THE PERSPECTIVE OF PERSISTENCE

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Summary   The term persistence, as used to describe the behaviour of
pesticides, is interpreted in both a positive and a negative sense. A
definition of the term is wanting. In this opening lecture, an attempt
is made to orient the term persistence to agricultural practice in
order to bring the kinetic aspect of degradability further into the
foreground. The discussion is centred chiefly on the agricultural aspects
of persistence, and in particular on their relationship to the formation
and fate of residues. The principal parameters, indigenous and external,
which influence the degradation or the persistence of pesticides are
discussed in relation to the question as to which models might suitably
be used in laboratories for measuring or predicting persistence phenomena
occurring in nature. The paper should be interpreted not as an estimate of
an ecological situation but as a stocktaking of possibilities likely to
contribute towards a more comprehensive evaluation of the behaviour of
pesticides.

INTRODUCTION

Any likely perspective of persistence is at present obscured by two contra-
dictory facts:

1.   The term persistence does not have a set meaning.

2.   While being overabundant, the information on what might be
     termed persistence nonetheless contains too many gaps.

For an individual to undertake an attempt to screen and classify the phenomena
of persistence described in the literature is almost tantamount to tackling the
impossible. One could try to classify the pesticides in groups – highly, moderately,
slightly and nonpersistent. But one would have to do this for plants, for soil, for
vertebrates, for invertebrates, for the atmosphere, for buffer solutions, for
ponds, lakes and streams, for the different seasons and for different climatic
zones, for target and non-target substrates. In the process, full account would
always have to be taken of analytical, biological and ecological aspects as a
joint criterion of assessment. Yet to attempt such a classification say in respect
of soils only would be highly complicated since the question immediately arises:
for which soil types, for which pH, for which moisture status? How should the
plants or how should the animals be subdivided?

I hope you will agree to my interpreting the title of my subject as signifying
some aspects of persistence, and viewing these perspectives chiefly through the eyes
of the residue chemist. I wish to express some thoughts on problems associated with
the definition, understanding, measuring and "prediction" of something that we
might call - or no longer call - persistence. It is simply an attempt and cannot be
more than that, and I hope it will prove as successful as possible.

It was the wish of the organizers of this Symposium that it be concerned more
with the implications of persistence in agriculture rather than with environmental
and toxicological aspects. This was a thankworthy decision, considering that the
nanogram concentrations of DDT in the environment still have the effect of arousing
scientific stimulus. In fact I doubt whether they have the alarming effect often
ascribed to or expected of them. All that is certain is that they can be analysed
easily.

Perhaps this Symposium will provide us with an opportunity of finding answers
to questions like:

What do we want to understand when we speak of persistence?

What criteria should be applied for assessing the phenomena of persistence?

Is there a necessity for "abolishing" persistence?

How can we study in a model what occurs as persistence in nature, in
other words how can we measure or predict it?

I shall try to explain why, in my opinion, these questions are justified.

DEFINITIONS

Persistence is something ambiguous. It is constantly encountered in two
distinct forms, one which is sometimes evil and one which is sometimes good, like
the split personality of Dr. Jekyll and Mr. Hyde in Robert Louis Stevenson's book.

The term "persistent" when used in a negative sense characterises both some-
thing static, that is when a compound is found at a location or at a time where or
when it is not expected, as well as something dynamic, in other words when a
compound undergoes degradation at a slower rate than is seemingly necessary or
desirable. When the term is used in a positive sense, it is understood to be
synonymous with residual activity, thus expressing that a compound possesses the
effect ascribed to it not only a priori but is also capable of retaining it for
a certain period.

Users of a pesticide expect it to persist for a while and to act accordingly.
To fulfil its purpose, the pesticide must be present during the period B at a
concentration within range A (Fig.1). Thus seen, three types of compounds may be
distinguished. Type 2 is present at a sufficiently strong concentration throughout
period B. Type 1 also satisfies this condition but it must be applied with much
greater "specificity" for it to fulfil the desired purpose between points a and b,
added to which its degradation must proceed exactly according "to schedule".
However, it is obvious that Type 2 has substantial relevance to the environment. At
harvest time E_1, the residue levels are twice as high as those of Type 1, and they
continue to persist beyond harvest time E_2, when compound 1 has already disappeared.
Problems of this kind are minimal with Type 3, although a compound of this partic-
ular type must be applied repeatedly. This already indicates that the perspectives
of application and those of environmental protection cannot be harmonized optimally,
and compromises must be made in either the one or the other direction.

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There is no organic pesticide which is basically and completely non-degradable in the conditions under which agriculture is practised, in other words which persists in the sense of existing continuously. Pesticides which have reached the South Pole, no matter how, cannot be expected to degrade. Consequently, we are faced with the question of deciding which pesticides we intend to term persistent, provided we wish to uphold this expression. After all it is well-established and handy. An ecologist (Rudd 1971) interprets the term persistent by saying, "For practical purposes those chemicals that survive for only a few days - or even weeks - can be termed nonpersistent. Those that survive for longer periods - months or years - are called persistent. Both use and hazard depend on how long and in what form pesticide chemicals survive. A nonpersistent chemical not only "disappears" in a short space of time but it has no opportunity to disperse widely. On the other hand, a sizable fraction of the original deposit of a persistent chemical remains. These residues become scattered so that they are no longer found only on the area where applied... The major evidence linking biological effect in the field and environmental contamination is correlative, not experimental. Ecologists regularly depend on correlation between events to reach conclusion; experimentalists seldom do".

As an experimentalist, I hesitate to define the term persistence in an absolute sense. Certainly, a compound could be termed "persistent" when it takes longer than time x to undergo 90 (or 99) percent degradation, and be called "non-persistent" when it takes less than time y to do so. Terms like quasi-persistent, semi-persistent or slightly persistent could be applied to those compounds which degrade (almost) completely in a time ranging between x and y. A view of this kind was advocated by Holden (1975) who stated: "Persistence cannot be defined precisely, but it is doubtful whether chemicals surviving less than six months should be so classified. The term should, however, be applied to a chemical not to its presence in a particular tissue, or geographical location."

To do this would be an arbitrary act of little expediency, nor would it be justified considered from the very nature of the matter since it would mean ascribing to a compound the characteristic of persistence like a physical property. However, persistence is not an inherent property of any one compound but is simply the description of a compound's behaviour. When we examine the behaviour of carbofuran in silt loam at four different pH levels (Fig.2), then we see that it would certainly be difficult to decide whether this particular compound should be termed persistent or not.

From all this, it follows that the obvious course would be to abandon the use of the term persistence for characterising a compound in the absolute sense. Its use should only be permitted for describing the behaviour of a compound under given conditions or in a statement of comparison to the effect that under certain conditions compound A is more persistent than compound B. It would be better still to replace the term persistent as hitherto used for describing a syndrome by the term "slowly degradable" or "difficultly degradable". By doing so, the more concrete kinetic aspect of degradability would at the same time be brought into the foreground. Of course, even this does not relieve us of the necessity of defining the term degradability. But before we try to define it, we must be able to measure it.

In the early days of residue analysis, Gunther Blinn (1955) clearly stated, among other things, "There appear to be two principal types of residues on and in plant parts, and doubtless also in soils; these are termed degrading and persisting residues. Both types of behaviour are illustrated in Fig.3. With degradation as portrayed by curve A, the fraction of the original amount of unchanged insecticide remaining at a given time after application is the same regardless of the magnitude of the initial deposit, under reasonable constant conditions and on the same variety of plant. Curve B is also a degradation curve. With persistence as portrayed by

curve C, a new and lesser slope is established. This new straight line represents the slow disappearance of the insecticide from within the plant part. Obviously, these two types of behaviour overlap, but it is convenient to consider that degradation curves demonstrate pictorially the sum of the parameters usually classified simply as weathering, whereas persistence curves demonstrate enzymatic or other metabolically induced fundamental alterations of the parent molecule. These two types of behaviour are collectively designated as disappearance behaviour." A typical degradation curve may be preceded by a more steeply sloping curve (X in Fig.4) which represents the physically displaced insecticide during the initial period after application. Although this more steeply sloping portion of a total disappearance curve may be frequently observed, the conditions under which it predominantly occurs seemingly have not yet been systematically elucidated.

Probably the first reported recognition that persisting insecticide residues obey first-order reaction kinetics is that of Gunther et al. in 1946, who found that the percentage decrease of DDT residues with time was independent of the quantity of DDT originally deposited (cited in Gunther and Blinn 1955, P.138). However, these interesting relationships do not seem to have received any particular widespread attention during the 1950's. In the meantime, they have become common knowledge. The majority of all pesticide degradation processes seem to obey, under natural conditions, a rule which can be expressed as an exponential function (Fig.5). By applying logarithms, the known relation for first-order reactions, $\log r = \log r_0 - k_1 t$, is obtained, in which k_1 represents the degradation rate (the slope of the regression line and always negative in sign) and r_0 is the apparent initial deposit obtained by extrapolating the line back to zero time. This form of representation is very convenient and permits the degradation rate to be characterised by the very handy term "half-life" (c.f. van Dyke 1975) and to be calculated easily. It is given by $\log 2$ (i.e. remaining fraction = 1/2) : k_1 = 0.3 : k_1. The time taken for a compound to undergo 90% degradation is given by $\log 10$ (remaining fraction = 1/10) : k_1 = 1 : k_1, etc.

It is, however, astonishing to note that these simple relationships have not been put to advantage for making quantitative determinations of degradation rates and, in particular, comparative assessments of degradation behaviour. Hoskins, working at the University of Berkeley, was the first to prepare, in 1961, a comprehensive study for expressing the persistence of insecticidal residues on plants. He evaluated available residue data for 47 insecticides by applying the relation I just referred to, and suggested that a distinction should be made among fast ($k_1 > 0.1$), medium, and slow ($k_1 < 0.01$) rates of loss (Hoskins, 1960/61; 1961). According to the definition of Hoskins, the half-life for rapidly degrading compounds would be < 3 days, for slowly degrading compounds >30 days, with the respective times for 99% degradation amounting to < 20 days and >200 days. Of course, these considerations can also be applied separately to the different steps of a degradation or persistence curve with a course possibly consisting of several parts. Table 1 provides an example of Hoskins' tabulation of his calculations. It seems a pity to me that hardly any use is made of this condensed and practical manner of summarizing and comparing (Table 2) degradation data. These relationships are also useful for detailed studies. If the effect of single parameters such as plant growth, evaporation, rainfall, etc. can be isolated by suitable experiments, even their separate effects can be calculated in the same manner (see also Hoerger and Kenega, 1972).

Little work has seemingly been devoted to investigating whether similarly frequent mechanisms of degradation basically exist, which could be expressed by relatively simple functions. It would, for example, be interesting to examine whether reactions which at first proceed very slowly and then at an increasingly faster rate, obey a power function. If so, they could be depicted, for example, by parabolic branches having the vertex r_0. Through the choice of appropriate exponents n and coefficients m, a behaviour of such kind theoretically can be depicted by any parabola (Fig. 6). Whether dependence upon such a functions is given can be

confirmed by establishing whether a straight-line is obtained when the remaining
residue $(r_0 - r)$ is plotted versus the time on loglog paper. The slope of the
straight-line gives the exponent; the value for m corresponds to the point at which
the straight-line intersects the ordinate at $t = 1$, corresponding to the equation
$\log (r_0 - r) = \log m + n \cdot \log t$. The time for complete degradation $(r = 0)$ would
be given by $n\sqrt{\dfrac{r_0}{m}}$, so that this would also be an alternative way of suitably classi-
fying degradation rates when such types of reaction occur.*

Robinson (1973) proposed, although against the background of pharmacokinetic
consideration, that a compound should be termed persistent when, under certain
circumstances and at a given time, the ratio of lapsed time to biological half-life
(n) is equal to or smaller than 0.01. When η is greater than 5, the compound should
be termed non-persistent, with intermediate stages being called quasi-persistent
and quasi-non-persistent. This form of characterisation appears rather unusual be-
cause it is oriented to the half-life while the usual conception is that the term
persistence characterises the behaviour of a compound rather than the time at which
the behaviour is studied.

Without doubt, persistence is a behaviour. Whether it is desired or undesired,
will depend upon how a particular pesticide is expected to perform in commercial
applications. For example, a field of application in which persistence is highly
desired is in the malaria eradication programmes of the World Health Organization.
Problems are posed by the use of the term persistence in that it cannot be tied
down to certain absolute periods of time. In agriculture, a possible reference
period would be the growing season. Here the question of persistence is of practical
importance. Pesticidal compounds which continue to remain active beyond the growing
season may cause damage to following crops grown in rotation. Since it is certainly
not desired that any practised system of crop rotation, or for that matter its
abandonment, should be governed say by the type of herbicides used, such a defini-
tion of persistence would, however, be tantamount to a negative rating. It would
also meet with difficulties in the case of total herbicides which are expected from
the very outset to display "possibly high" persistence. It must also be borne in
mind that the length of the growing season differs for crops from one climatic zone
to another, added to which double-cropping systems are practised in some regions so
that here a completely different definition of persistence would be needed.

In the search for a definition oriented to agricultural practice, consider-
ation might be given to a proposal I should like to put forward, namely that the
characterisation of the degradation behaviour of a compound should be oriented to
its use. Assuming that a compound, as mentioned earlier (Fig.1), is expected to act
for a period B, it could be made a condition that upon expiry of period B the
compound is very largely degraded within a reasonable interval. Compounds which
satisfy this condition would then be "normally degrading" (or sufficiently persist-
ent) compounds, those which take longer would be "insufficiently degrading" (or
over-persistent), and those which are active for less than period B would be "non-
persistent". This line of thought could be applied just as well to the treated
object (e.g. the plant) as to its immediate surrounding, e.g. the soil. I should
like to explain this in more detail.

A pesticide must persist in order to act for a desired period. This property
which from the agricultural aspect is positive, is termed residual effect. At the
end of this period (Phase 1a), a further residueal effect is unnecessary; the
pesticide then persists, still possessing biological activity against the pest
target, but without its presence being needed any longer (Phase 1 b). However, it
may not always be possible for the two phases to be distinctly separated. Even after
the persisting biological activity has abated, the compound will usually still be

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* For a short review of other mathematical expressions which were proposed to
explain the disappearance of pesticides, see Edwards, 1972.

detectable by analytical methods for a certain time. During this time (Phase 2), it may still be biologically active against non-target organisms, and then assume the character of a chemical unnecessarily present in nature. Additional properties which the compound may possibly still develop during its continued existence, and which are detrimental to the environment, may even make its present undesired during this phase. I would refer to the entire time the pesticide is analytically detectable as the "practical existence time" (P.E.T.). To avoid confusion in terminology, the three phases should each be expressed by a different term, e.g. residual effect for Phase 1 a, pesticidal (biological?) persistence for Phase 1 b, and analytical persistence for Phase 2. The object of my proposal is to find a definition which is oriented to Phase 1 and uses the end of Phase 2 as the classification criterion.

The subject of persistence can only be discussed logically on the assumption that pesticides are applied according to what is termed good agricultural practice. However, questions pertaining to overdosing should not be overrated. A pesticide which degrades from 10 ppm to 0.1 ppm in 100 days when applied at the normal concentration also ought not to take more than 150 days to degrade to a level of 0.1 ppm when applied at 10 times the normal dose. Therefore, assuming that the pesticide is used as directed, its application will be made so that the biologically requisite concentration is present at time "zero" (Fig. 7). It corresponds to the analytically determinable initial value of the residues, the "depot", which we shall put at 100%. The pesticidal effect continues up to the end of period B (Phases 1 a + 1 b), when the pesticide is still present at concentration c_1 or c_2. When we refer to the P.E.T. of a pesticide as being that period of time the product takes to be degraded down to a level equivalent to 10% of the initial value, then we find that the practical existence time increases with the duration of activity (I versus II) and with the difference between the biological threshold concentration and the 10% residue level (I versus III); it is inversely proportional to the effective concentration range which is known or can be determined empirically (cf. Jeppson and Gunther, 1970). If we simply assume that the degradation proceeds steadily in accordance with a first-order reaction, then the P.E.T. of the residue can be estimated from the degradation in the range between 100% and the threshold concentration c during Phase B. The constant k_1 of the degradation rate is = log 100 − log c divided by the interval B. The time for a 90% degradation is then given by $1/k_1$ or $\dfrac{B}{2 - \log c}$. One can decide to choose the period up to 90%, 95% or even 99% degradation (t_{90}, t_{95}, t_{99}) as the criterion for the P.E.T. Table 3 provides some examples of the relationship between B, the threshold concentration c and the P.E.T. for 90%, 95% and 99% degradation.

A definition of persistence oriented to biological performance can now be formulated to suit our convenience. One could take any multiple of the time B as the threshold for a phenomenon to be called persistence. In other words, a compound could be termed ("over-") persistent when, for example it takes more than time 5 B to undergo 90% degradation. The requirements for "non-persistence" ("sufficient persistence") would then be satisfied in respect of the multiples of B given below the dividing line in Table 3.

Of course this approach is not devoid of problems. It is assumed that the effective concentration range is known and that degradation proceeds steadily. For degradation curves which at first have a steep slope followed by a gradual but steady slope (Fig.3, B + C), the principle of this approach can be upheld by correspondingly shifting the range given by B and the effective concentration parallel to the x- and y-axis. For degradation curves which first exhibit a lesser slope at a later stage of degradation (Fig. 4 , portion Z), the P.E.T. would have to be determined empirically and then related to B. At all events, such an approach or one similar in principle would have the advantage of uniting two essential parameters, the kinetic aspect with the agricultural need. The term persistence could, therefore, be relativized better, and a certain pesticide need be classified as "(over-)

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persistent" only under given conditions. A compound which is to be used for a certain purpose but is considered persistent on the grounds of this proposal, would have to be substituted by one which undergoes degradation at a faster rate. Such a model could be used also for establishing safety intervals.

No matter what one may agree on, for the practical purposes of this perspective I shall use the term "persistence" throughout my paper in its conventional catchword meaning.

PERSISTENCE AND FORMULATION

There has been no lack of attempts to formulate pesticidal compounds so that they will display longer residual activity than conventional products (Neogi and Allan, 1974). To achieve this, it is necessary to create, in addition to a freely available and hence biologically active amount of active ingredient, a depot from which the active ingredient, very largely unexposed to environmental influences, is released in a controlled manner. Its rate of release from the depot should be equal to that at which the freely available and hence biologically active ingredient disappears from its area of effectiveness. This latter condition is of great importance. If the rate of release is too high, the duration of activity becomes shortened or else excessively high amounts of active ingredient must be applied. If the rate of release is too low, the concentration of freely available active ingredient will soon fall below the effective threshold level so that no effect is produced even though there is still sufficient active ingredient present in the depot.

I should like to illustrate this by giving a few examples:

1. It is possible to formulate solid solutions of active ingredients in polymeric delivery systems from which the active ingredient is released by diffusion. With such systems, however, there is the risk of the rate of release at first being too fast and later too slow.

2. A steadier release can be achieved by encapsulating active ingredients. With this system, the active ingredient can be released by diffusion through the walls of the capsule. The rate of delivery can be controlled by suitable choice of the capsule material as well as by its thickness and porosity.

3. Steady release of an active ingredient can also be achieved by incorporating it in a matrix which, with progressive delivery of the active ingredient, loses its structure integrity or disintegrates with the result that new surfaces are exposed to the environment.

As the mechanisms of release and disappearance of a pesticidal compound may differ very greatly, it frequently hinges upon the prevailing environmental conditions whether the desired balance between these two factors is reached. Thorough field experiments must be carried out before it can be finally decided whether the level of success justifies the usually very much higher cost of such formulations.

A proposition more difficult than lengthening the duration of activity of fast-degrading pesticidal compounds is to shorten the longevity of persistent products. For example, DDT was formulated together with a compound which catalyzes its degradation upon contact with water. However, this does not provide any advantage when the active ingredient is already degraded before it has had any opportunity at all of producing its effect. It remains to be considered how ways and means can be found of then bringing an active ingredient into contact with a degradation catalyst once it has already performed its task.

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PERSISTENCE AND RESIDUES

Technical errors in analysis have also contributed towards the image that has been created of persistence. Included among these are, in my view, the false interpretation of phantom peaks, the demonstration of translocation and distribution of "residues" in the form of radioautograms, and the lack of attention many analysts devote to confirming the identity of allegedly found residues by means of other physical or chemical methods. "Persistence phenomena" on plants must be well understood and interpreted especially as residues are generally expressed as concentrations so that consequently it need not always be an indication of a genuine degradation when the concentration drops. The influence of individual factors, including plant growth, on residue decline constitutes a phenomenon to which little systematic study has been devoted as yet, even though such individual influence has long been known. Fig. 8 illustrates, for example, the influence of the stage of growth of clover at the time of treatment on the decline of residues. The effect of growth dilution can be so important that other smaller influences may not be noticed. The half-life on citrus fruits may, for example, differ by more than a power of ten depending upon whether the fruit was treated in spring or in late summer (van Dyk, 1975). A study of the effect of environmental factors on the disappearance of pesticides on tree fruits thus requires both fruit and leaf samples, because the effect of climate can only be obtained with mature leaf samples.

Persistence problems of a special nature are those linked with the question of the post-harvest fate of residues. Maximum permissible residue limits relate as a rule to the situation on the field at harvest time. Fears among the general public and also calculations, e.g. of the WHO (FAO/WHO, 1974), concentrate on the potential daily intake by which is meant that all residues amounting to the tolerance levels will indeed reach the mouth of the food consumer. This line of thought is unrealistic in most instances as total diet studies have repeatedly demonstrated. Studies on the distribution and the decline of residues during transportation, storage, processing and preparation of foods should be conducted more systematically and on a broader basis also in other countries. The importance of doing so is underlined by the fact that recent studies with dithiocarbamate residues have revealed that negative effects can also come to light during such procedures. Significant amounts of ethylenethiourea were formed during boiling or cooking of food containing ethylenebisdithiocarbamate residues (Newsome and Laver, 1973; Watts et al., 1974). Unfortunately, information about this special important aspect of persistence is scattered, and only a few review articles are available (Stobwasser et al., 1968; Kirchhoff, 1972; Geisman, 1975). Another area that has received little attention as yet is that concerning intentional removal of residues (Gunther, 1969; Burnside, 1974; Gomaa and Faust, 1974), e.g. also by composting (Müller and Korte, 1976), and more studies on it should be encouraged. The growing awareness that the actual intake of residues with the daily diet only seldom reaches the level of the toxicologically acceptable amounts may also make the task of legislators easier when it comes to granting approval of pesticides or establishing tolerances in such cases where good agricultural practice leads to residues which one would rather see at a lower level.

It would be desirable for closer contact to exist between legislators and analysts in some countries. Analysts tend to take pride in detecting increasingly smaller concentrations and reporting increasingly greater sensitivities for their methods. The legislator is all too inclined to follow the analyst into the realm of arithmetical acrobatics. It is all too seldom realized that persistence may also be a function of analytical performance and reproducibility in inexperienced hands. The quality of residue analysis results and their interpretation in the sense of a "good analytical practice" (see Bates, 1975) should be improved. Legislators should gain a better general understanding of the "biological" and "analytical" complexity

of a certain residue or "environmental" situation. There also should be widespread realization that safety intervals are not necessarily a reflection of persistence just as low tolerances do not necessarily signalize high toxicity.

The purpose of conventional residue analysis as an aid to agriculture is to clarify what is present and how much of it is present (provided toxicologists and/or legislators have informed the analyst what to search for). It is not a matter for conventional residue analysis to answer the question as to what is no longer present and where it is. At this point, not only does residue analysis link up with environmental analysis but above all the question of relevance again arises. It has been calculated that in the Antarctic 1 kg. of snow contains 1 ng. of DDT (Peel 1974); furthermore, it is suggested that in the Antarctic there is about another 250 grams of DDT moving about in the guise of penguins (Wunderlich, 1975, P. 28). It is reported that in a sandy loam soil which initially contained between 30,000 and 95,000 ppm of parathion, the "residues" did not drop below 1,500 ppm even after 5 years (Wolfe et al., 1973). I consider these to be typical problems of relevance.

There is relatively little information to indicate what proportions of an applied pesticide a) impinge on a plant and b) adhere to it. Still less information is available providing an indication of the amount of losses which then occur due to evaporation or as the result of the pesticide being washed off the plant surface (c.f. Ebeling, 1963; Hull, 1970). It is not until the true initial deposit has formed that the analyst becomes active. Persistence has two distinct characters also in this context. A pesticide may be non-persistent in the sense that it rapidly "becomes less" in the analysed substrate. But from the environmental standpoint, this apparent non-persistence might not be genuine in that substantial proportions of the residues or the metabolites have evaporated in the atmosphere where they raise completely different problems. It is only recently that a start has been made to investigate reactions to which pesticides are exposed under the combined parameters of atmospheric influences (see Moilainen and Crosby, 1975). Therefore, the practice ought to be adopted of distinguishing between "genuine persistence" and "pseudo-persistence". This point will be raised again in the discussion of balances.

CHEMISTRY AND PERSISTENCE

To avoid the problem of persistence, pesticides are needed which display high biological activity at low rates of application, and which can be used as selectively and as economically as possible. An equally important requirement is that the pesticides decompose to "environmentally" acceptable products in a reasonable period of time in order to reduce residues present in non-target substrates.

Persistence is characterized by molecules, mostly lipophilic, resisting chemical and biological breakdown and tending to move from their site of application. A low breakdown combined with a partition coefficient favouring lipophilic solvents are factors that result in increasing concentrations of residues reaching non-target, and particularly higher, organisms. Photodecomposition, volatility, enzymatic and/or microbial metabolism, adsorption and leaching are the main factors for determining the persistence of a compound. Obviously, the extent to which these parameters may become effective is governed by the chemical structure of the compound.

It is probably naive to believe that we can design pesticide molecules which degrade rapidly in the environment to produce compounds which do not, in turn, represent environmental and residual hazards. As an empirical approach, emphasis is laid on structures which are known, or can be demonstrated to be, readily degradable, such as esters or anilides. Furthermore, incorporation of polar groups often reduces lipid solubility and may facilitate degradation (cf. Kearney and Plimmer, 1970). Metcalf has repeatedly stressed the need "to replace DDT and other

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persistent non-degradable (hard) insecticides with persistent yet biodegradable substitutes" (Metcalf, 1972). His efforts to achieve this by replacement of aryl chlorine atoms with "degradophores" such as methoxy, ethoxy, methyl or thiomethyl groups have aroused some attention. Such moieties are substrates for multifunction oxidases which through their action on these substituents, convert the lipid soluble compounds into a variety of water-partitioning derivatives (Metcalf, 1976). An ether linkage, chlorine atoms, branches carbon chains or substitutes amino groups as substituents increase resistance to (microbial) degradation (Cripps, 1971). A finding which also appears interesting is that chloro-substituted aromatic compounds are degraded, by microorganisms, mainly by cometabolism because of the inertness of halogen substituents against nucleophilic attack, and that halogen substituents can be replaced more easily after loss of aromaticity by the action of dioxygenases (Knackmuss, 1975).

Such investigations may probably be helpful in obtaining a better theoretical understanding of degradability. Viewed more pessimistically, these need not necessarily be seen as presenting the solution to the problem of persistence. Extensive research studies have demonstrated that the cyclodiene compounds are metabolized also to polar compounds (cf. Porter, 1971, 1972; Porter and Korte, 1974, 1975; Korte and Porter, 1976). However, this finding has not yet resulted in this class of compounds being accepted as environmentally safe.   Interesting chemical aspects of persistence might be discovered by conducting intensive studies on the degradation of metabolites especially when they are applied as such to the plant. It is known that the oxones of thiophosphates generally degrade at a faster rate (example: parathion group; Möllhoff, 1968). With omethoate, as compared with dimethoate, this rather seems to be the reverse. Demeton-methyl-sulphone degrades more slowly when it is applied as such than when it forms as a metabolite after the application of sulphoxide or demeton-methyl. For the present, it can only be established that, but not explained why, compounds show slower rates of loss than would be expected from their chemical structure, particularly if it is that simple as methamidophos (O,S-dimethylphosphoroamido-thionate; Horler et al., 1975).

SOIL AND PERSISTENCE

Soil is the dream substrate of all research workers investigating persistence. It embodies all the parameters which may influence persistence yet, on the other hand, it has also proved to be the undoing of attempts to classify the major pesticides into categories of persistence. The graph of Edwards (1966) has meanwhile become famous (Fig. 9). His data in respect of dieldrin and heptachlor have been confirmed by new ones (Freeman et al., 1975) although other authors report different life spans for these compounds. Compilations of data published by Alexander (1969) and Kearney and Kaufman (1969) in respect of representatives of all the major pesticide groups do not agree (Kunc, 1975), and all attempts at a summarized presentation of this kind provide only limited information, as demonstrated by two examples of graphs by Kearney et al., 1969 (Fig. 10) and by Higgins and Burns, 1975. Nonetheless, pesticides like other environmental chemicals, are very largely judged by the way they behave "in soil" which, in such context, is treated as a uniform substrate in a most astonishing manner. Symposia or review articles on "Pesticides in soil" are most common. Understandably, hardly any symposia or review articles on "Pesticides in plants" are held or published. However, I doubt whether the difference between peat and sand is any less than that between cotton and apples. I have the impression that it would be very useful indeed, for the purpose of assessing pesticide chemistry and persistence phenomena in soil, to classify the different soil types in groups such as we have long been accustomed to doing for plant material. The classification of crops into suitable residue or tolerance groups such as practised in the U.S.A. and in the Federal Republic of Germany after all has the advantage that the different members of each group can be related for the assessment of residue behaviour and that they can be treated alike for regulatory purposes.