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PHYSICAL LOSS AND REDISTRIBUTION OF PESTICIDES IN THE VAPOUR PHASE

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Summary The importance of losses of pesticide as vapour is illustrated by evidence of volatilisation losses during application, and from deposits on crops and in soil. The main physico-chemical principles governing volatilisation of pesticides are discussed. The volatilisation potential of new pesticides in specified conditions can be estimated from physico-chemical data. Although their absolute behaviour under varying conditions of natural environments can only be predicted approximately, nevertheless their properties relative to those of compounds of known behaviour should enable the likely contribution of volatilisation as a determinant of persistence to be estimated with adequate precision for practical purposes.

INTRODUCTION

From the earliest days of the use of organic pesticides, vapour phase transfer and redistribution have been recognised as important attributes affecting the biological performance of fumigant pesticides. In contrast, undesirable volatility has been a cause for concern in the use of growth-regulating herbicides, and organophosphorus insecticides with high mammalian toxicities. Despite recognition of the biological consequences of vapour transfer, it has only been grudgingly accepted within the last decade that, with a few exceptions, the volatility of pesticides is sufficient for loss as vapour to be important in limiting their persistence in the target area.

Many factors have combined to slow progress in understanding the importance of volatilisation as a route of pesticide loss. Those concerned at first-hand with the practical use of pesticides have not always had a good understanding of the physico-chemical principles involved. The physical chemist, familiar with the individual principles, has tended to study the factors mainly in isolation from each other in the belief that their individual influences can eventually be combined to describe the whole system. Natural environments are, however, physically complicated and the interactions of the relevant factors are so complex that, simplifying generalisations are necessary to limit the detail incorporated into mathematical models for predictive purposes. An understanding of the behaviour of pesticides has not been helped by the unfortunate tendency to describe them in quantal (all-or-nothing) terms. References to compounds as being toxic or non-toxic, systemic or non-systemic, soluble or insoluble in water, persistent or non-persistent in the environment and, in the context of this paper, volatile or non-volatile abound in the literature and in technical conversation. The hundreds of pesticides now in use represent such a wide range of properties that these characteristics form almost continuous scales and to be meaningful, each must be qualified at almost every mention. There has also been a deplorable tendency for research concerned with aspects of pesticide behaviour to be confined to particular groups — insecticides, fungicides, herbicides, nematicides — according to the prime interest of each team of workers, and relevant findings in closely related fields of study seem often to have been disregarded. It is of no consequence to physico-chemical behaviour that one chemical should be placed in soil to control an insect pest and another weeds. The interplay between the physical properties of chemicals and those of the environment determine their fates.

Observations of biological effects provided early evidence that some 'non-fumigant' pesticides transferred into, and were transported as, vapour in biologically-important amounts. During the late 1930's vapours of some hormone-like chemicals were seen to affect plants within paper bags. The fumigating effect of lindane was observed in the mid-1940's, and subsequently 'fumigant action' by parathion, chlordane and TDE was reported . Vapours of esters of 2,4-D and 2,4,5-T have often resulted in damage to non-target plants near treated areas and there are many other more recent instances of unsolicited biological effects arising as a result of the movement of pesticides as vapour.

Attempts to measure the concentrations of vapours were a natural consequence of the early reports of biological effects. Small animals have been used to assess the concentrations of parathion vapours in citrus groves after spraying, and sensitive test plants such as tomato have often been used to determine volatilities of herbicides. By the early 1960's it was realised that volatilisation possibly accounted for a substantial part of insecticides disappearing from soil and by the mid-1960's improved methods of analysis had revealed that some organochlorine compounds were present in the atmosphere continuously at very low concentrations. It must now be accepted that appreciable concentrations of vapours of most pesticides will occur in the atmosphere of, and near to, target environments during, and for some time after, application and that some of the widely used and stable compounds are continuously and ubiquitously present in the earth's lower atmosphere.

The theoretical principles governing volatilisation have been described by Hartley (1969) and Hamaker (1972). The subject of pesticide volatilisation was reviewed thoroughly by Spencer et al. (1973) and, in its wider context, by Wheatley (1973). The Environmental Protection Agency in the U.S.A. has recently Anon.(1975) prepared guidelines of Proposed Rules showing the type of information on volatility now needed for pesticide registration and how the relative volatilisation potential of new pesticides can be estimated from physico-chemical data. Except where otherwise stated, the information presented in this paper is contained in the above review sources which acknowledge the original contributions. The purpose of this paper is to provide a much-simplified account of pesticide volatilisation as it affects their persistence in use.

EVIDENCE OF VOLATILISATION LOSSES

Volatilisation of pesticides is encouraged whenever they are distributed in a system which has a large surface (interface) exposed to air, whether directly or in aqueous solution. Some loss occurs while sprays or granules are being applied, even though the exposure to air is only very brief between the applicator and the target. The deposited pesticide, whether on plant or other surfaces or in soil, is ideally presented to realise any potential it may have to transfer into the vapour-phase.

Volatilisation during application: Almost invariably, comparisons of the amounts of pesticide reaching a target (the initial deposit) and the amounts applied have shown that material is 'lost' between the applicator and the target. Only part of the loss occurs as small particles or droplets drifting away from the target area, rarely amounting to even 5% of the applied amount of pesticide during ground operations, and more usually $< 2\%$. Consequently, when larger losses are observed, either faulty measurement technique or direct volatilisation of pesticide into the atmosphere must be inferred. When several compounds have been compared under comparable conditions, the excess (non-drift) loss has usually correlated well with their relative saturation vapour pressures, confirming that volatilisation most probably caused the loss. Decker *et al.* (1950) recovered on average (relative to DDT = 100%) only 85, 84, 56 and 45% of camphechlor, dieldrin, aldrin and chlordane respectively. Even when DDT was collected at the nozzle of a laboratory sprayer, they recovered only 88%, and less at 1.2 m from the nozzle. Their recovery of DDT from crop foliage was thus probably incomplete and consequently the true recoveries of the pesticide would have been less than those indicated above. Similar results have been obtained in several other studies, whether the chemicals were applied as sprays or as granular products. Even when sprayed directly towards the soil surface, only 60% of thionazin and 76% of fonofos have been recorded as reaching the soil. Initial losses of 16 and 18% have been reported for dimethoate and disulfoton respectively. In an extreme case, only 22-30% of aerially-applied DDT was found on targets at the level of maize tassels 2.5 m above-ground, and only 35 and 49% of diazinon and ethion. There is little doubt that these are not isolated examples and that loss of pesticide as vapour during application must often account for a very significant proportion of the applied chemical vanishing before it reaches the target.

Losses during application are further corroborated by measurements of pesticide vapours at concentrations of several hundreds of $\mu g/m^3$ in the vicinity of target areas during application (Wheatley, 1973). Unfortunately, the data needed to estimate the actual amounts involved are not available but even a crude calculation shows that the observed concentrations in air would relate sensibly to the proportions being lost. Assume that an average pesticide burden of 1 mg a.i./m^3 air is confined to a 3 m depth of air over 1 ha; that a sprayer fitted with a 10 m boom travels at 8 km/ha and sprays 1 ha in about 7.5 min; then a 3 m deep layer of still air would contain 30 g of the pesticide/ha. If the air were moving at 1 m/s, it would change over a ha square in about 100 s, or about 4.4 times in the period needed to treat 1 ha, removing about $4.4 \times 30 = 132$ g of entrained pesticide, representing 13% of a 1 kg a.i./ha application. Direct loss during application reduces the initial deposit below expectation, with a comparable reduction of persistence of its biological activity by what may often be the equivalent of a 'half-life' or more.

Volatilisation from deposits: The potential rates of volatilisation of certain organochlorine insecticides and some herbicides have been studied under controlled laboratory conditions. When the surface from which the pure substances are vapourising is relatively 'inert' (non-sorptive), for example glass or metal, similar environmental factors affect their volatilisation. Volatilisation rates of p,p′-DDT (calculated and observed) at 20°C are 1.3 ng/cm^2h from glass, equivalent to about 14 - 46 days for 1.12 kg a.i. to volatilise from a continuous deposit spread over 1 ha of inert surface. This is in reasonable agreement with measured rates of loss of DDT from plant surfaces and several studies have indicated little difference in the rates of vapour loss of this and some other pesticides from inert and plant surfaces, although this is not invariably so.

The decline of pesticide residues from treated plant surfaces has been measured both in the laboratory and in the field, but evidence for loss by volatilisation is mainly circumstantial. Other factors being equal, rates of residue loss from plant surfaces are often positively correlated with the vapour pressures of pesticides. The correlation is not necessarily perfect because the effective vapour pressure of a deposited pesticide is reduced by many factors including the nature of the plant surface, the deposit and adjuvants in the formulation. Diminution of pesticide deposits on plant surfaces usually show two or three phases distinguished by rather abrupt changes in the rates of loss. It was believed that the rapid initial loss of deposited material occurred by particles being dislodged in the few hours immediately following application, but it now seems certain that much of the recorded loss is attributable to volatilisation into the atmosphere. A slower loss then continues, often lasting several days or weeks, attributable to continued loss of particles, volatilisation and degradation of surface deposit. Finally, when the surface deposit has virtually disappeared, material adsorbed into the plant can be lost only at a much reduced rate and the loss may cease as the residue equilibrates with prevailing ambient concentrations of the pesticide.

It is almost certain that much of the loss from deposits at all stages is as vapour, often of degradation products rather than parent active ingredient, as with DDT. This is amply confirmed by measurements of pesticides in air downwind of treated areas, ng/m^3 concentrations continuing in some cases for several weeks after the treatment.

By far the greatest attention has been given to vapour loss of pesticides from soil, and the conditions which govern the rates of loss. Detailed measurements have now been made of losses of dieldrin, heptachlor, lindane, DDT, EPTC, propham, chlorpropham, and s-triazines, to cite but a few. As with deposits on plant surfaces, a high initial loss of a chemical often, but not invariably, occurs during the first few minutes or hours after it is applied to soil and much of the residue's subsequent fate depends on whether it remains on the soil surface or is incorporated. Incorporation greatly suppresses volatilisation and, although it is well-known that some of the more volatile herbicides such as EPTC, chlorthiamid, dichlobenil or trifluralin, must be promptly incorporated after application, this has not been widely recognised as essential for many other compounds such as aldrin, dieldrin, phorate or disulfoton. Substantial loss of these can, however, occur immediately after application, presumably as vapour. Much depends on the temperature and soil moisture status at the time. Detailed measurements of the flux of dieldrin concentrations in air in and over a maize crop revealed a marked diurnal pattern whereby the transfer to air occurred only during the daytime in a well-defined cycle peaking about 11.00 h and probably closely related to insolation and water movement and loss from the soil (Parmele, et al., 1972).

FACTORS INFLUENCING VOLATILISATION

The physical principles underlying volatilisation have been well described and discussed by Hartley (1969),Hamaker (1972) and Spencer et al. (1973). Although most of the important principles involved are probably recognised, the structure of interactions of the individual factors has been less well analysed. Difficulties are encountered in attempting to deduce from the basic properties of chemicals, substrates and deposits how they will behave amid the dynamic influences that occur in natural out-door environments. The degree of volatilisation affects not only the persistence of pesticide deposits but also their redistribution within the target area and the environment at large.

As with other chemicals, each pesticide has a fundamental tendency to become distributed between the liquid, solid and gaseous states of matter in its environment. Its distribution between phases will accord with its affinities for each and redistribution will continue in a static, closed system until an equilibrium is reached between the concentrations of the pesticide in each phase. This is discussed in greater detail in the complementary papers of this Session of the symposium. Suffice it to say that the rate of transfer of pesticides from one phase to another is directly related to the difference between the concentration in each phase at any moment and the equilibrium concentrations for the system. Transfer from one phase to another is a passive, diffusion-controlled process which, in practice, is generally enhanced by mass movement of the air and/or liquid phases.

Nature of chemical: For the present purpose it is assumed that the chemical is relatively stable, or that the physico-chemical properties of its immediate breakdown products can be used in the same manner as those of the parent compound to estimate the importance of volatility on overall persistence of the deposit. Physico-chemical properties of a pesticide molecule determine its potential behaviour in any system. They can be determined by appropriate methods, and obey well-understood physical principles.

The *molecular weight* (M) of most pesticides is between 90 and 400. Since the rate of loss of a pesticide by evaporation in standard conditions of ventilation is approximately proportional to $p\sqrt{M}$, where p is its saturation *vapour pressure*, differences in M can only account for about a two-fold difference between loss-rates, a very minor factor. The amount (g) of vapour that can be held in a litre of air (saturation vapour concentration: SVC:g/l.) is, however, approximately $M/22.4 \times p/760 \times T/273$ where T is the temperature in ^{o}K, and in this context differences in M may account for up to four-fold differences in amounts moved by mass transfer in air, as by wind. The SVC of any pure substance is for practical purposes independent of the composition of the disperse gas phase at any given temperature. It increases markedly as p increases with temperature and p is therefore the most important property determining the potential of a pesticide to evaporate directly into air from an inert surface. In practice, this ideal may not often occur. The pesticide will most usually be on or in a substrate which is not inert so that its SVC will be less than the theoretical value. The *solubility characteristics* of the pesticide (approximately referred to as polarity) become important in modifying the saturation vapour pressure. Relatively non-polar pesticides have an affinity for, and dissolve in, waxy (lipophilic) surfaces of plants, insects and soil constituents. The physico-chemical structure of the pesticide molecule also determines its potential for being adsorbed on solid phase surfaces in the polyphase system within which it will normally be operating. The combined effects of both its potential to dissolve in a liquid phase and to be adsorbed on surfaces of solids in the same substrate system is to reduce p, and therefore the SVC, and so to reduce its volatilisation to less than the expectation implied by its vapour pressure and molecular weight.

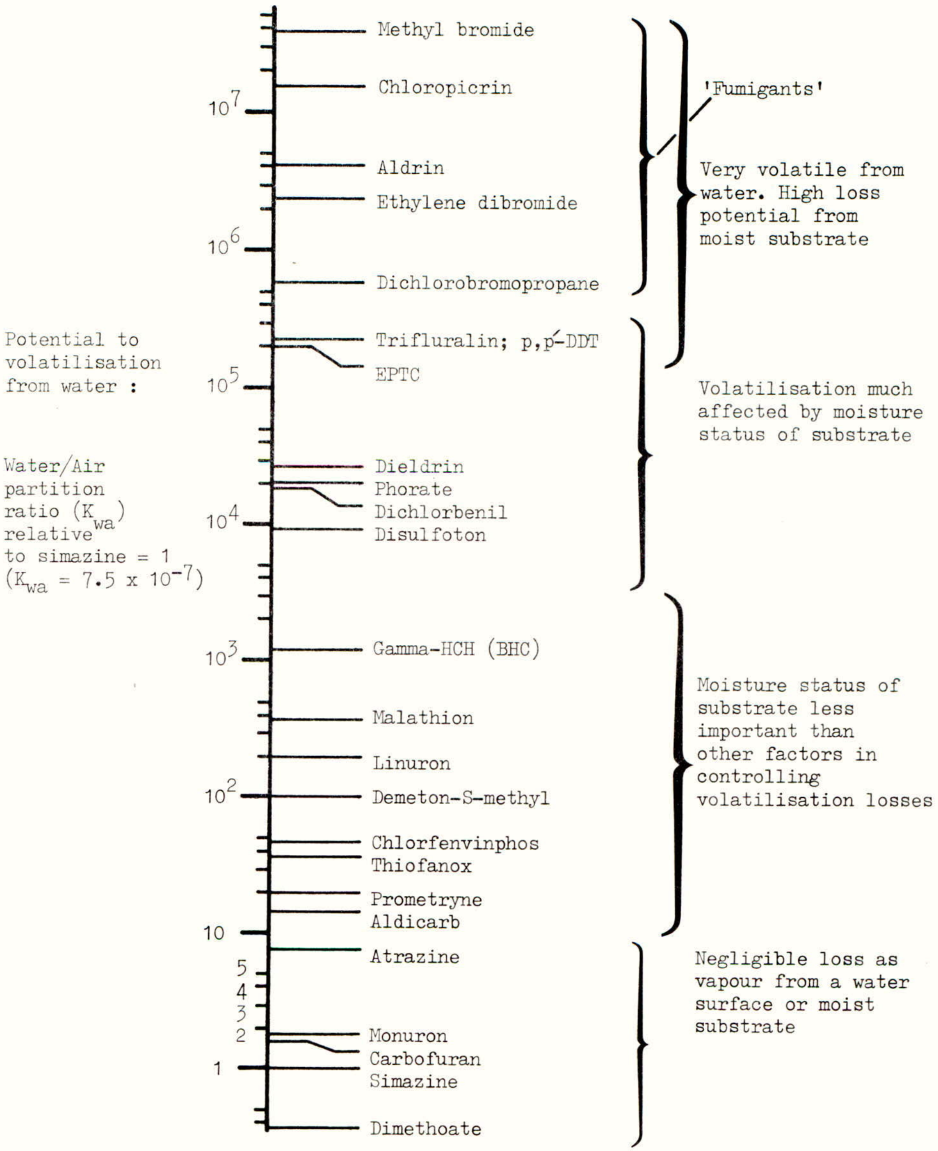
Nature and state of substrate : Few substrates on which pesticides are deposited are inert, not interfering in any way with the volatilisation behaviour of the pure pesticide. Even glass is slightly adsorptive. The complex waxy microstructures coating plant and insect surfaces affect the behaviour of pesticide deposits. The nearer the chemical properties of a surface wax are to those of a pesticide the more readily will the chemical diffuse into, through and across the surface. 'Like substances dissolve in like', so that relatively non-polar pesticides tend to be dissolved in and have reduced SVC's over relatively non-polar waxy surfaces.

Soil comprises a very heterogeneous mixture of mineral and organic materials. The organic matter may participate as an adsorbent, or even as a solvent (residual lipoid waxes from degraded organisms) for the pesticide. Pesticides disappear as vapour most rapidly from sands or soils containing little organic matter and very slowly from soils that contain a large proportion of organic matter. In soils containing little organic matter, adsorption onto the mineral complex, particularly clays, is an important factor affecting volatilisation. The vapour concentrations of pesticides are greatly reduced over most agricultural soils, and their moisture status is a most important modifying influence. In wet soil the interface for evaporation is water-film/air, not soil-particle-surface/air or pure pesticide/air. Water molecules compete more successfully than the pesticide molecules for the active adsorption sites, and therefore moisture reduces the sorptive tendency of soil or other substrate. The "co-distillation theory" developed to explain apparently enhanced loss of DDT or certain other pesticides from water surfaces has now been discredited and is not needed to explain why most pesticides are lost much more rapidly from wet than from dry soils. Moisture flux from soils may, however, be a reliable guide to the likely flux of pesticide vapour (Hartley, 1969; Parmele,*et.al.*,1972) since the same environmental factors affect both. Volatilisation from a water/air interface is very common and Fig. 1 illustrates the range of potential of various pesticides in this respect. The logarithmic scale is relative to simazine = 1 and contrasts several of the more persistent *s*-triazine and substituted urea herbicides with compounds such as trifluralin which is notoriously volatile when not promptly incorporated into soil but relatively persistent after incorporation. Four recognised soil fumigants have a potential to volatilise from water 6-7 orders of magnitude greater than that of simazine, and this sets the range of water/air volatilisation potential between pesticides. The relatively high water solubility of demeton-S-methyl and malathion should suppress the tendency for either to volatilise from a water/air interface, suggesting that in moist soil decomposition rather than volatilisation, or from plant surfaces direct vapour loss to the atmosphere from dry deposits, should be a more important route for loss. The relatively high potential for DDT to be lost from a water/air interface seems to conflict with its low vapour pressure (1.9×10^{-7} mm Hg at 20°C) but it is explicable by its very low water solubility (c.1.2 µg/l.) Its water/air partition ratio is thus about 320/1 compared with 75 million/1 for simazine. However, the relatively high potential of DDT to be adsorbed will normally greatly suppress its vapour concentration and, being chemically relatively stable, DDT is therefore relatively persistent in soil. In fact, most is probably 'lost' as p,p′-DDE which is about 8-9 times more volatile from soil than p,p′-DDT. In contrast, aldrin has a water/air partition ratio of about 18 but is much less adsorbed and it is lost fairly rapidly from soil as vapour, especially from moist soil. It is, however, rather surprising to find that its calculated water/air partition ratio is similar to that of such fumigants as chloropicrin or ethylene dibromide (Fig. 1). It was the detection of loss of aldrin vapour from soil that first led Harris and Lichtenstein (1961) to attribute much of the disappearance of this and certain other organochlorine pesticide residues to vapour-loss. During the early 1960's evidence of vapour loss of herbicides from soil was also accruing, particularly concerning EPTC, allidochlor, trifluralin, propham and chlorpropham, showing how temperature, moisture, cultivation, wind, cation exchange capacity and organic matter content of soil can greatly influence loss to the atmosphere.

Nature of deposit : An important feature to bear in mind with pesticide deposits is that they are usually distributed over very large areas of substrate surface. The greater the area of deposit, the more rapidly will a given amount of pesticide be volatilised until, in a confined system, the SVC is reached. Hence volatilisation of a film-deposit proceeds most rapidly while it is continuous. The rate of loss will change as it becomes discontinuous, and get progressively slower. Finely crystalline or particulate deposits generally disappear more quickly than those of large crystals or particles. Phillips (1971, 1974) has discussed these and other factors, presenting experimental evidence of the extent to which they modify rates of loss of deposits from inert and plant surfaces.

An important distinction must be made between pesticide deposits which remain undisturbed on the surface of soil and those which are mixed intimately into the soil. Even when pesticides are only 1-2 cm deep they volatilise very much more slowly than from the soil surface. Pesticide mixed deeply must first move to the soil surface to be lost into the atmosphere. Diffusion processes, particularly in water, are relatively slow and it seems that pesticides are moved to the surface mainly by mass flow of vapour in soil, or in solution in water rising to the surface (the evaporative 'wick' effect of Hartley, 1969). Relatively insoluble pesticides such as DDT or trifluralin do not dissolve in the soil water sufficiently for much to be carried to the surface in the mass flow of evaporating

Fig. 1. Potential of a selection of insecticides and herbicides to volatilise from water/air interface in the absence of substrate adsorbtion calculated from physical constants given mainly by Martin and Worthing (1974) for temperature 20 - 25°C.



water. In dry soil, both tend to be strongly adsorbed, and there is little tendency for them to be carried upward by mass flow of air created by pressure differentials through, and across, the soil matrix. Both chemicals therefore tend to be very persistent when incorporated into soil, particularly DDT (Edwards, 1966) which is not rapidly biodegraded. Numerous other factors concerned with the nature of the deposit and its distribution modify the tendency of pesticides to volatilise from the substrate on which, or in which, they are placed.

Environmental factors : Although the overall effects of environmental factors are readily appreciated, for instance the much increased volatility of compounds at high ambient temperatures, the dynamic and stochastic (distribution) characteristics have created a significant barrier to the application of physical principles to predict the persistence and volatilisation of pesticides. The relationship between vapour pressure and temperature is known for many compounds and it is also appreciated that wind movement creating a mass-flow effect carrying the pesticide rapidly away from the diffusion-restricted boundary layer over substrate surfaces is also important, up to moderate wind speeds. Relative humidity has, in some instances, affected rates of volatilisation of pesticides but it is not generally credited with great importance unless the affinity for water of either the compound or the substrate modifies adsorption (i.e. water vapour dissolves in the compound or substrate layer). An important feature controlling volatilisation, and one which may account for the marked diurnal flux in loss of dieldrin from soil (Parmele, et al. 1972), is the saturation deficit of the air with respect to a particular compound at the prevailing ambient temperature. Wind and turbulence are particularly important in lowering the saturation deficit. Diffusion through the boundary layer at the substrate/air interface is most rapid when the concentration of pesticide in the ambient air tends to zero as during mass movement of the air (wind).

REDISTRIBUTION OF PESTICIDE IN VAPOUR PHASE

The actual extent to which a pesticide can redistribute itself within a target area, or disappear as vapour is not known. Although many pesticides appear not to be very volatile, nor to have particularly high SVC's, the opportunity for the continuous loss of vapour into air means that it can transport considerable amounts of many pesticides from a source to a sink. Residues of dieldrin in maize foliage probably arise by vapour transfer from dieldrin in the soil, rather than by translocation up the plant from the roots. This is an example of equilibration of the chemical between phases; the concentration in the air is higher than the corresponding equilibrium concentration on the plant surfaces so that vapour moves onto the plant to achieve the appropriate partition equilibrium. In a recently treated crop, much of the foliage will have near-zero concentrations of pesticide, thereby attracting the pesticide from the vapour phase. It seems likely that a considerable amount of redistribution of pesticide in the vapour phase must occur within the crop canopy. This ability of crop plants to 'scavenge' pesticide vapour from the atmosphere is perhaps best recognised in the damage caused by vapour-phase transfer of esters of certain growth-regulating herbicides. However, pesticides are only transported as vapour from one point (of high concentration) to another (of low concentration); biological activity can only occur after the vapour has condensed or been sorbed onto, or dissolved in, target surfaces.

Although the absolute volatilisation behaviour of pesticides cannot yet be very accurately predicted, sufficient observations exist on chemicals representing ranges of properties for comparisons to indicate the likely behaviour of new compounds with adequate precision for many practical purposes. To state that a new pesticide behaves similarly to, say, trifluralin in soil makes use of much existing information to provide helpful guidelines of immediate practical value.

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PHYSICAL PROCESSES ASSOCIATED WITH FORMULATIONS

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Summary The persistence of deposits and biological effects of pesticides depends upon the physical processes which control the initial dosages, any redistribution after application and the transfer of chemicals to the pests. Ways in which the characteristics and constituents of the main types of formulations can influence these processes are discussed.

INTRODUCTION

The term persistence can refer to the way in which the amount of active ingredient changes or to the duration of a biological effect (they need not be simply correlated) and either can be modified by formulation. Various basic physical processes, such as evaporation, solution, adhesion, absorption, and adsorption are those which are important in situations discussed in other papers, namely those at surfaces, in solution and in the vapour phase. Therefore rather than deal with the processes as they affect various formulations I have chosen the opposite approach and have taken the different formulation types in sequence. A possible sub-division which is relevant to the title of this symposium is between those whose main function is to transport and distribute the chemical in an efficient manner: solutions, emulsions, water-dispersible powders and dusts and those which are intended to control persistence, such as polymeric matrices and capsules. The latter are described in much greater detail by other speakers but will be mentioned briefly because they are the main examples of such formulations.

Many comparisons have been made on the effect of formulation on persistence but it is not easy to find examples which are simple to interpret in terms of physical processes. The difficulty lies in the complexity of the inter-relationships of pest, chemical and environment in space and time and to the varying relative importance of the various factors depending upon the particular case which is being examined. Some effects have been investigated in detail, for example, the influence of particle size on insecticidal activity, the behaviour of sprays on vegetation and dispersal from granules but many have not. Examples are the adhesion between deposits and surfaces and the way this controls both persistence and toxicity or the effect of deposit constituents on passage of chemical to, over and into the pest. There are also areas where a large amount of work has been done, such as the effect of surfactants on herbicide penetration, without any clear picture emerging (see for example the review by Hull (1970)).

GENERAL COMMENTS

The initial dosages decay by various means such as evaporation, chemical break-down, abrasion, leaching and adsorption and absorption onto and into surfaces while those on vegetation are also diluted by plant growth. Each process is further influenced by the climatic variables of temperature, humidity, air movement and rainfall (see David (1959) for a useful summary).

At any given time during the life of a deposit the biological effect it produces will also depend upon the intrinsic toxicity of the chemical to the pest; the physical characteristics of the deposit, such as liquid or solid, crystal size and shape, packing of the particles from a suspension, adhesion of particle to particle and particle to insect and competitive processes which are occurring at the same time and reduce the amount of chemical available to the pest, for example diffusion in other directions.

Graphs have been published, for example by Gunther in the 1950's and discussed by him (1955, 1969) and more recently by Phillips & Gilham (1971) which show in detail the rates of loss from various deposits and surfaces. It is common for the rates to change markedly during the life-time of a deposit. They can be of zero order for high dosages but become dependent in varying ways on the mass or concentration remaining as the latter fall. The changes probably reflect the heterogeneity of the spray deposit itself as well as altering ratios of chemical to the effective area of the substrate. Phillips has observed double as well as single exponential rates and even those which follow a logistic equation because there is an initial lag. If decay plots are sufficiently detailed they may be used to identify formulation-associated processes and factors which are important in the life of the deposit. They are obviously very relevant to such matters as total crop residues but would be of greater value in interpreting variations in biological activity if the kinetics of pesticide-pest interactions were also known and associated with various stages of loss. These, however, are relatively unknown.

SOLUTIONS

There may be additional components in these formulations but the main influence on the persistence of the active ingredient is exerted by the solvent or solvents. They will affect atomization, when spraying is the method of dispersion; changes in the size of air-borne droplets and so their size and distribution when they reach the sprayed surface; spreading of the drops; penetration into porous substrates and, if the solvent is persistent and remains with the chemical, its evaporation, redispersion and biological activity. If the solvent is water and the target vegetation the spray will probably be applied at medium and high volume rates and include surfactants to improve wetting. Persistence will depend upon the retention of such sprays and this is a subject more conveniently dealt with under emulsions and water-dispersible powders which are invariably water based and contain surfactants.

Solutions containing other solvents than water are becoming popular as a result of the interest in low and ultra-low-volume techniques. They are often derived from petroleum but many recent formulations contain other chemical types either as primary or secondary solvents. Their volatility must be low enough for at least part of the emitted spray to reach the target and so it and other properties such as viscosity and surface tension will control drop size and so impaction, spreading and penetration of substrates. Even if the solvent soon evaporates from the spray residue the rate at which this happens can influence the crystal size and habit of the pesticide, if this is a solid, and these variations in structure of a crystalline deposit will have their effects on activity and persistence. Small concentrations of polymers and resins in a given solvent also modify crystal growth.

If a solvent has a very low volatility so that it remains with a pesticide for at least the time during which control is needed it can have two main influences on persistence. The rate of evaporation of the active ingredient is reduced and a solution often has a greater activity, certainly with insecticides, than that shown by the same amount of material in a dry deposit.

This increased biological activity is due to a much greater transfer of insecticide from deposit to insect since non-volatile solutions are usually comparatively viscous and adhesive. Evaporation of pesticide is commonly exponential since it is concentration dependent. It is also often suggested, following Raoult's Law, that a very high molar fraction of solvent is needed to produce a substantial improvement in persistence and this would limit the usefulness of such a formulation but this high dilution is not always necessary. For instance, 25 to 40% solutions of endosulfan have half-lives which are up to 4 times longer in low-volatile solvents such as the longer alkyl-chain phthalates or vegetable oils compared with the dry deposits left by volatile solvents. There are probably specific diffusion rate effects as well as reduced vapour densities which themselves are not in exact proportion to molar fractions. Active chemicals do not have to be completely in solution in low-volatile solvents to improve persistence and activity. There can be advantages from formulations of suspensions in poor solvents or, a situation which is equivalent, solutions in mixed solvents from which the good solvent evaporates and leaves the chemical to crystallize or separate in the poor solvent. In either case rates of loss should be more uniform as a result of the constant concentrations in solution.

EMULSIONS

Some of the comments on solvents and solutions also apply to emulsions. Potentially any solution could be emulsified but the solvents used in pesticidal emulsions are normally there as simple carriers and not intended to alter activity or persistence. Exceptions are the oils of very low volatility used in treating fruit trees where the oil is the active component. The more usual emulsified solvents are always less volatile than water. Consequently there is a changing ratio of oil to water as the latter evaporates and often an inversion of phases before an oil film remains. The exact sequence of events will depend upon the types and concentrations of surfactants which are present and could well modify the resultant deposit. Finally the solvent itself evaporates and the rate at which this happens can again change the crystal size and habit of solid insecticides as mentioned for solutions. There have been few detailed investigations of these phenomena.

A main distinguishing feature of emulsions compared with most solutions is, of course, the presence of surfactants. These influence distribution and retention on vegetation and penetration into leaves, soil and other porous substrates. They are therefore important factors in determining the size of initial deposits, their persistence and their redistribution. Much theoretical and experimental work has been devoted to the subject of surfactants and spray application, especially by Furmidge and his co-workers and is too extensive to be adequately considered here. Particularly useful summaries have been provided by Johnstone (1973) and Ford et. al. (1965). Briefly it can be noted that there are optimum wetting agent concentrations for a particular surface which will give the greatest retention. At lower concentrations there is reflection and roll-off while at higher concentrations drops will coalesce and drain from the surface too readily. There may be preferential deposition of the dispersed phase at high volume rates and this can also depend upon emulsion stability with low stability giving the greater deposits.

A useful survey of additives, including surfactants, in herbicide formulations has been provided by Kanellopoulos (1974).

Surfactants have also been used in special formulations where they are used to solubilize active ingredients. On dilution these can produce suspensions or remain solubilized. Either way they are likely to modify the properties of the deposit and so persistence.

WATER-DISPERSIBLE POWDERS

The particle-size distribution of solid pesticides in these formulations is determined during manufacture and alterations in this distribution might seem to be an ideal way of controlling persistence. Unfortunately, of course, such changes would also have other, usually unfavourable, effects. Persistence will certainly be extended by increasing particle size and so reducing the rate of evaporation which is a main cause of loss from many spray deposits. Leaching would also be reduced. Such a change however would also make uniform application more difficult and in most cases reduce activity. In fact a suitable size range for meeting the suspensibility tests given in many specifications and to give optimum activity on a variety of surfaces means that evaporation rates will be relatively high for a given chemical compared with thoseshown by less available deposits. There is an opposite relationship to particle size with adhesion and so resistance to abrasion. This increases with decreasing size and may extend life butcan also become strong enough to decrease activity on some surfaces.

The amount and type of inert carriers in water-dispersible powders varies greatly depending upon the properties of the active ingredient and the economics of formulation production. They could have an effect on persistence where they remain in a spray deposit but, of course, are not included for this purpose. The ratio of carrier to active ingredient certainly influences biological activity but this is a consequence of changing opportunity for pick-up of active particles. Deposits with a high proportion of carrier are less effective. A longer residual life might also be expected both because of the greater thickness of deposit and consequent reduction in surface area and by a reduction in vapour density of pesticide mixed with carrier but this possibility does not seem to have been investigated.

The surfactants needed in these powders to promote wetting and dispersion can change persistence in various ways. As with emulsions they control gross spray retention on vegetation and, after the spray has dried, its subsequent resistence to removal by rain. Deposits from suspensions can be more sensitive to rainfall than those from emulsions. The preformed particles can be re-suspended in the presence of surfactant residues whereas the dried-out active ingredient solids of emulsions are not so easily redispersed. This is one reason for emulsions being preferred to dispersible powders for tsetse fly control in areas of high rainfall. Resistence to rain is not so important in dry regions and since the deposits from powders have a greater toxicity they would be the formulation of choice.

It might be expected that the influence of a surfactant on activity and persistence of suspensions would be reduced when porous surfaces are sprayed. Most is dissolved in the water and can drain away from the solid particles. However enough remains attached to the active ingredient to greatly increase its adhesion to the substrate when the water has evaporated and so reduce availability to many resting and walking insects. If the active ingredient is a liquid the surfactants also displace it from the carrier and form an emulsion in the water phase. They may therefore be said to modify persistence indirectly. When such a mixture is applied to a porous surface most of the pesticide is carried into the substrate with the water and very little remains in the surface deposit which is available to the pest. A solid insecticide stays in the surface deposit and gives a persistence more dependent on its own volatility properties. Formulations have been described in the patent literature where this difficulty is reputedly overcome but do not seem to have been produced on a large scale.

DUSTS

The initial deposition is so inefficient that they start at a considerable disadvantage when compared with sprays in that the initial dosages are low. Deposition can be improved by giving the particles a negative charge but the equipment for doing this is not common in pesticide applications. Once suitably small particles have reached a surface however they can adhere well and there are no surfactants to promote redispersion in rainwater for example. Dusts usually contain low concentrations of pesticides. Presumably the high ratio of carrier will encourage both absorption and adsorption of the active ingredient and so increase persistence although reports of work on this particular aspect have not been found.

POLYMERIC MATRICES

This is the most extensively developed class of formulation by which control over concentrations in media such as air, soil or water can be obtained. They may also be used to maintain pesticides on surfaces which are subject to excessive wear and tear that conventional formulations could not withstand or because they can replace non-pesticidal decorative surface coatings. Their properties are described elsewhere in this symposium but they can hardly be omitted from a survey of ways in which formulation can influence persistence and perhaps a few general observations can be allowed here.

Many devices have been claimed and patented in recent years. They combine such chemicals as insecticides, fungicides, molluscicides, pheromones and attractants with paint and lacquer bases, polyvinyl chloride, polythene, rubbers and resins or may even have pesticidal moieties covalently bonded to polymers. Most are relatively large in size, for example strips hanging in air spaces or extended coatings on surfaces but some are dispersed as pellets or even fine suspensions.

The polymer itself can disintegrate and release the active ingredient but it more often remains entire so that the chemical must diffuse outwards. The ideal rate of release would be a constant mass in unit time. In many devices the rate is diffusion controlled and so decreases with time as the concentration falls although if the active ingredient is present as a separate phase, liquid or solid, the rate is much more constant. Rates at a given concentration naturally depend upon the particular system used. Control can be obtained by choice of polymer type, modification of the polymer especially by cross-linking, adding non-polymeric components such as plasticizers and altering the geometry of the device. The polymer may be already formed before the pesticide is added or can be produced in monomer-pesticide mixtures.

In these ways diffusion of the pesticide can be controlled over a very wide range. At one extreme it is little less than from a conventional formulation. At the other the rate of loss is negligible and the pesticide is effectively locked-in. A simple example is provided by insecticides which are active in the vapour phase, such as gamma-BHC, in urea-formaldehyde lacquer films. Films containing a high ratio of polymer to plasticizer are hard, retain the chemical indefinitely and are biologically inactive. Outward diffusion, and so biological activity, increases as the ratio of plasticizer increases and the film is more flexible and less highly cross-linked. This illustrates a requirement for many insecticides used against non-chewing insects which seems self evident but is not always overtly recognised: an insecticide must be able to diffuse from a particle or a film of polymer if it is to have a biological effect. The polymer cannot diffuse.

A suitable value for rate of loss is clearly dependent upon the way in which the pest will acquire a dose which causes death or desired response. It may also be stating the obvious to notice that the active ingredient is diffusing all the time whether a pest is there or not but this has implications for the kind of situations where these formulations and, incidentally those based on micro-capsules, should be used. The chemical does not accumulate on the outside but evaporates into air, dissolves in water, or diffuses into soil or other porous substrates. Where this diffusion into outside media is necessary for control the devices can be a very suitable and adjustable way of prolonging action by metering pesticide. Where a potentially lethal concentration must be maintained in a spray deposit and pest exposure times are relatively short, say minutes or hours rather than days, they are less suitable and often markedly inferior to conventional formulations where a greater mass of chemical is more readily available.

CAPSULES

Another important method of controlling persistence is by micro-encapsulation. Again this will be described in another paper but a few comments may be appropriate. Many of the considerations already noted with polymeric matrices apply but an advantage of capsules in a micro form, say up to 50 micrometres or so in diameter, is that they are prepared in a slurry form already suitable, after dilution, for application with the usual spray gear. Capsule walls may be meant to disintegrate and release the contents but many have walls which are intended to remain and release the active chemical by diffusion. Control of this diffusion is by choice of polymer, cross-linking, capsule size and relative wall thickness. An example of the range of control is provided by some recent tests on the release of fenitrothion, malathion and diazinon through walls with various degrees of cross-linking. Evaporation rates of the insecticides into the surrounding air varied from a value which was very similar to the same components in water-dispersible powder deposits to negligible rates. It was interesting that the rates for different insecticides through the same wall compositions were not in the order of their normal, free evaporation rates and suggest some specific insecticide-polymer effects. Other factors include the nature of the core (neat chemical, solution or suspension) and the effect of diffusion of air or water inwards. As with polymer matrices rates of loss should ideally be tailored for a particular use so that a pest will receive a toxic dose during its time of contact with the surrounding air, water or soil. This can be extremely difficult to derive by calculation since the outside concentration depends upon such events as decomposition, evaporation, adsorption, solution and other dispersive processes and field trials are obviously essential in these complex situations.

GRANULES

The term 'granules' refers to size and not composition but most granular formulations are based on such inorganic materials as clays. Organic polymer-based granules have been used more recently especially with mosquito larvicides but will be discussed elsewhere in this symposium. A valuable review on pesticide residues from granules has been given by Walker (1971).

Granules have been most often employed for treating soils and water. They do have advantages over conventional formulations for these purposes, especially as regards application, since they are safer to handle, reduce drift hazards and can be placed on the target more accurately. They can also be prepared in ways which allow various rates of release of the active chemical and so could potentially be modified to give the optimum performance for a given situation. Where control of release rates is important there would appear to be considerable scope for this kind of granule based on inorganic carriers because a large number of suitable ones are available. These may be preformed and subsequently impregnated or mixed with pesticides and formed into granules of suitable sizes. Additives can be easily included to control diffusion, wetting and breakdown and although granules are more expensive to make and transport than conventional formulations they should be cheaper than other controlled-release devices.

Unlike the situation with fine particulate deposits the pesticide must move from the inert carrier before it can act. This movement may be through volatilization, solution in bulk water or migration in surface water films and should be controlled by characteristics of the pesticide, carrier, any additives, environment including soil and climatic variables. Furmidge (1972) has provided a very useful guide to the general principles of granular formulation and Osgerby (1972) has calculated the theoretical rates of loss from some basic classes of formulation, including controlled-release, into water and soils. Granule size, dosage, concentration, density and release characteristics can all play their part in determining whether and for how long a biologically-effective concentration is reached but granule release rates are only important in soils when adsorption by the soil is relatively low. It follows that while granules, and controlled-release formulations in general, can give improvements they would need to be capable of a wide variation in release properties to suit given combinations of pest, pesticide and soil. Osgerby concludes that provision of such a wide range of granular formulations is not a practical possibility. Other investigators with granules in soils, for example Graham-Bryce et. al. (1972), support the conclusion that biological performance is determined more by the properties of the chemical and the environment than by the formulation.

Granules have been used for many years for the control of mosquito larvae and here the situation is probably simpler in that although silt or mud can adsorb dispersed insecticide it does not have the immediate and over-riding influence shown by adsorption processes in soils. There are many reports on the effect of variations in pesticide, carrier and additives but none of these have used the fundamental approach of Furmidge and his colleagues for granules in soils. The findings however do agree with expectation for the most obvious properties such as an increased rate of solution with decrease in size or with increased solubility of active ingredient in water. An interesting feature, demonstrated by Mulla (1960) and Mulla and Axelrod (1960) is the effect of the solvent used in impregnation of granules on release rate. Their suggestion that volatile solvents produce a superficial deposit which dissolves readily while the less-volatile carry the insecticide much deeper into the granules and so make it less available, combined with partitioning effects between solvent and water, seems reasonable. It is not so obvious why different carriers provide such a wide range of release rates but presumably they vary in porosity and disintegration rates among other things. Much less work has been done on disintegration than on solution from the intact granules.

ADDITIVES

Many of the formulations, including solutions, emulsions and water-dispersible powders, have been used with various non-toxic additives apart from those which are required for dispersion and application such as solvents, carriers, surfactants or thickening agents.

Adhesives are a common additive to improve rain-fastness and general resistance to abrasion. They include synthetic polymers, natural gums, oils, proteinaceous materials and even low molecular weight but hydrophobic compounds such as fatty acids. They certainly do increase persistence but often at the expense of reduced biological activity. How much this reduction in activity will counterbalance the value of an increase in persistence will depend upon the pest being controlled.

Other additives are concerned with chemical rather than physical processes but can perhaps be mentioned since they are constituents of formulations and are intended to increase stability and persistence. They include stabilizers to inhibit light and oxygen-promoted and other decomposition reactions. Various workers have used light-absorbers and anti-oxidants with labile compounds such as the pyrethroids and have been able to demonstrate a protectant action. Some of these formulations have been patented and may have been used on a commercial scale. One of the great difficulties in this kind of system is in matching the properties of the additive with those of the pesticide so that the former lasts at least as long as the latter. The protectant must also be in intimate contact with the pesticide if it is to work efficiently and be active at low concentrations. This means that a light-absorber, for instance, should re-emit the absorbed light at a different non-damaging wavelength and not suffer decomposition itself. Although light and oxygen protectants have not been much used with conventional formulations they could very conveniently be added to controlled-release types such as polymer matrices and capsules.

Synergists can be present in substantial amounts, at least equal in weight to the active chemical. Their potentiation of the insecticidal action will itself serve to increase the toxic life of a deposit but they are also likely to chemically and physically stabilize the chemical and so extend its physical life.

It is unlikely that the stabilizers needed in some formulations to give adequate shelf life will also extend persistence in deposits. They are usually volatile or water-soluable, for example, epichlorhydrin, glycols, urea or hexamethylenetetramine. Many stabilizers have been added to dichlorvos-polymer strips but whether they are protecting dichlorvos or changing its emission rate is not clear.

CONCLUSIONS

Persistence can be influenced by the constituents and characteristics of conventional formulations and even controlled by some of the newer ones in favourable combinations of pest, pesticide and environment. It is still preferable to use formulation to improve the performance of a pesticide which already has the appropriate basic properties for a particular application and not to overcome serious deficiencies in these.

Future research and development work should give more attention to the ways in which the toxicant is transferred from the formulation residue to the pest as well as to the purely physical aspects of application, persistence and dispersal on the one hand and toxicological responses of the pest on the other. Gerolt (1970, 1975) has been showing the way to deal with part of this problem, the movement of insecticides over and into insects, and perhaps his approach can be extended to a general study of the influence of formulation variables on transfer and absorption.

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