{-4}	1×10^{-4}	10^{-10}	1×10^{-4}	7.2×10^{5}	8.3	1.7×10^{1}		1×10^{-4}
		10^{-12}		7.2×10^{7}	8.3×10^{2}	1.7×10^{3}		1×10^{-4}
		10^{-14}		7.2×10^{9}	8.3×10^{4}	1.7×10^{5}	1.9	1×10^{-4}
		10^{-10}	1×10^{-2}	7.2×10^{3}		1.7×10^{1}		1×10^{-2}
		10^{-12}		7.2×10^{5}	8.3	1.7×10^{3}		1×10^{-2}
		10^{-14}		7.2×10^{7}	8.3×10^{2}	1.7×10^{5}	1.9	1×10^{-2}

Table 5 Cont'd

Theoretical Release Data for Encapsulated Chemical

Core radius cm	Wall thickness cm	Diffusion constant $cm^2\ s^{-1}$	Solubility in the wall $g\ cm^{-3}$	Time to release 50% s	Time to release 50% day	Time to Steady State s	Time to Steady State day	K_p
		10^{-10}	1×10^{-1}	7.2×10^{2}		1.7×10^{1}		1×10^{-1}
		10^{-12}		7.2×10^{4}	.83	1.7×10^{3}		1×10^{-1}
		10^{-14}		7.2×10^{6}	8.3×10^{1}		1.9	1×10^{-1}
5×10^{-3}	1×10^{-4}	10^{-10}	1×10^{-4}	8.5×10^{6}	98	1.7×10^{1}		1×10^{-4}
		10^{-12}	1×10^{-2}	8.5×10^{6}	98	1.7×10^{3}		1×10^{-2}
		10^{-13}	1×10^{-1}	8.5×10^{6}	98	1.7×10^{4}	0.19	1×10^{-1}
1×10^{-4}	2×10^{-4}	10^{-12}	1×10^{-4}	1.2×10^{7}	138	6.7×10^{3}	0.08	1×10^{-4}
5×10^{-4}	2×10^{-4}	10^{-10}	1×10^{-4}	1.2×10^{6}	13.8	6.7×10^{1}		1×10^{-4}
		10^{-12}	1×10^{-2}	1.2×10^{6}	13.8	6.7×10^{3}		1×10^{-2}
5×10^{-3}	2×10^{-4}	10^{-10}	1×10^{-4}	1.7×10^{7}	196	6.7×10^{1}		1×10^{-4}
		10^{-12}	1×10^{-2}	1.7×10^{7}	196	6.7×10^{3}		1×10^{-2}
5×10^{-4}	1×10^{-3}	10^{-13}	1×10^{-4}	4.6×10^{6}	32	1.7×10^{3}	0.02	1×10^{-4}
		10^{-13}	1×10^{-1}	4.6×10^{6}	53	1.7×10^{6}	20	1×10^{-1}

From equation (18) the time to the steady state can also be found. It will be noted in Table 5 that the time to the steady state is usually short compared with the time for release of any large quantity and that it is the wall thickness and diffusion constant that govern the time to steady state. Thus in concept a particular time-lag before extensive release occurs can be arranged. Also by adjusting the size of the core the length of steady state release can be predetermined. This may involve an unfavourable mass ratio of wall material to pesticide in some instances.

From Table 5 it is immediately apparent that some of the release times are of high interest, for example 32 days to 50% release, implying about 64 days to total release. Remember, however, that some of the latter material will not be released in the steady state as all the inner wall will not be 'wetted'. In these calculations the assumption is that the wall is initially free of chemical; however, on storage it will reach an equilibrium concentration. Thus the steady state will not be delayed as much as the calculation suggests.

Some Practical Considerations

Several methods can be used to produce spheres containing a chemical.

(i) Rapid cooling of molten solid droplets by producing them at an orifice above the surface of a water column. The liquid falls through air and spherical drops form which are cooled on passing down the water column. Certain larger sizes of spheres can be produced this way and a 'dimpled' flattened portion occurs owing to impact with water.

(ii) Emulsion polymerisation to form spherical particles has been reported by several workers. Good spheres can be obtained for some systems but great care is necessary to obtain good results.

(iii) An aerosol of molten solid can be created using hot air to disperse a jet of the hot liquid, the small particles formed condense while airborne and can be collected as a solid. Paraffin wax has proved ameanable to this treatment and the product is a distribution of sizes of spheres. These can be readily fractionated into narrow bands. The cooling rates can influence the quality of the product considerably.

Method (iii) was chosen to produce a series of wax spheres containing the dye Phenol Blue and five size ranges of spheres from 10 to 700 μm were produced. The sizes and distributions were established by photographing the spheres at particular magnifications and taking measurements by hand.

The release of dye into water or acetone/water mixtures could be followed spectrophotometrically.

Vigorous mixing of the spheres in the 'extraction medium' was necessary as they float and are difficult to wet.

From the data produced and the empirical equation (8) the diffusion constant was established, assuming Fickian Diffusion. When acetone/water mixtures were used for extraction some of the wax must be dissolved as the particles, when dried, after four days extraction suffered about a 10% weight loss.

Thus the acetone/water experiments will give a high value for the diffusion constant.

Water	Acetone	D cm^2 s^{-1}
90%	10% v/v	4.3×10^{-14}
100%	0%	3.4×10^{-14}

M_∞ was found by examining the partition constant of the dye between paraffin wax and the solvent system independently. Such experimentation gives some feeling for the type of data that can be obtained. Other sources should be consulted for more detailed practical work, for example the Controlled Release Pesticide Symposium (1974).

CONCLUSIONS

So far consideration has been given to the control of release of the chemical. Thus the placement of the chemical in the environment as a 'protected material' is the concept used to control persistence. This in no way controls the surrounding environment, however, and the chemical once released becomes subject to all the usual mechanisms listed in Table 1. Thus once released the chemical will be destroyed by the same processes with the same rate constants as will a conventionally applied chemical.

The steady-state release from encapsulated material provides a source of pesticide which, if decomposed by first order processes, will yield a fixed input rate of chemical into the environment. This will remain constant until the source becomes depleted. Thus if the release is fast a higher concentration will exist for a shorter duration than when release is slow. As diffusion in the environment is a continuous process the sphere of influence of the chemical increases as time passes but at increasing dilution. Which particular combination of concentration, time of exposure and sphere of influence is appropriate for optimal pest control and crop protection is not immediately obvious.

To gain some insight into this requires some examination of the space/time relationship of the potentially effective material remaining. Such a system is difficult to handle rigorously but a crude approximation highlights the important parameters. Soil will be taken as the medium to which the pesticide is applied.

The breakdown of pesticides in the soil is often found to follow a first order kinetic process. This may be modified by adsorption but only a simple first order process will be considered here. This does not mean that only one breakdown pathway is considered but that they are all gathered together as one constant. Thus if a quantity Q exists in the environment and its rate of breakdown $\frac{dQ}{dt}$ is due to three processes with different rate constants then this is expressed as

$$\frac{dQ}{dt} = -k_1 Q - k_2 Q - k_3 Q \qquad \ldots\ldots (19)$$

where k_1, k_2 and k_3 are the rate constants. This becomes

$$\frac{dQ}{dt} = -Q \left[k_1 + k_2 + k_3\right] \qquad \ldots\ldots (20)$$

and $k_1 + k_2 + k_3 = k^1$, a further constant.

For encapsulated material the rate of imput will be given, in the steady state, by $\frac{Q_o}{t_o}$ for a particular system; where Q_o is the amount released in time t_o. The time for which this steady state exists should also be considered of course. If we now assume that the rate of change of the quantity present, Q, is due to the constant imput, $\frac{Q_o}{t_o}$, and the rate of decomposition k^1Q, then,

$$\frac{dQ}{dt} = \frac{Q_o}{t_o} - k^1Q \qquad \ldots\ldots (21)$$

and

$$Q = \frac{Q_o}{k^1 t_o} \quad (1 - e^{-kt}) \qquad \ldots\ldots (22)$$

at long times e^{-kt} tends to zero and a steady state is set up with

$$Q = \frac{Q_o}{k^1 t_o} \qquad \ldots\ldots (23)$$

This holds only as long as the source is delivering pesticide at a constant rate. After this period Q will decrease with time exponentially.

Table 6 is constructed as follows.

(a) Data of interest concerning the controlling parameters are taken from Table 5 and the steady state release is calculated. This is the value of $\frac{Q_o}{t_o}$ averaged over one square centimetre taking into account the density of capsules per square centimetre.

(b) A range of possible decay rates are assigned such that appropriate half lives are covered. Here 0.08 day (10^{-4} s^{-1}); 0.8 day (10^{-5} s^{-1}); and 8 day (10^{-6} s^{-1}), and 80 day (10^{-7} s^{-1}), are included.

(c) The steady-state amount available, Q, is calculated from equation (23). This steady-state amount will diffuse as time passes and during this time it should interact with a pest to give an effective response.

(d) Q is considered as a constant chemical source for diffusion as an amount per square centimetre in a plane within the soil, that is, incorporated.

(e) The concentration is averaged over the depth at this time.

(f) The concept of a fixed CT value to give a biological response is now invoked, recalling the constraints considered earlier in association with Fig 5. It is assumed that a constant CT of 1×10^{-6} gram of chemical per gram of soil (1 ppm) for 10 hours exposure gives effective control. Such numbers are derived from laboratory experiments in which the chemical is intimately mixed with the soil at zero time, thus diffusion is likely to be a minor factor in the system.

(g) It is assumed that the pest occupies the chemically treated region continuously in the time period of interest.

(h) The concentration depth profile is averaged by considering the smooth curve as a 'square wave' to obtain an average concentration as shown in Fig 9.

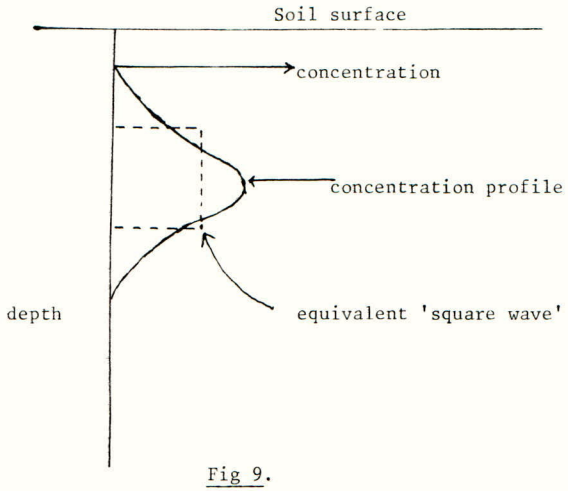

Fig 9.

Chemical Diffusion in Soil with Simplified Profile

(i) It is assumed that the chemical dilution over this time period of pest interaction remains constant at the average value.

(j) Once released into the soil the chemical is assumed to diffuse to encompass a further 1 cm soil depth every 50 days.

(k) The time this concentration would take to give a lethal dose (Lethal time) assuming the CT value of 10 ppm hour, is then calculated.

From these results a range of controlled release systems can be assessed, bearing in mind the crude assumptions made. An insect pest will sweep out a volume with time encountering chemical while a plant will call upon a zone of influence for water supply. Provided the CT relationship is determined from appropriate experimental procedures with the chemical then the details of this pick-up need not be known to chose an appropriate controlled release system.

Several questions remain:

(i) What is the sphere of influence of one capsule and how long will it take before chemical from adjacent spheres interpenetrate? This is very much a function of the capsule size and density.

(ii) For any particular chemical the overall rate of decomposition can be interpreted as a half-life. If this half-life is short compared with the time for release of 50% of the chemical then benefit accrues from having controlled release. If the rate of breakdown is such that the half-life is long compared with the 50% release time then the question must be asked - Why employ controlled release%

Table 6

Persistence Control and Pesticidal Effectiveness

Case 1

Basic Data	Decay rate s^{-1}	Steady state amount available g cm^{-2}	Depth - Time cm	day	Averaged concentration g cm^{-3}	Lethal time day
Core radius 1×10^{-4} cm	1×10^{-4}	5.7×10^{-9}	0.2	10	2.9×10^{-8}	14.6
Wall thickness 1×10^{-4} cm			1.0	50	5.7×10^{-9}	73
D 1×10^{-12} cm^2 s^{-1}			2.0	100	2.9×10^{-9}	146
K_p 1×10^{-4}	1×10^{-5}	5.7×10^{-8}	0.2	10	2.9×10^{-7}	1.46
Q_o/t_o 5.7×10^{-13} g cm^{-2} s^{-1}			1.0	50	5.7×10^{-8}	7.3
			2.0	100	2.9×10^{-8}	14.6
Steady state lasts 190 day	1×10^{-6}	5.7×10^{-7}	0.2	10	2.9×10^{-6}	0.146
Amount applied 1 kg ha^{-1}			1.0	50	5.7×10^{-7}	0.73
active ingredient			2.0	100	2.9×10^{-7}	1.46
	1×10^{-7}	5.7×10^{-6}	0.2	10	2.9×10^{-5}	0.015
			1.0	50	5.7×10^{-6}	0.073
			2.0	100	2.9×10^{-6}	0.146

Table 6

Persistence Control and Pesticidal Effectiveness

Case 2

Basic Data	Decay rate s^{-1}	Steady state amount available g cm^{-2}	Depth - Time cm	day	Averaged concentration g cm^{-3}	Lethal time day
Core radius 5×10^{-4} cm	1×10^{-4}	4.2×10^{-9}	0.2	10	2.1×10^{-8}	20
Wall thickness 2×10^{-4} cm			1.0	50	4.2×10^{-9}	99
D 1×10^{-11} cm^2 s^{-1}			2.0	100	2.1×10^{-9}	200
K_p 1×10^{-4}	1×10^{-5}	4.2×10^{-8}	0.2	10	2.1×10^{-7}	2
Q_o/t_o 4.2×10^{-13} g cm^{-2} s^{-1}			1.0	50	4.2×10^{-8}	9.9
			2.0	100	2.1×10^{-8}	20
Steady state lasts 260 day	1×10^{-6}	4.2×10^{-7}	0.2	10	2.1×10^{-6}	0.2
Amount applied 1 kg ha^{-1}			1.0	50	4.2×10^{-7}	0.99
active ingredient			2.0	100	2.1×10^{-7}	2.0
	1×10^{-7}	4.2×10^{-6}	0.2	10	2.1×10^{-5}	0.02
			1.0	50	4.2×10^{-6}	0.099
			2.0	100	2.1×10^{-6}	0.2

Table 6

Persistence Control and Pesticidal Effectiveness

Case 3

Basic Data	Decay rate s^{-1}	Steady state amount available g cm^{-2}	Depth - Time cm	day	Averaged concentration g cm^{-3}	Lethal time day
Core radius 5×10^{-3} cm	10^{-4}	6.8×10^{-9}	0.2	10	3.4×10^{-8}	12
Wall thickness 1×10^{-3} cm			1.0	50	6.8×10^{-9}	60
D 1×10^{-12} cm^2 s^{-1}			2.0	100	3.4×10^{-9}	120
K_p 1×10^{-1}	10^{-5}	6.8×10^{-8}	0.2	10	3.4×10^{-7}	1.2
			1.0	50	6.8×10^{-8}	6
Q_o/t_o 6.8×10^{-13} g cm^{-2} s^{-1}			2.0	100	3.4×10^{-8}	12
Steady state lasts 160 day	10^{-6}	6.8×10^{-7}	0.2	10	3.4×10^{-6}	0.12
Application rate 1 kg ha^{-1}			1.0	50	6.8×10^{-7}	0.6
active ingredient			2.0	100	3.4×10^{-7}	1.2
	10^{-7}	6.8×10^{-6}	0.2	10	3.4×10^{-5}	0.012
			1.0	50	6.8×10^{-6}	0.06
			2.0	100	3.4×10^{-6}	0.12

(iii) The pest may be repelled from a chemical area but not killed. The pest chemical encounter may be over a time period with intermittent entering of the chemical region. In these circumstances the CT is not adequate as metabolism of compound occurs in the pest when the pest is in chemical-free area, while the chemical in the soil also continues to be degraded.

(iv) For short 'lethal times' the steady state may not have been achieved and thus the answers are in large error.

(v) When large numbers of capsules are present per square centimetre the concentration profile will approach an even plane source; however, for large capsules widely spaced the assumptions are inadequate.

As far as the physical losses are concerned, for any surface deposit the rate of appearance of chemical on the surface of a capsule in the 'useful' region is 1×10^{-6} g s^{-1} ha^{-1}, that is rate of loss from one times the number of them. A vapour pressure of 5×10^{-9} mm Hg or above could readily accommodate for this removal of chemical from a surface. As most pesticides have a vapour pressure in excess of 5×10^{-9} mm Hg at ambient temperatures the chemical is best incorporated in the soil or, for plants, a very high partition into foliage would be required (McFarlane, 1975).

Some of the 'lethal times' in Table 6 are obviously nonsense as the time of exposure required for kill is often comparable to the pest's natural lifetime. Thus to be exploited fully the concepts presented here need to be improved; however, it is hoped that the value of considerations of this type is apparent, and some areas of interest are highlighted by Table 6.

A considerable amount of knowledge is yet required if good use is to be made of controlled persistence and until it is available the practice of screening is as good as any other for finding out if improvement in effectiveness can be achieved. Some theoretical considerations are worth while, however, if only to reduce the amount of experimentation by discarding the inappropriate, and, it is hoped that this paper has indicated some of the ways to approach the selection.

Thus while encapsulation and controlled release in general are at first sight very attractive their usefulness in improving the effectiveness of biological activity must be considered suspect unless the release/time profile is appropriate to the target and this is coupled with optimal placement. They remain attractive of course for other reasons such as safety.

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