FACTORS THAT AFFECT THE PERSISTENCE OF PESTICIDES IN PLANTS AND SOILS

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ABSTRACT

Some of the factors that influence the persistence of pesticides are common to both plants and soils. These are, firstly, the characteristics of the pesticide, including its over-all stability either as parent compound or metabolites, its volatility, solubility, formulation, and the method and site of application. A second group includes the environmental factors, particularly temperature, precipitation (and humidity) and air movement (wind).

The other factors depend on the properties of the plant or soil. Characteristics influencing the persistence of pesticides in plants include the plant species involved, the nature of the harvested crop, the structure of the cuticle, the stage and rate of growth and the general condition of the plant. Corresponding soil characteristics are the soil type and structure, its organic matter content, clay content, acidity or alkalinity, mineral ion content and degree of aggregation and its microbial population.

Of these factors, the most important seem to be related to the chemical stability and physical characteristics of the pesticide; its stability exerting the greatest influence, otherwise volatility being more important in soil and solubility in plants.

Of the plant characteristics, the species and rate of growth seem most important, and in soil, adsorption on to organic matter or clay minerals, and the populations of soil microorganisms present exert the greatest influence.

I. INTRODUCTION

Vast quantities of pesticides are applied to plants and soils to control nematodes, insects, pathogens or weeds. At one time, it was considered desirable for such chemicals to be persistent, because a single treatment would protect a crop for a whole season or even successive crops for several seasons. However, it has become obvious that persistence is desirable only when the chemical does little harm to other organisms, and, currently, the aim is to use chemicals that are as specific as possible, and persist no longer than is absolutely necessary to control pests. It is now generally accepted that not only must the pesticide be harmless to non-target organisms, but also its metabolites should not present any environmental hazards. In recent years our knowledge of pesticide metabolism has increased greatly, and many reviews on this subject have been published[1-6].

However, our knowledge of the biological, physical and chemical factors that affect the deposition, penetration, translocation, movement between media, metabolism and effectiveness, of the many pesticides in use, has not developed as quickly, and has not been thoroughly reviewed. With more

information on how these factors act, it should be possible to use smaller quantities of pesticides, in ways that avoid killing beneficial arthropods, harm wildlife or man, and contaminate the environment unduly.

There are now more than 1000 different pesticides in general agricultural use, of which about 100 are insecticides and acaricides, 50 fungicides, 50 herbicides and 20 nematicides. These include compounds of greatly different complexity of structure, and with persistence in plants and soils that ranges from a few hours to many years (*Figure 1*). It is impossible within the scope of this paper to consider more than a few of these chemicals, so I shall
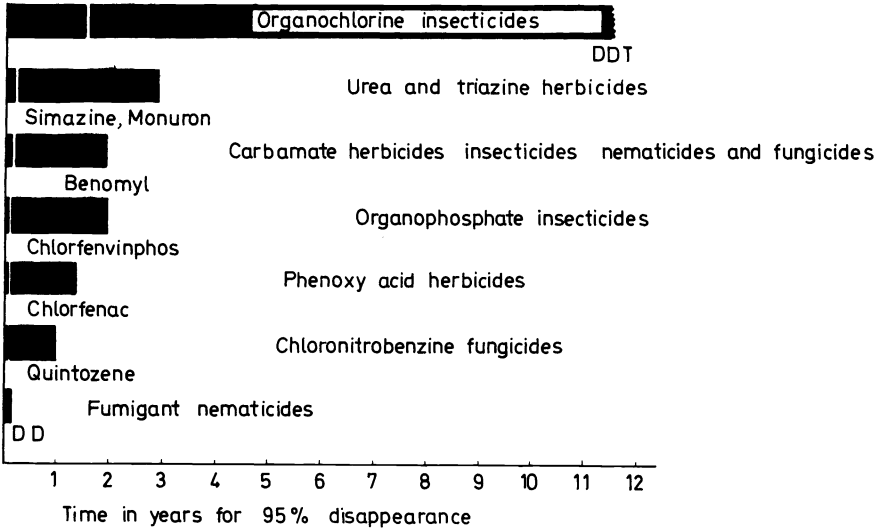

Figure 1. The persistence of pesticides in soil.

confine my discussion to the factors that influence the disappearance of the more persistent compounds. Fortunately, many of these factors tend to exert a similar effect on widely dissimilar pesticides, so it is unnecessary to discuss details of how they affect all compounds. It is also outside the aims of this paper to discuss the detailed metabolism of pesticides, so that only the ways in which chemical, plant, soil and environmental factors influence the metabolism will be considered.

When a pesticide is applied to a crop or soil, it enters a dynamic ecosystem and immediately begins to be moved from one part of the system to another, degraded *in situ* or moved out of the system into other systems. It is important to determine the relative importance of these processes, because, whereas pesticides that are completely degraded become harmless, those that move to other systems and persist may do some environmental damage.

A pesticide can disappear from soil by volatilization, leaching, surface run-off, uptake by plants or the migration of invertebrates or small mammals with residues in their bodies. Comparable pathways of loss of pesticides from plants are that residues may volatilize, pass to the soil in root exudates or be

removed when the crop is harvested. Only the residues that remain in the plant or soil are metabolized, and often, for persistent pesticides, these represent only a small proportion of the whole.

Pesticides tend to persist much longer in soils than in plants or animals. The growing plant or active animal can metabolize or dilute residues much more rapidly than a comparatively static system such as soil, where the residues become tightly adsorbed on various soil fractions, and even transient pesticides may be retained much longer than they would on unreactive surfaces. Many of the major pathways of metabolism of organic compounds are similar in plants, microorganisms, insects and mammals, although there are exceptions to this rule.

Insecticides can be classified according to their stability and persistence in plants, as: (1) *stable*—those that are not metabolized or decomposed in the plant; (2) *endometatoxic*—those that disappear in the original form but persist in the plant as toxic metabolites; (3) *endolytic*—those that remain in the plant until they are decomposed or ingested by a pest[7]. However, the first category is no longer a valid one, because even DDT becomes partially metabolized in plants. The great majority of compounds are in the last category, because with a few exceptions only the true systemics, such as dimethoate, disulfoton, demeton methyl, fenthion and menazon, can be classed as endometatoxic and completely decomposed in the plant. There is much more information on the metabolic pathways of organophosphates than on those of organochlorines. For instance, the degradation of demeton, disulfoton, phorate, mevinphos and dimethoate has been well documented[8].

The disappearance of pesticides from plants or soils may occur initially according to the law of first-order kinetics, but it is usually a two or more step reaction with an initial phase that has been termed 'dissipation' and a slower phase called 'persistence'. The first phase is probably due to volatilization, adsorption or translocation, and the second to chemical, photochemical or microbial degradation[1, 4].

The factors that affect pesticide persistence, i.e. chemical, plant, soil and environmental factors, will be discussed in turn and their extremely complex interactions considered. Finally, the relative importance of these factors will be compared and assessed.

II. CHEMICAL FACTORS

A. Chemical stability

(a) *Structural stability*

Pesticides range in stability from unstable to extremely stable, and their basic structure is fundamental in influencing their persistence in plants and soils. A readily metabolizable pesticide breaks down rapidly in plants and soils no matter how the environmental factors vary, and a stable chemical will persist for long periods even under the most unsuitable environmental conditions. Some pesticides can be partially broken down, then become extremely persistent, as when aldrin is epoxidized to dieldrin and heptachlor to heptachlor epoxide; both the breakdown products being more stable than the parent compounds. A few pesticides are extremely stable, in respect of

all but some single factor such as pH. Pesticides may interact together to form compounds either more or less stable than either of the parent compounds, although usually the new compounds are more complex and more stable than their precursors.

(b) *Volatilization*

Pesticides range in volatility from extremely low to the very high vapour pressures necessary for fumigant action. It has long been realized that there is a strong correlation between the rates of loss of pesticides from plant surfaces and their vapour pressures[9] but most of the earlier workers believed that there was very little volatilization of so-called 'non-volatile' pesticides such as DDT[10]. However, it is now clear that even a compound with a low vapour pressure, when distributed over a large surface area, such as the surface of a leafy crop, disappears quite rapidly[11], and it is possible for even the least volatile pesticides to disappear completely by volatilization within one growing season. Of course, this is unlikely to happen in practice, because the pesticide becomes adsorbed on to the plant surfaces and absorbed into its tissues as well as being affected simultaneously by many other processes.

Similarly, it was believed that only minute quantities of 'non-volatile' chemicals could be lost from soil, where they are even more tightly adsorbed, but many workers have now shown that it is possible for a major proportion of many of the pesticides applied to soils to disappear by volatilization[12-18] and that there is a strong correlation between the vapour pressure of a pesticide and its persistence in soils. Pesticide residues that remain on the soil surface volatilize up to 10 times faster than the same amounts cultivated into soil[19]. However, even those residues that have been cultivated into soil can disappear by volatilization and it has been suggested that the rate of volatilization of persistent insecticides from soil is controlled by diffusion of the pesticide and by mass flow of water to the soil surface. The humidity of the air above the soil surface influences the rate of loss of water, and increased rates of water loss in turn accelerate the volatilization of pesticides, but only after the soil surface has become depleted of pesticide. This has been likened to a 'wick' effect, such that pesticides move to the soil surface by mass flow, in water which moves to the surface to replace that which has evaporated. At very low relative humidities, the pesticide can accumulate at the soil surface, then very rapidly volatilize when the surface is again moistened and the pesticide released. There seems little doubt that volatility is a major factor influencing the loss of pesticides from plants and soils.

(c) *Solubility*

Pesticides range from very soluble compounds to extremely insoluble ones such as DDT.

Solubility greatly influences the persistence of pesticide residues on plants, because almost all of a comparatively soluble spray can be washed off a crop within 24 hours, unless it is absorbed on to the plant surface. There seems to be quite good correlation between water solubility and persistence of pesticide residues on plant surfaces[2]. However, the influence of solubility may be complicated, because rainfall is sometimes heavy enough to wash pesticide deposits off leaves as particulate matter. For example, although

DDT is very insoluble in water, its apparent solubility may seem quite high, owing to the occurrence of micro-particulate DDT in suspension in water (less than 0.5 μm diameter).

There is also a reasonably good correlation between the water solubility of pesticides and their persistence in soils[4]. Soil is an excellent filter of fine particulate matter and there can be little carriage of undissolved pesticides in leachates. However, soluble pesticides pass down through the soil in large quantities, as water drains downwards, and are lost in the drainage water, whereas less soluble ones are hardly leached at all.

B. Method of application

The total quantity and form of a pesticide reaching plants or soils depends on the site and method of application, the type of equipment used and the formulation of the pesticide.

(a) *Site of application*

Pesticides can react with, or become adsorbed on to, a wide variety of materials, and this relationship has a considerable influence on the persistence of these chemicals. The adsorption and absorption of pesticides depends mainly on their molecular polarity; for instance, polar aqueous compounds cannot penetrate waxy hydrophobic layers of plants as easily as non-polar lipoid-based compounds. This relationship can be changed by the addition of surfactants to the pesticide. Probably, the surfactants enable pesticides to be absorbed more readily by orientating themselves with the polar portion towards the water phase and the lipophilic portion attracted to the cuticular waxes, so increasing the permeability of the cuticle to the pesticide[8]. Different parts of plants and soil fractions differ in their ability to adsorb or absorb pesticides, so the site to which a pesticide is applied influences its persistence very much. The woody parts of plants, particularly the bark of trees, can readily adsorb pesticides and so can soil organic matter.

(b) *Method of application*

The persistence of a particular pesticide depends greatly on the method by which it is applied. In the course of time, the gradual increase in efficiency of equipment for applying pesticides has led to a corresponding decrease in the dosage of actual toxicant used per unit area. There has also been a progressive tendency to use less liquid to carry pesticides, and this usually implies applying smaller particles of pesticides to crops. The commonest methods of applying pesticides to plants are, in order of decreasing particle size, as dusts, sprays, mists, fogs or smokes. Control of pathogens tends to require a more even and thorough coverage by a pesticide than control of insect pests or weeds. At either end of the droplet scale of size, there is risk of loss of the pesticide, the larger droplets tending to coalesce and run off the surface of leaves and the smaller ones to become lost owing to wind and air movements. More concentrated, ultra-low-volume applications tend to penetrate leaves more readily than greatly diluted water emulsions[20].

Soil pesticide treatments have gradually progressed, from a broadcast application thoroughly cultivated into the soil, to 'spot' or localized treatments. They range from in-row treatments with dusts or sprays, long-lasting

granules or microcapsules, to root dips, injections or seed dressings. As with aerial treatments, more efficient placement has enabled much smaller dosages to be used. In general, all treatments incorporated into the soil will persist much longer than those left untouched on the surface[21].

(c) *Formulation*

The ways in which pesticides are formulated considerably influence their persistence. Formulations, in order of increasing persistence on plants and increasing size of particles, are as water-soluble liquids, emulsions, miscible liquids, wettable powders, dusts, microcapsules or granules. The reasons for the differences in persistence of these formulations are many and varied. Water-soluble formulations are more readily washed from plants by rain, and wettable powders and dusts persist longer, because they are less readily absorbed into plants, less liable to photodecomposition on the plant surface, and less readily volatilized. Granules and microcapsules are specifically designed to delay release and breakdown of the pesticide. In soils, the rate of adsorption on to various soil fractions, particularly the organic matter, is *inversely* related to the particle size of the pesticides in the formulation. Hence although water-soluble formulations are not persistent in soils, because they can be easily leached away, emulsions tend to persist longer than wettable powders or dusts, because they are more readily adsorbed on to soil fractions and so not appreciably degraded.

III. PLANT FACTORS

The morphological and physiological characteristics of plants greatly influence the distribution, retention and uptake of pesticides into their tissues.

A. Plant species

(a) *Structure of plant*

Plants differ greatly in habit, size and morphological features. Those structural features that influence the distribution, retention and uptake of pesticides[22] have been listed as: (1) plant form (erect, spreading, prostrate); (2) leaf shape (broad, narrow, large, short, linear); (3) leaf position and density (horizontal, upright, pendulous); (4) leaf surface and margins (hairy, waxy, sculptured).

Features that do not favour the retention of pesticides are narrow, waxy or sculptured leaves, whereas broad and hairy leaves retain pesticides much better. The leaves of different species of plants differ greatly in wettability, and, within a given species, immature leaves tend to be more difficult to wet than mature ones, and the lower surfaces of leaves are more difficult to wet than the upper ones[2]. The density of the foliage is another important factor, some species having such a dense growth habit that it is virtually impossible for sprays to reach the innermost leaves. Thus, specific plant differences considerably affect the uptake and persistence of insecticides. Not only do different species of plant take up insecticides at different rates, but so also do different varieties. For instance, different varieties of carrots take up endrin at different rates[23].

(b) *Nature of crop*

Crops are grown not only for foliage, which provides food for man or animals, but also for their fruits or seeds, and underground portions such as storage roots, bulbs, rhizomes or tubers. There is translocation of nutrients to most of these organs from the foliar parts of the plants, and studies with radioactive insecticides have shown that this movement of nutrients can be accompanied by translocation of pesticides, so that storage organs tend to contain much larger pesticide residues than other parts of the plants. There is a tendency for most of the residues to be concentrated in the skin, peel or rind of the storage organs[8]. Moreover, roots take up pesticides from soil, and these residues tend to be retained in root storage organs, and, once in these organs, the pesticides persist much longer than they would in the plants' leaves or stems. The amount taken up depends upon the crop: for instance, carrots usually take up more organochlorine residues than other root crops such as potato, radish, turnip and beet, and most of the residues are in the peripheral zone of the upper half of the carrots.

(c) *Ease of penetration*

Pesticides that remain on the surface of plant organs can disappear quite rapidly through various forms of weathering, and the speed at which they penetrate into plants considerably affects their persistence. For many pesticides, the ease with which they are taken up into plants depend upon the wettability of the cuticle, but this changes with ageing and differs on different parts of the leaf, and usually monocotyledenous plants can be wet less easily than dicotyledenous ones[24]. Since most non-ionic organic insecticides are soluble in plant oils and waxes, they can penetrate to some extent into the cuticular and subcuticular tissues of the treated parts of plants, even if they are not truly systemic. The mechanism of foliar penetration by solutions has been thoroughly reviewed[24].

Pesticides can be taken up from sprays applied to the foliage, stem, seeds and fruits or through the roots, but to be absorbed by these organs the chemical must first penetrate the plant cuticle. This probably occurs most easily through the absorptive areas of roots, although it also occurs quite readily through the leaves, stems and fruits. Residues of demeton methyl absorbed through roots persisted in plants for more than a month, those of phorate for more than 47 days, those of schradan 10 days, those of dimethoate 42 days and those of disulfoton 86 days[8]. Some systemic organophosphates (dimethoate and phorate) were transported from soil so efficiently that they persisted in the nectar of the flowers for up to 20 days[25] and sometimes even longer. Roots absorb lipid-soluble pesticides much less readily than water-soluble ones, but leaf absorption differs, because absorption of pesticides by leaves is usually hindered by wax particles, hairs, thorns or other protuberances that produce air pockets that prevent the spread of pesticides. Water does not readily penetrate the unbroken cuticle, and various hypotheses have been made as to the main route of entry of pesticides into the leaf. It has been suggested that entry occurs through the stomata, through modified epidermal cells that lie above the veins, through cracks in the cuticle, through stretched areas of cuticle or through plasmodesmata, or protoplasmic threads[26, 27].

Recently there is evidence that compounds with low vapour pressures are taken up into leaves in the vapour phase[28].

Pesticides can also penetrate the seed coats of many seeds, and for a short time the amounts entering some plants in this way can be quite large, because seed dressings consist of large concentrations of pesticides applied directly to the seed. Pesticides are sometimes applied to the trunks of trees, but usually they are poorly absorbed unless applied to cuts or holes in the bark. There are reports that insecticides applied to trees by trunk injection can persist for very long periods. For instance, phorate persisted 20 months in cacao trees[29] and amiton 12 months in white pine[30].

B. Metabolic activity

There is now much information on the metabolic fate of organic pesticide chemicals in plants. However, such data often concern the breakdown of chemicals that are relatively easy to study, rather than those that are most commonly used. Plants can degrade many of the organic pesticides, although some are broken down much more readily than others. However, it is not always the most complex compounds that are the most resistant to breakdown. The degradation may often be mediated enzymically, but can also occur by reactions with normal plant constituents or by photodecomposition. Many aspects of the physiological activity of plants, including the rates of growth, translocation, excretion and storage of reserves, influence the persistence of pesticides in them.

(a) Rate of uptake

The rate at which pesticides are taken up into plants is correlated with the ease with which they can penetrate the cuticle, and is influenced by environmental factors, particularly light, temperature and moisture. For instance, some pesticides can penetrate pea plants grown in the dark much faster than those grown in light, and there is evidence that the rate of uptake of many organophosphate insecticides is enhanced if the cuticle is kept moist. Similarly, plants take up much more insecticide from soil when the soil moisture level is at field capacity, with a gradual reduction in uptake as the moisture level approaches the wilting point or if the soil becomes waterlogged[31].

The rate of uptake of pesticides from soil is greatly influenced by the type of soil to which the pesticide is applied. For instance, the rate of uptake of dieldrin into the roots and shoots of corn was inversely related to the amount of organic matter in the soil[32]. A good example of the influence of soil type on uptake of pesticides was when wheat, orchard grass, alfalfa and corn plants were grown in sand containing dieldrin and accumulated two to six times more insecticide than the same species grown in soil under the same conditions and for the same time[33].

(b) Rate of growth

The rate at which a crop grows greatly influences the persistence of pesticide residues on the leaves and other parts. This is obvious, because residues become spread over a much greater surface area as the leaves and other organs grow and become much more exposed to weathering. Moreover, if a plant doubles in weight, the pesticide residue concentration is halved, even if there

is no increase in the rate of its breakdown. For example, when red clover plants were sprayed at three stages in growth, residues disappeared more slowly on the older plants[9].

(c) *Translocation*

Once a pesticide has penetrated the leaf cuticle, the absorptive area of the roots, or some other site of uptake, it can be carried through the plant tissues in several ways. It may be translocated via the non-living continuous cell wall phase (apoplast), via the living continuous protoplasmic phase (symplast) or across the mesophyll and into the phloem and then be translocated in the assimilation stream[2].

Many herbicides, most of the organophosphate and organochlorine insecticides, and some carbamate insecticides, translocate through plants, although they are often present in only non-lethal amounts. The term systemic insecticide as a special category is of dubious value, because most pesticides penetrate plant tissues to some extent and are translocated through plants.

Not only the pesticides but also their metabolites may be translocated, and these can persist longer in the plant and be more readily transported than their parent compounds.

Translocation of pesticides can be upward or lateral (acropetal) or downward (basipetal), but upward movement is more common, particularly because many pesticides are applied to the soil. As would be expected, most of the downward translocation of pesticides is via the phloem and their upward movement via the xylem. Most of the upward translocation is to the terminal leaves and growing parts, which are areas with a high rate of metabolism and have a greater potential for degrading pesticides. Insecticides can move through plants quite rapidly: for instance, demeton moved upwards through plants at a rate of 10 cm/h and downwards at 2.5 cm/h[34]. The rate of transport depends on the rate of transpiration, temperature, plant metabolism and the chemical concerned[35].

(d) *Storage*

There is not much information on the storage of pesticides in plants. Such evidence as we have is that storage organs such as potato tubers[36], sugar beet[37], carrots[38], turnips[39] and rutabagas (swedes)[40] have a considerable affinity for pesticides and contain much higher concentrations and over-all larger residues than the rest of the plants which bear them. There is a general tendency for persistent pesticides to be translocated and stored in the lower portions of plants such as wheat[41] and beans[42].

(e) *Excretion*

Pesticides can be excreted from various plant organs in guttation droplets from leaves or in root exudates. A number of pesticides have been reported in leaf guttation fluid; these include lindane from wheat[41] and a variety of other crops[43]; schradan from wheat, strawberries and Brussels sprouts[44]; and chloramben from grasses[45]. Reports of pesticides in root exudates include diazinon in exudates from bean roots[42] and picloram in those from ash and maple[46]. No doubt these phenomena are quite common, but it is doubtful whether very large pesticide residues are lost by excretion.

IV. SOIL FACTORS

The persistence of pesticides in soil is markedly influenced by the type of soil to which they are applied, and particularly by soil characteristics such as particle size, mineral and organic content and hydrogen ion concentration. Their residual life also depends upon the biological activity of the soil, since the breakdown patterns of many pesticides are mediated by enzymes.

A. Soil type

Soils are classified according to the proportion of mineral particles of different sizes present. Pesticides become readily absorbed on to soil particles, thus making the pesticide persist much longer than it otherwise would, and include (1) physical adsorption, (2) chemical adsorption (ion exchange or protonation), (3) hydrogen bonding, (4) coordination (metal complexes). In any one soil, several mechanisms or combinations of mechanisms may exist[47].

(a) Soil structure

With a few exceptions, the smaller the particles a soil is composed of, the longer pesticides persist in it. The way in which particle size and structure influences persistence in soil is complex, because structure is also intimately linked with such features as hydrogen ion concentration, organic matter and clay content. One comparatively simple approach was to show that there was a significant correlation between the persistence of dieldrin in a range of soils and the available adsorptive surface area, which itself corresponded with a decrease in size of the soil particles[48].

Several other workers have studied the relative persistence of pesticides in a range of soil types. For instance, aldrin and lindane were adsorbed least in Springfield sand and in increasing amounts in silty clay loam, light sandy clay loam, coarse silt, silty clay, sandy loam, clay loam and muck, doses many times larger being needed in the heavier and more organic soils[49]. Other workers have found that DDT, camphechlor, chlordane, dieldrin, heptachlor and aldrin are progressively adsorbed by a number of soil types ranging from Monmouth loam, Lakewood sand, Downer sandy loam, Bucks silt loam, Sassafras sandy loam, Annandale silt loam, Collington sandy loam, Croton silt loam, Weeksville sandy loam, Cokesbury silt loam, to muck[50]. In another experiment, one week after several soils were sprayed with heptachlor, 31 % of the amount applied still remained in muck soil, 11 % in silty clay loam and only 8 % in silt[51]. Similar results have been obtained for organophosphate insecticides; when thionazin was applied to an organic soil, a sandy loam, a silty loam and a clay loam, the time taken for 50% to disappear was 10, 6, 4 and 1.5 weeks, respectively[52].

Adsorption by smaller particles may also lessen the uptake of systemic insecticides by plants. For instance, drenches of mevinphos, phorate, schradan and demeton were more toxic to aphids and plants grown in sands and sandy soils than in silt loam, clay loams or muck[53].

Soil structure also affects leachability of pesticides, because the pore size and pore size distribution greatly affect the movement of water through soil. The availability of moisture also affects the degree of adsorption on to soil fractions. Not all pesticides are adsorbed in the same way: for instance, heptachlor and DDT seem to be adsorbed by the clay fraction; diazinon and

parathion by the sand and silt fractions; and dichlofenthion by both fractions[54].

(b) *Clay content*

The smallest particles in soil (0.002 mm) are called clay, and soils with more than 40 % of clay particles are referred to as clay soils. Such soils have a much larger internal reactive surface area than other soils, thus providing a greater surface area for adsorption of pesticides. Many workers have obtained data showing strong correlations between the amount of clay in soils and their ability to bind and retain pesticides[49, 55–58].

The relationship is complex, because much clay is associated with organic matter as soil colloids. The possible mechanisms of adsorption on to the soil colloids have been reviewed extensively[47] and are outside the scope of this paper. However, it would be appropriate to list the factors that can influence the amount of adsorption of pesticides by soil colloids. These include : (1) the physicochemical configuration of the colloids, (2) the physicochemical configuration of the pesticide, (3) the dissociation constant of the pesticide, (4) the water-solubility of the pesticide, (5) the size of the pesticide molecule, (6) the soil hydrogen ion concentration, (7) temperature, (8) the electrical potential of clay surface, (9) the moisture content of the soil, and (10) formulation.

There is little doubt that clay is one of the two most important soil constituents (organic matter being the other) influencing the persistence of pesticides in soils.

(c) *Organic matter content*

The amount of organic matter in soils ranges from less than 1 % to more than 50 %. There is now much evidence to show that soil organic matter is extremely important in adsorbing pesticides, and many workers have reported strong correlations between the persistence of pesticides in soils and the amount of organic matter in them[48, 49, 54, 58–62]. Supplementary evidence has been provided by workers who have demonstrated that the uptake of pesticides by plants is inversely related to the amount of organic matter in soil[32, 53, 63].

Most of soil organic matter consists of humic compounds that have not been completely characterized but have a very high cation exchange capacity. The humic compounds have functional groups such as carboxyl, amino and phenolic hydroxyl, which provide sites for hydrogen bonding with pesticide molecules. Together, these characteristics provide a very considerable capacity for pesticide adsorption and increased persistence.

It has also been suggested that sodium humate can lower the surface tension of water in much the same way as sodium lauryl sulphate, so it is possible that sodium humate might help to solubilize compounds that are very water-insoluble. A 0.5 % sodium humate concentration[64] can increase the water solubility of DDT by a factor of at least 20.

(d) *Hydrogen ion concentrations*

The hydrogen ion concentration of soil has complex effects on pesticides. It can affect the stability of clay minerals, the ion exchange capacity and the

rate at which both chemical and bacterial breakdown occurs. It is not a simple relationship, because whereas some workers have reported that pH does not influence the persistence of pesticides[65-67], others have said that they degrade more rapidly in acid soils[58, 68, 69]. However, the great majority of workers have reported that pesticides are adsorbed less and break down more rapidly in alkaline than in acid soils. These include herbicides[70, 71], organochlorine insecticides[56, 72-74] and organophosphate insecticides[75-77].

Clearly, the influence of pH differs with different pesticides and soils, the effect depending on the nature of the adsorption mechanism.

(e) *Mineral ion content*

The kind of minerals present in a soil is closely linked with soil type and structure, and the structure of clay minerals depends on mineral ions such as aluminium, iron, magnesium, lithium, chromium, zinc and silicon. Therefore, it is not surprising that the mineral ion content can influence the degree of adsorption[78], but different minerals can also act catalytically and accelerate decomposition. Examples of this include iron and aluminium[79, 80] and magnesium[55, 80]. Much more work is necessary before we understand the full relationship of mineral ions to pesticide adsorption and breakdown in soils.

B. Metabolic activity

Although pesticides can break down in soils by purely chemical action, it is becoming increasingly evident that soil organisms are very important in degrading these chemicals enzymically.

(a) *Soil microorganisms*

The importance of microorganisms in breaking down pesticides in soils can be established readily by comparing the rates of degradation in sterilized and unsterilized soil[36, 59, 68, 81, 82]. Additional evidence of microbial breakdown can be obtained by careful study of the kinetics of breakdown. If extracellular chemical breakdown occurs, it begins shortly after the pesticide reaches the soil, and either the rate of breakdown remains constant or it gradually declines with time. By contrast, microbial degradation does not begin until populations of microorganisms build up; then the rate of loss increases with time, eventually becoming logarithmic, particularly when only a single species of microorganism is involved[83].

There are instances where a particular microorganism specifically breaks down a particular pesticide, but, more usually, the breakdown is non-specific, and a wide range of microorganisms, including most of the common genera of soil-inhabiting bacteria, the three main genera of actinomycetes and many fungi, are all able to degrade any particular pesticide.

Some pesticides, such as aldrin and heptachlor, become more toxic to pests after microbial breakdown, whereas others, such as BHC, DDT and isobenzan, are less toxic after microbial attack. Although microbes may be able to degrade certain herbicides or organophosphate insecticides completely, and there have been reports that they can cleave the benzene ring of some organochlorine insecticides, there have been few substantiated reports of this occurring[84].

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It has been shown that populations of some species of microorganisms increase after repeated applications of pesticides to soil, but it is not yet clear whether such increases occur because the pesticides are a source of food for them, or because the pesticide eliminates certain competing species. There have been a number of reports of this accelerated breakdown of pesticides after repeated treatments of soil with the same pesticide[85]. These include parathion[86], diazinon[87], lindane[88] and a number of herbicides[89], and it seems very probable that this is due to build up of appropriate populations of microorganisms.

Many workers have reported that accelerated degradation of pesticides occurs when additional energy sources are added to soils. These include increased breakdown of DDT by addition of ground alfalfa foliage[90, 91], or of cattle manure[92], and of parathion by addition of glucose[81]. Other workers have shown that microbial breakdown of pesticides progresses faster under anaerobic than aerobic conditions. These conditions are usually produced by flooding soil, and this has accelerated the breakdown of BHC[93-95], DDT[90, 96], heptachlor and methoxychlor[95].

There seems little doubt that microbial activity is a major factor in the degradation of pesticides in soil.

(b) *Soil invertebrates*

Many pesticides are taken up into the tissues of invertebrates that live in soil, either through their cuticles or in their food. Some of these, particularly the insecticides, become, at least partially, degraded in the tissues of these animals. Unfortunately, very few data on the magnitude of this breakdown are available, but it has been shown that DDT can be degraded to DDE in the bodies of mites[97-99], earthworms[100, 101] and many insects. There is circumstantial evidence that such uptake occurs with many other pesticides.

(c) *Free soil enzymes*

Enzymes are of biological origin but some can also exist for considerable periods outside living organisms. They may be released from dying organisms, from microorganisms, from the roots of plants or in excreta from soil animals, and still remain active. Whereas heat sterilization inactivates both enzymes in living organisms and those free in soil, other forms of sterilization such as gamma-radiation[102] and chemical inhibitors such as sesamex piperonyl butoxide and piperonyl cyclonene[103] tend to be much more specific and either inactivate only enzymes in living organisms or particular enzymes. We do not know how extensive is the breakdown of pesticides by free soil enzymes, but there is evidence that microorganisms do not account for more than 40 % of the breakdown of persistent pesticides, and it is unlikely that relatively simple chemical reactions can add much to this. Probably, free soil enzymes make an important contribution to over-all pesticide degradation.

V. ENVIRONMENTAL FACTORS

The influence of the climatic factors—temperature, precipitation, radiation and wind—on pesticide breakdown is extremely complex, because not only do they affect most of the chemical, plant and soil factors, but they also interact with each other (*Figure 2*).
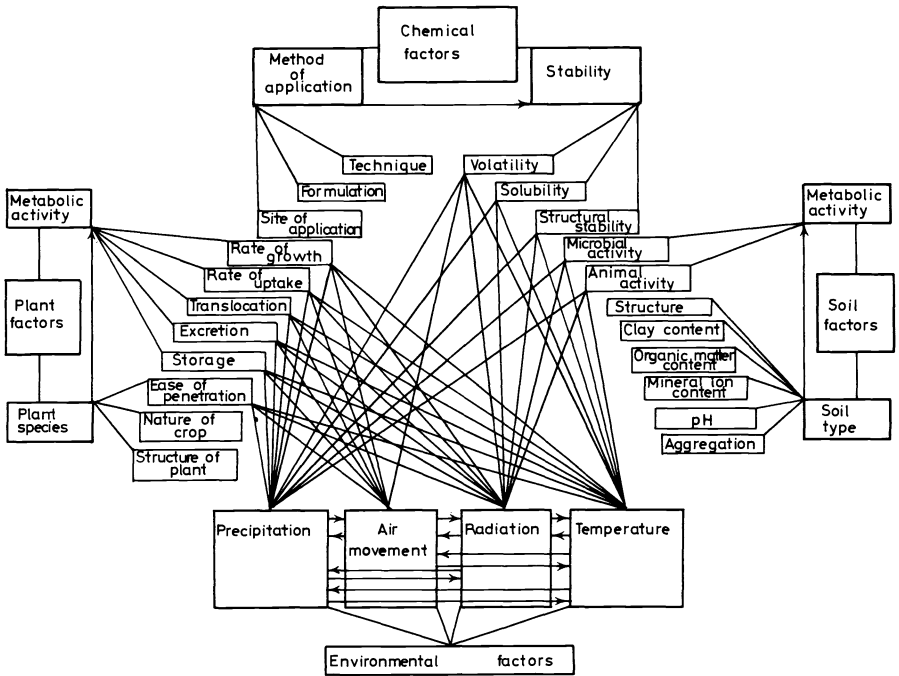
Figure 2. Interactions between factors that influence the persistence of pesticides in plants and soils.

A. Temperature

There are many reports in the literature of increases in temperature resulting in pesticides losing their effectiveness faster[2]. Such loss of effectiveness may be due either to physical loss from plants or soil or to accelerated degradation.

All of the plant, soil and chemical processes of pesticide breakdown are affected by changes in temperature. Higher temperatures increase the rate at which pesticides volatilize from soil or plant surfaces and also their water-solubility. They increase the rate at which pesticides break down on the plants, penetrate the plant cuticle or are taken up by the roots, and also the rate of growth and translocation; all these are factors which accelerate the degradation of pesticides. Both microbial and animal activity in soil are dependent upon temperature, activity virtually ceasing in very cold soils. Also, increased temperatures in soils usually decrease the amount of pesticide that is adsorbed in them, although this is a complicated relationship, because increased temperatures usually cause soils to dry out and this drying greatly increases adsorption.

Increased temperatures are caused usually by increased radiation, and changes in temperature greatly influence other climatic factors such as wind and precipitation.

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B. Precipitation

The influence of rain, hail and snow can be either direct, due to mechanical effects of the precipitation on the plant and to the leaching of moisture through the soil, or indirect, due to its effect on soil and air humidity. Heavy precipitation washes surface residues off plants, so preventing their uptake, but this may be compensated for, because pesticides are taken up faster from moist plant surfaces, and uptake of pesticides (both of those that have been applied to soil and those that have been washed off plants) is much greater from moist than from dry soil. Plants with surplus moisture excrete water from both leaves and roots, another mechanism that results in increased pesticide loss. The increased soil moisture resulting from precipitation causes faster plant growth and translocation, which also results in increased pesticide loss.

Moisture favours both microbial and animal metabolic activity in soil; in dry soils, many microorganisms pass into a resting stage and are inactive, thus slowing down pesticide breakdown; in flooded soils microbial activity is mainly anaerobic and favours the breakdown of pesticides.

Water is a very polar molecule and can compete with pesticides for adsorption sites on soil colloids and other fractions. In dry soils, pesticides are tightly adsorbed, whereas in wet ones they are released and thus may be more readily lost or degraded; this seems to be a reversible process for most pesticides.

The changed humidity resulting from precipitation affects pesticide loss in several ways. There is much less volatilization from the surface of plants when humidity is high, but the stomata open more, so there is probably more transport into the plant and less is lost by leaf excretion or guttation.

Air humidity also affects the volatilization of pesticides from soil very much, and the greater the humidity the less pesticide volatilizes. It also influences the diffusion of pesticides in soil, because when the air above the soil is dry, there is diffusion through soil towards the surface, and when it is very moist and the soil is dry, there is diffusion from the soil surface into the deeper soil layers[104, 105].

C. Radiation

In recent years, much data have accumulated on the effects of sunlight—in particular, ultra-violet light—on breakdown of pesticides on plant and soil surfaces. Even the most persistent pesticides such as DDT will degrade, at least partially, under the influence of radiation, and non-persistent compounds such as some pyrethrins are very susceptible to ultra-violet decomposition. Radiation increases the volatilization of most pesticides from leaf surfaces. It may decrease uptake through the plant surface but increase the rate of growth and translocation of these chemicals.

D. Air movement

The movement of air in the form of wind can affect the persistence of pesticides in plants and soils quite considerably. One of its greatest effects is on volatilization from plant surfaces and from soils. Moreover, there may also be physical removal by wind of deposits of dusts or sprays on plant

surfaces. The effect of wind on loss of pesticides from soil is considerably influenced by the presence of a cover crop; when there is no crop, much more pesticide is lost from the soil surface than when it is protected by a crop.

Wind can also decrease the rate of uptake of pesticides from a plant surface by causing closure of stomata and diffusion through the plant surface.

VI. CONCLUSIONS

In such extremely complex interacting systems, involving a vast range of crops, pesticides, soils and environmental conditions, it is very difficult to make generalizations as to the relative importance of the different factors influencing the persistence of pesticides in plants and soils. However, it is possible to assess factors that have a very general effect on pesticides in either plants or soils. One factor that stands out as of primary importance is the fundamental structural stability of the pesticide, particularly relative to its volatility and solubility. In plants, the solubility of the pesticide is probably of greatest importance, followed by volatility, but in soils the order is reversed, volatility tending to be more important than solubility. These factors together are of major importance.

Factors that are next in importance in affecting persistence of pesticides in plants are, in order of decreasing influence: the metabolic activity of the plant, the temperature regime, the amount of precipitation, and the amounts of wind and radiation. In soil comparable factors are the adsorption of pesticides on to clay or organic fractions, precipitation, temperature and microbial activity.

The nature of the crop and the method of application of the pesticide are of much lesser importance affecting persistence in plants, whereas in soil the less important factors are the hydrogen ion concentration and also method of application. The other factors that have been discussed in this paper can be considered as of very minor importance.

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