

PESTICIDE DEGRADATION IN AQUATIC ENVIRONMENTS AND THE AIR

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INTRODUCTION

The title of this paper describes a very wide area of pesticide science, and a somewhat daunting one for an author whose research interest in pesticides embraces only one small part of this subject. Nevertheless an attempt will be made in this paper to present a view of what can happen to pesticides in water and air environments to affect their persistence (or existence) as biologically active molecules. It is hoped that the material discussed may give some indications of the reactivity of these environments and their components towards pesticides, with particular reference to their potential to degrade the pesticides.

Pesticides must, of course, persist in order to exert the desired effect. On the other hand, there are compelling voices which argue on ecological grounds against excessive persistence of such toxic synthetic chemicals in natural environments. From either standpoint it is desirable that degradative aspects of the fate of pesticides in the environment should be thoroughly characterized and understood.

AQUATIC ENVIRONMENTS AND THE AIR

Before discussing pesticide degradation in aquatic environments and the air, the nature of the environments will be outlined. Although for most purposes in this paper the air and water are considered as separate entities, there is of course considerable juxtaposition, not to say merging, of the two in the 'total' environment. Considering that over 70% of this planet is covered by water, the area of contact between the hydrosphere and the atmosphere is vast. This is then considerably extended by including those situations representing overlap between the two (e.g. mists or raindrops in the air, and air bubbles in turbulent water).

The aquatic environments which pesticides may enter include both static (lentic) and mobile (lotic) systems, e.g. ponds and ditches, streams, rivers, canals, lakes, reservoirs, drainage channels, irrigation systems, paddy fields, fish-farm ponds, estuaries and the sea. Any particular aquatic system will be characterized by interfaces with both living and inanimate systems; quantities of sediments and suspended particulate matter; the degree of light penetration; the temperature profile; the aeration status, ranging from a high degree in surface waters to the anaerobiosis of mud and sediments; the turbulence and movement; the hardness and salinity; and the types of living organisms, including microbes, plants, invertebrates, and vertebrates. Of the microorganisms, the micro-algae assume importance due to their diversity, high numbers, and prime position in the aquatic food chain.

Natural, unpolluted air comprises 78% nitrogen, 21% oxygen, 0.3% carbon dioxide and traces of inert gases. The components of the atmosphere which pesticides enter are divisible essentially into (1) the open air (2) enclosed and

semi-enclosed atmospheres such as those inside buildings and glasshouses. The open atmosphere comprises several layers ranging from the stratosphere to the lower atmospheric layers, or troposphere. The thickness of atmospheric layers varies according to climatic conditions, whilst the air density, temperature and barometric pressure all decline with increasing height. The troposphere, which extends from ground level up to heights of the order of 10 km (Gregory, 1973), is the significant zone in relation to pesticide distribution and persistence. The troposphere contains organic and inorganic particulate terrestrial material in addition to living particles, such as microbial cells of all types, fungal and microbial spores, pollen grains and spores of bryophyte and pteridophyte plants. The presence of such a range of particulate material in the air, together with the presence of light and possibly water vapour, suggests a potential for reactivity of this medium with pesticides. The enclosed air inside greenhouses will have restricted movement, reducing the tendency for random distribution of particles and infinite dilution, with the likelihood that as in other types of buildings, dust and microorganisms may accumulate. Whilst the possible existence of true air-inhabiting microbial populations remains speculative, there is no discounting the air's content of transient living organisms, ranging from microbes to insects and birds; neither can we ignore the fundamental fact that all free-living terrestrial surface life forms are in intimate and perpetual association with the air.

Further aspects of the air and water as environments have been discussed by Gray, Jones & Wright (in press), and of the behaviour of pesticides in them by Hill & Wright (in press).

PESTICIDE ENTRY AND MOVEMENT IN WATER AND AIR

Water

The ways in which pesticides are intentionally and unintentionally introduced into aquatic environments have been summarized by Ware & Roan (1970), Frank (1972) and Hill & Wright (in press). The principal direct mode of pesticide entry is through application of various sprays and granular formulations to control water-inhabiting pests such as vascular weeds, algae, insects and snails. Included in this category are the herbicides and insecticides applied to the irrigation water of crops such as rice which are cultivated in an essentially aquatic environment. In all such cases the levels of pesticides entering the water are controlled, usually of the order of a few parts per million or lower, calculated to have the desired effect and approved for the purposes used. Other ways in which pesticides may intentionally though undesirably, enter waters include the disposal of pesticide wastes and containers still containing small volumes of pesticide concentrates (Stojanovic, Kennedy & Shuman, 1972), in industrial effluent discharge, and through on-site cleansing of application and mixing equipment. High levels of pesticides may enter water in this way, but only in very localized situations.

Pesticides may unintentionally or indirectly enter aquatic environments by drift from adjacent aerial or ground applications and as wind-blown droplets or particles. Entry in surface drainage (run-off) water following applications to crops or land is possible, especially where high rainfall occurs soon after application of herbicides (Barnett, et al., 1967; Bovey et al., 1974; Willis et al., 1975), although the concentrations of pesticides in surface drainage waters from treated land are generally low (Merkle & Bovey, 1974). With proper use on agricultural land, herbicide run-off posed little threat to adjacent aquatic areas (Willis et al., 1975). It is also possible for soil-applied herbicide to move into underlying ground water (La Fleur, McCaskill & Adams, 1975). Other modes of unintended entry of pesticides into water include movement into irrigation and drainage water passing

through treated areas; application mal-practice and spillages, although these are infrequent contributors (Frank, 1972); accidents with water-borne pesticide cargo; in industrial effluents; sheep dips, and in particles deposited by rainfall. The extent to which agricultural applications of pesticides infiltrate adjacent waters will be determined by intrinsic factors such as the formulation and application rate and by extrinsic factors including climate, the terrain and the physico-chemical properties of the soil (Balicka, 1974). In general terms, the quantities of pesticides entering natural waters indirectly are far less significant than those applied directly. For example, natural waters contain very low concentrations (e.g. less than 1 ppb) of organochlorine pesticides (Hartung, 1975; Holden, 1975), even though these are the most commonly detected group of pesticides (Merkle & Bovey, 1974). The mode of entry and quantities of pesticides in freshwater, estuaries and the sea have been reviewed by Edwards (1973).

The distribution of a pesticide in water will be determined by its chemical properties, solubility and the type of formulation in which it is applied. Additional factors which may affect the pesticide's aquatic fate include, dilution; movement by currents or turbulence; chemical and photochemical degradation; adsorption to particles and other surfaces; metabolism, accumulation and transportation by living organisms; biological magnification in food chains; and concentration in bottom sediments and at the water-air interface. It is also possible for pesticides to be 'lost' from water to the air by volatilization and aerosol formation. Several of these factors relevant to the redistribution and altered availability of pesticides are the subjects of other papers in this Symposium. Although biological uptake of pesticides does not necessarily remove pesticides from the water environment as a whole, such processes (considered later in this paper) do, of course, remove or scavenge pesticides from the water as such. Further aspects of the behaviour of pesticides in the aquatic environments have been discussed by Hassett & Lee (1975).

Air

Agricultural use is an important source of entry of pesticides into the atmosphere (Robinson, 1973). There is evidence that most pesticides have the opportunity of entering the atmosphere, and some evidence that atmospheric contamination is global (Wheatley, 1973). The atmosphere is essentially a reservoir for pesticides, and in it they may be transported far from the site of application (see, for example, Cohen & Pinkerton, 1966), although with the exception of air within and close to zones of usage, the background concentrations are usually very low. There have been considerable practical difficulties in determining pesticides in the air, however some sampling and quantification procedures are now established (van Dyk & Visweswariah, 1975); Seiber, Woodrow, Shafik & Enos, 1975).

Pesticides occur in the air in vapour, gaseous or particulate form (Crosby, 1973). Appreciable amounts of the very small particles in dust formulations, and even the smallest droplets of liquid sprays, can drift into the atmosphere during application to targets. Entry of pesticides into the atmosphere by volatilization from the surfaces of treated soil, water and plants is probably responsible for a considerable proportion of residues in the atmosphere. Pesticide volatilization, extensively reviewed by Spencer, Farmer & Cliath (1973), is usually most marked in the period shortly after application, depends on the chemical's vapour pressure and is favoured by air turbulence and increased temperature, but reduced in the presence of sorptive surfaces (Lichtenstein & Schultz, 1970). There are some pesticides which rely on volatility to place them into the atmosphere in relatively high localized concentrations, e.g. some fumigants, moth-proofing chemicals and insecticides in resin-impregnated strips. It has recently been found that pesticide storage areas can contribute to the pesticide levels in surrounding air and adjacent situations (Winnett & Siewierski, 1975).

Wind erosion may contribute pesticides to the atmosphere adsorbed on soil particles, whilst some contaminated plant particles (e.g. pollen) and microorganisms are also small and light enough to be wind-blown. Pesticides can travel vast distances on dust particles (Risebrough, Huggett, Griffin & Goldberg, 1968). Physical removal from the atmosphere is mainly by wash-out in rain or by dry-deposition of particles (Wheatley, 1973; Robinson, 1973; Seiber *et al.*, 1975). There may also be transfer of pesticide from one phase to another within the air e.g. from vapour to the adsorbed state (Pitter & Baum, 1975). A model for the dispersion of aerial spray was given by Bache & Sayer (1975), and Crews, Brewer & Petersen (1975) have reviewed methods for modelling atmospheric diffusion.

PESTICIDE DEGRADATION

The term 'degradation' is analogous to 'decomposition' and 'breakdown' and strictly implies destruction of a chemical to simpler components, and possibly even complete mineralization. However, for the purpose of this section in the symposium 'degradation' is to be interpreted more widely. Thus, in so far as the persistence and biological activity of a pesticide may be affected by any change, however slight, to the compound's molecular structure, the term 'degradation' is extended to cover those processes which might otherwise be individually described as 'transformations', 'inactivations' or 'detoxifications'. The terminology used to describe pesticide degradation is discussed by Hill (*in press*). The factors which effect pesticide degradation are divisible into chemical, photochemical and biochemical reactions. Whilst for the purpose of establishing, and to some extent discussing, such processes it is necessary to consider them separately, it is soon apparent that it is invalid to do so since inter-play and interdependence of the different factors is likely in the natural environment. Furthermore, the likelihood of extensive and rapid dilution and dispersal of pesticides in water and air points to the fact that, with localized exceptions, the concentrations of pesticides and any transformation products in these environments will be very low. This is endorsed by the analytical data, and may in turn be interpreted in terms of such environments having relatively lower degradative significance than say, soil, on the grounds that only very low levels are present anyway. Some aspects of the ensuing discussions could, however, dispel such a view of the reactivity of these environments.

DEGRADATION IN THE AIR

The susceptibility of pesticides to abiotic transformation will be determined by their molecular structure and chemical properties (e.g. solubility), and also possibly by the manner in which they are formulated, the types of chemical impurities present, and whether other pesticides or their transformation products are also present. Information on the aerial degradability of pesticides is required, especially for compounds which might be applied under meteorological conditions favouring abiotic reactions (e.g. strong sunlight). The degradative potential of the atmosphere will be influenced, if not determined by, the presence of light, heat, moisture, oxygen, ozone, other gases and oxides of nitrogen, free radicals, particulates and hydrocarbon pollutants (Crosby, 1973; Moilanen, Crosby, Soderquist & Wong, 1975).

Chemical degradation

The free availability of oxygen in the atmosphere suggests a potential for oxidative transformations, including epoxidation, of susceptible pesticides.

Furthermore, although evidence is lacking, there is the possibility that normally non-susceptible pesticides may be sensitized by naturally occurring chemicals to the extent that photo-oxidations may occur (Crosby, 1973). Although many pesticides are known to undergo oxidative changes on exposure to air (see Crosby, 1973), information on the operation of such factors within the atmosphere is lacking. Other abiotic reactions which may occur on surfaces exposed to air, but which do not seem to have been reported for the atmosphere itself include: photo-reduction e.g. reduction of aromatic halides by hydrogen replacement of halogen substituents, and reduction of aromatic nitro-compounds to the corresponding amines; hydrolysis, which may occur with vapourized or particulate chemicals in damp atmosphere; reactions of elimination and isomerization. With the availability of particulate or aerocolloidal material there is a tendency for pesticide transfer from the vapour to the adsorbed state. For adsorbed pesticides, chemical oxidations, hydrolysis and catalytic decomposition may be promoted (Pitter & Baum, 1975).

Photochemical degradation

To undergo photodecomposition a pesticide must absorb light energy. Although the sun's emission spectrum is broad, most of the u.v. radiation below 285 nm is unavailable owing to absorption by ozone in Earth's atmosphere (Plimmer, 1970; Rosen, 1971). Consequently, only those molecules which can absorb sufficient light above 285 nm to activate chemical bond fission can be degraded by sunlight. The absorbed light energy may be released through chemical reactions, often involving chemical bond fission and free-radical formation (Plimmer, 1970; Rosen, 1971). The free radicals are unstable and reactive and the overall photochemical reactions may be manifest in isomerization, substitutions or oxidations. The wide range of pesticides known to be susceptible to photodegradation suggests the potential importance of such reactions, given suitable circumstances. The available wavelength range (285 nm to approx. 450 nm) does, in fact, have sufficient energy to cause photodegradation of organic molecules in the atmosphere, where there is no shortage of oxidant or catalytic surfaces (Crosby & Li, 1969; Crosby, 1973; Moilanen, Crosby, Soderquist & Wong, 1975). Many pesticides have aromatic moieties which absorb in this wavelength region, whilst other substances having lower absorption can be rendered susceptible to light by natural photosensitizers (Rosen, 1971).

Technical difficulties frustrate investigation of pesticide photodegradation in natural atmospheres, and although a few field experiments on herbicide photochemical reactions have been attempted (see Crosby & Li, 1969), large-scale photodegradation of pesticides within the atmosphere is not established (Wheatley, 1973). However, the technology for laboratory photoreactor studies of pesticides in the vapour phase has been developed (Crosby & Moilanen, 1974; Moilanen *et al.*, 1975), and it is possible to at least speculate on photodegradation of pesticides occurring in the atmosphere on the basis of results of laboratory investigations.

Vapour phase photochemical transformations of the cyclodienes aldrin, dieldrin and photoaldrin include epoxidation of aldrin to dieldrin, isomerization of dieldrin to photodieldrin, isomerization of aldrin to photoaldrin, and epoxidation of photoaldrin to photodieldrin, the latter representing a stable product (Crosby & Moilanen, 1974). The photoisomerization reactions of aldrin and dieldrin may be particularly significant since photoaldrin and photodieldrin express higher insecticidal activity than their precursors, due to metabolism to a ketone by the insects (Rosen, 1971). The same workers (Moilanen & Crosby, 1973) reported the photochemical transformations of vapour-phase *pp*-DDT in which the first reaction, occurring readily, was the well-known dehydrochlorination to form *pp'*-DDE, followed by reactions via 4,4'-dichlorobenzophenone to the stable product dichlorobiphenyl. However, although in vapour phase the organophosphorus insecticide parathion was stable to persistent u.v. irradiation, it was rapidly photodegraded when adsorbed on dust particles in air (Moilanen *et al.*, 1975). One of the products, paraoxon,

was an established photooxidation product of condensed-phase parathion. These observations signified the possible importance of particulate surfaces in determining, via adsorption, the photochemical transformations in the atmosphere. Other pesticides, such as DDT, are known to be photodegraded in the adsorbed state and it is likely that this could also occur on particles in the atmosphere (Pitter & Baum, 1975).

Moilanen et al. (1975) have suggested that pesticides may be subject to photodegradation and the action of natural photosensitizers in the thin organic films at water-air interfaces and in similar films which coat airborne particles.

Pesticides are deposited on the aerial surfaces of terrestrial and aquatic plants during pest control operations and to a smaller extent from vapourized and particulate atmospheric sources and rainwater. The persistence of pesticides in this rather specialized aerial situation will be governed by the extent of their uptake by the plants and by factors, such as wash-off and volatilization, which physically remove them. However, pesticides or plant and microbial metabolites thereof on plant surfaces are also exposed to sunlight, and may be subject to photodegradation. For example, photochemical degradation of the herbicides diquat and paraquat adsorbed on plant surfaces may occur (Calderbank, 1968), a principal product in the case of paraquat being 4-carboxy -1-methylpyridinium chloride (Slade, 1966).

Through the entry and transport of pesticides and their products, in vapour and particulate form, in the atmosphere, they are placed in a situation where there is distinct potential for the absorption of u.v. energy. Crosby & Li (1969) considered that representatives of most classes of herbicides can be decomposed by u.v. light, and that although influenced by a number of factors, it is possible for photochemical reactions, which often liberate products similar to those of chemical and microbial attack, to occur in the air. It is therefore possible that under appropriate conditions the atmosphere may be a significant medium for the degradation of some pesticides, especially in those aerial situations where photosensitizing compounds are likely to be present.

Biological processes

Considering the general very low levels of pesticides in the atmosphere and the fact that this environment is not densely populated by free-living organisms, the opportunities for biological scavenging or intervention in the fate of air-borne pesticide may at first appear remote. If, however, we extend our view of the biological systems in the atmosphere to include all microbial, plant and animal forms perpetually exposed to the atmosphere, then a number of possibilities are opened-up. The fact that the air is inhabited and contacted by a wide range of living forms suggests a potential for partitioning of pesticides from the air into biological systems, wherein there are many opportunities for 'degradation'. However, in terms of the contribution to the overall fate of pesticides in the environment, the scale of such events occurring 'free' in the air is probably small and the significance doubtful.

The small size and spatial distribution of the microbiological components of the atmosphere reduce the chances of their contact with pesticides. For this reason, coupled with the lack of available nutrient and energy sources, the extent of microbial transformation of pesticides in the atmosphere is likely to be very small except possibly in the rare situations where high numbers of microorganisms exist in localized aerial situations concurrent with pesticides. However, a different picture emerges when considering the microorganisms which populate the aerial surfaces of plants (the phyllosphere). In these situations both the numbers of heterotrophic microorganisms and quantities of pesticides may reach levels commensurate with requirements for microbial degradation. There is also the

possibility that leaf-surface microorganisms may degrade the products of photochemical transformations of pesticides occurring on leaf surfaces. For example, 4-carboxy -1-methyl-pyridinium chloride (N-methyl isonicotinate), which is formed photochemically from paraquat on leaf surfaces, can be degraded by bacteria in pure culture (Orpin, Knight & Evans, 1972; Wright & Cain, 1972) and it is conceivable that this could occur on leaf surfaces.

The other life forms which move through the atmosphere are flying insects and birds. The discharge of insecticidal dusts, sprays and aerosols into the air and onto plants to combat insect pests represents the most obvious direct mode of contact and uptake of pesticide by airborne insects. It is also an indirect route for pesticides into animals, including birds, which prey upon the insects (Robinson, 1973). Furthermore, insects and birds may take up other pesticides, e.g. herbicidal sprays, not aimed at them, by inhalation or absorption through the body surface.

Degradation of insecticides by target insects seems unlikely to represent significant 'removal' of insecticides from the air. It is possible, however, that with a greater potential for uptake and accumulation of residues, carnivorous birds may make a small contribution even though the numbers of birds involved in any particular instance would be very low. Pesticide metabolism by wild birds does not seem to have received as much attention as the toxicology and residue accumulation. Some aspects of insecticide metabolism by avian species have, however, been reviewed by Stickel (1973) and Walker (1975).

DEGRADATION IN AQUATIC ENVIRONMENTS

Much of the interest in pesticides in aquatic systems has concerned their concentration levels and persistence, their uptake and magnification in organisms at various levels in the food chain, and their toxicity to aquatic life ranging from plankton to fish and fish-eating birds. By comparison there are fewer data on degradative processes, reaction rates and products. This is not entirely surprising in view of the difficulty in distinguishing between the actions of some physical, chemical and biological forces upon the compounds in what is often a fairly complex environment. Therefore, although for the purpose of this discussion, degradation processes are mainly considered separately, it should be recognized that biological and physico-chemical reactions may overlap (some examples of which will be given). Thus it is conceivable that biodegradation products may be further degraded or modified chemically, or *vice versa*. It is not easy to project from simple 'one-member' laboratory systems to the complex situations in natural aquatic environments.

Chemical reactions

Water is a suitable medium for chemical reactions, and a variety of factors such as solute concentration, salinity, temperature, pH and light, together with the presence of particulate adsorbing sites and soluble organic compounds, suggest a potential for chemical reactions in natural waters. Such reactions involving pesticides may occur in solution, in water surface films, on the catalytic surfaces of suspended particles and in bottom sediments. The degradative reactions which pesticides might undergo in water include: Oxidation, reduction, hydrolysis, elimination, isomerization and decarboxylation.

Many natural waters have a slightly alkaline reaction, and some pesticides, including carbamates, dinitrophenol esters, and organophosphorus esters, are susceptible to alkaline hydrolysis (Crosby, 1973). The insecticide carbaryl (1-naphthyl methylcarbamate) undergoes chemical and photochemical hydrolysis to 1-naphthol (Crosby, Leitis & Winterlin, 1965). The hydrolysis of carbaryl occurs in water (Back, 1965) and sea-water (Karinen, Lambertson, Stewart & Terriere, 1967),

whilst the related compound PCMC (p-chlorophenyl N-methylcarbamate) also undergoes spontaneous hydrolysis in aqueous solution to p-chlorophenol (Westmacott & Wright, 1975). Both 1-naphthol (Bollag & Liu, 1972; Walker, Janes, Spokes & Van Berkum, 1975) and p-chlorophenol (Westmacott & Wright, 1975) are degraded by microbial cultures. It is therefore possible that in the aquatic environment the degradation of these insecticides may be initiated by chemical or photochemical hydrolysis, to be followed by further chemical or microbial degradation.

Because of their susceptibility to hydrolysis in water (and soil) the organophosphorus insecticides are not considered to pose a long-term environmental threat. The hydrolysis of organophosphorus compounds such as diazinon and malathion is pH-dependent. For example, malathion is rapidly hydrolysed under alkaline conditions but is stable below pH 7.0 (see Paris & Lewis, 1973). Hydrolysis of the ester linkage of parathion (0,0-diethyl-0-p-nitrophenol phosphorothioate) in lake water yielded diethylthiophosphoric acid and p-nitrophenol (Graetz *et al.*, 1970). Similarly, esters of 2,4-D (2,4-dichlorophenoxyacetic acid) hydrolyse to the acid in alkaline solutions.

Strictly chemical reductions (i.e. not photo-chemical) of pesticides are not widely encountered, although the fact that iron porphyrins added to lake water reduced DDT to DDD (Miskus, Blair & Casida, 1965) may be of significance in view of the distribution of porphyrin compounds in biological systems.

Photochemical degradation

Considering that many pesticides likely to enter aquatic environments have molecular configurations (e.g. aromatic rings) which absorb u.v. energy, the photodegradation of such compounds in water is possible. This applies only at depths penetrated by sufficient light energy of appropriate wavelengths. There have been several studies of the photodegradation of pesticides, especially herbicides, in aqueous solution under controlled conditions. Indeed, with appropriate 'hardware', such experiments and the analysis of photodegradation products would seem to be a comparatively straightforward procedure. The study of pesticide photodegradation in natural waters poses greater problems in experimentation and data interpretation. Under such conditions it is difficult to envisage how, if at all, the strictly photochemical reactions can be distinguished from chemical and biochemical processes which may either produce common products (Crosby & Li, 1969), or which might collectively transform the pesticide. The situation becomes even more complicated with compounds such as some phenoxy herbicides, which may undergo different photochemical reactions (e.g. photo-oxidation, photo-reduction and hydrolysis). Furthermore, apart from depending on the intrinsic properties, the photochemical degradation of pesticides in natural waters will be affected by factors such as the quantity and quality of light energy passing through the water, the pH (Aly & Faust, 1964), the presence of adsorbing surfaces, the availability of dissolved oxygen and reducing sources, the physical and biological factors which may remove photolysis products, and the presence of photosensitizing, or even desensitizing, substances.

With the recognition of the fact that diverse naturally occurring substances can act as photosensitizers, there is reason to believe that photosensitization of pesticides could occur in aquatic environments (Crosby & Li, 1969). Soderquist & Crosby (see Moilanen *et al.*, 1975) found that the rice herbicide MCPA (2-methyl-4-chlorophenoxyacetic acid) underwent photolysis more rapidly in sterile rice paddy water than in buffered distilled water. Although sterilized paddy water is not 'natural', this indication that agricultural waters contain photosensitizers suggests that photosensitization may be important in pesticide photodegradation in the environment.

The photodegradation of some of the widely used phenoxy acid herbicides in aqueous solution has been extensively studied under laboratory conditions. From

these studies (see Crosby & Li, 1969; Moilanen et al., 1975) it is evident that several types of photolytic reactions occur and that the products of some of these are the same as those generated by chemical and microbial action. Thus, the photolysis of 4-CPA, 4-chlorophenoxyacetic acid, (Crosby & Wong, 1973) included side chain photo-oxidation, followed by hydrolysis firstly to 4-chlorophenol and then hydroquinone. Another reaction was photoreductive dechlorination releasing phenoxyacetic acid, which is also photo-oxidized to hydroquinone, whilst photonucleophilic hydrolysis of the pesticide was followed by oxidation and hydrolysis, again to hydroquinone. The hydroquinone is then oxidatively polymerized to humic acids (Crosby & Wong, 1973). Photochemical reactions in 2,4-D degradation include ether bond cleavage to form, 2,4-dichlorophenol (also a microbial metabolite), or stepwise dechlorination of the aromatic ring. Either way, the subsequent product, 1,2,4-benzenetriol, is unstable to air (Crosby & Li, 1969). Aly & Faust (1964) showed that photolysis of both 2,4-D and 2,4-dichlorophenol occurred more rapidly at pH 9 than at pH 7 or 4.

Most studies on 2,4-D photodegradation have been made using u.v. light at 254 nm. Although this wavelength is absorbed by 2,4-D, it is well below the sunlight lower limit. For this reason Aly & Faust (1964) considered that the sunlight energy might be insufficient to effect such reactions in aqueous solutions, and since suspended particles and organic matter might further reduce the effects, they inclined to the view that sunlight would not be significant in the decomposition of 2,4-D in surface waters. Sunlight photolysis of 2,4-D is known to occur in the presence of a light-absorbing photosensitizer such as riboflavin (see Crosby & Li, 1969), and whilst this could possibly occur in natural waters it would be difficult to prove. Rosen (1971) points out that photosensitizers may act either by altering the products of direct irradiation, or by causing photolysis of pesticides which do not absorb appropriate light on their own.

Propanil (3',4' -dichloropropionanilide), is used in the selective control of broad-leaf weeds in cultivated rice. The photodegradation of aqueous solutions of propanil exposed outdoors to natural sunlight was investigated by Moilanen & Crosby (1972), who identified several unstable degradation products. The main reactions, each of which give non-phytotoxic products, were: replacement of aromatic chlorine substituents by -OH groups; formation of propionamide; reductive dechlorination; and amide hydrolysis (aniline formation). The condensation product, 3,3',4,4'-tetrachloroazobenzene (TCAB) and a humic acid were also detected. The photolytic formation of 3,4-dichloroaniline (DCA) and its condensation to TCAB is interesting in view of the fact that 3,4-dichloroaniline is also formed from propanil by soil microorganisms, and TCAB is formed in propanil-treated soil (Bartha & Pramer, 1967). It is, therefore, possible that sunlight and microorganisms may synergistically effect the degradation of propanil in rice paddy water, and the possible intervention of photosensitizers is again suggested by the finding that riboflavin phosphate can induce photolysis of DCA in aqueous solutions (Rosen, 1971). Considering the apparent suitability of some other propanil photolysis products to microbial metabolism (e.g. the hydroxypropionanilides, propionic acid and propionamide), there may be a considerable degree of interplay between abiotic and biotic factors in propanil degradation.

Some of the photochemistry of herbicides has been studied *in vitro* with aqueous solutions and suspensions (see Crosby & Li, 1969) and such reactions might relate at least in part to events in natural water environments. Photodegradation may reduce the persistence of some pesticides in water, but there may be cases where this is disadvantageous, e.g. with compounds applied for pest control in waters. However, photochemical changes in pesticides need not necessarily be extensively degradative, and it is possible for structurally complex substances with unknown toxicity to be generated (Rosen, 1971). Although photodecomposition may cause some loss of pesticide residues in clear surface waters exposed to long periods of sunlight, photolytic processes are much less significant in turbid waters lacking in light penetration (Gomaa & Faust, 1974).

Biological Degradation

(a) Uptake

Most aquatic environments support diverse and often numerous forms of life, so that there is appreciable potential for biological involvement in the aquatic fate of pesticides. Aquatic organisms can affect pesticide fate by physically removing the compound, in whatever phase, from the water. This, the biological uptake of pesticides, is also highly relevant to the degradation or metabolism of pesticides by living organisms.

Microorganisms have in general a high surface area: mass ratio which, coupled with the low water solubility and lipophilic nature of many pesticides, may account for significant removal of pesticide from water by adsorption on cell surfaces, whether or not intracellular absorption occurs. Aquatic organisms higher up the scale, including invertebrates, fish, reptiles and mammals, may either ingest pesticides in their food or prey, or absorb the pesticides directly from the surrounding water. Fish can absorb pesticides from the water via the gills and skin, and high levels of insecticides such as DDT are concentrated in fatty tissues (Edwards, 1970). Organochlorines are also absorbed from water by invertebrates such as oysters and sea squirts (see Edwards, 1970), crustacea and insect larval stages (Crosby & Tucker, 1971; Johnson, Saunders, Sanders & Campbell, 1971) and protozoa (Gregory, Reed & Priester, 1969). In fact, direct uptake of organochlorine insecticides from water by aquatic animals is probably often more important than ingestion of pesticide-contaminated food (Edwards, 1970; Moriarty, 1975; see also Kerr & Vass, 1973; Hartung, 1975). Fish can also absorb pesticides from contaminated sediments (Kobylinski & Livingston, 1975). It is also possible for fish to transfer pesticide residues to the offspring (Burdick *et al.*, 1964), and for fish eggs to absorb pesticides directly from water (Heisinger & Green, 1975).

Plants, including the macroscopic algae or seaweeds, floating and submerged aquatic weeds, and the water-edge shrubs and trees, may also take up pesticides from the surrounding water. Uptake of herbicides from water by target aquatic weeds may be especially significant. Upon the death of organisms containing pesticides or their metabolites, autolysis and decomposition will release residues back into the water. Dead organisms containing pesticide residues may also sink, (Wojtalik, Hall & Hill, 1971), and this can have an important bearing on the microbiological degradation of pesticides under the anaerobic conditions of bottom sediments.

The uptake and concentration of pesticides from aqueous media or aquatic environments has been widely reported for the primary-producer micro-algae and phytoplankton. The pesticides taken up by algae include several chlorinated hydrocarbon, cyclodiene, and organophosphorus insecticides; phenoxy-acid, triazine and hydroxybenzotriazole herbicides (see Wright, *in press*). In general, pesticide uptake by aquatic bacteria and fungi has received less attention. However, the accumulation of DDT and dieldrin from water by fungi, bacteria and actinomycetes (Chacko & Lockwood, 1967), and DDT and methoxychlor by bacteria (Johnson & Kennedy, 1973), has been shown.

The adsorption of pesticides onto suspended particles and sediments in water bodies has the initial effect of removing the pesticide from the aqueous phase, although desorption may also occur to the extent that a continual supply of pesticide is passed back to the aqueous phase (Huang, 1971). Whereas adsorption of a pesticide onto colloids may reduce the likelihood of microbial attack, desorption would favour it. The adsorbed state may increase the chance of pesticide ingestion by filter-feeding animals and detritivores, whilst adsorption to sediments places the pesticides in a situation for potential anaerobic degradation.

Pesticide degradation by plants is discussed in another contribution to this

Symposium and will not be considered further here. However, in aquatic situations there are also diverse animal species which are exposed to pesticides.

(b) Metabolism by aquatic animals

Some foreign or toxic chemicals may resist metabolism by animals and either be accumulated or excreted unchanged. In many cases, however, the animals are able to metabolize the chemicals and excrete metabolites. Usually the process involves detoxication, but it is also possible for toxication reactions to occur (Walker, 1975). The potential toxicity of pesticides to aquatic animals, especially fish, and the possibilities for metabolism and metabolite accumulation, are aspects studied thoroughly prior to acceptance of pesticides for registration.

The principal metabolite of DDT in mature freshwater crustacea such as Daphnia sp. and Gammarus sp., and in nymphs and larvae of aquatic insects, was the dehydrochlorination product DDE, whilst in some cases smaller amounts of the dechlorination product, DDD, were also formed (Johnson et al., 1971). Neudorf & Khan (1975) have also reported conversion of DDT to DDE in the freshwater flea, Daphnia pulex.

In the metabolism of DDT by fish it is apparent that both qualitative and quantitative differences exist between different tissues (e.g. liver, brain, and eggs) of individual fish, between species and habitats, and according to the degree of exposure to the pesticide (Johnson, 1973). Fish from the higher trophic levels show a greater tendency to metabolize DDT than those from lower levels, the predominant metabolite being DDE, with occasional reports of DDD (see Johnson, 1973). Malone (1970) reported that DDT is also converted to DDD by fungi and bacteria from the gut of fish. As occurs in aquatic invertebrates (Johnson et al., 1971) and microorganisms, there is a marked tendency in fish for epoxidation of aldrin to dieldrin, in which form it may accumulate (Johnson, 1973). The fact that pesticides can be transformed to other toxic compounds at this low level of the aquatic food chain suggests the possibility of biological magnification of such metabolites, in addition to the parent compounds, in the higher trophic levels.

A common feature in vertebrate transformation of toxic foreign compounds is the operation of essentially two phases, in which the compound is first converted into a metabolite, which may then be conjugated with endogenous molecules. Both phases usually, but not always, lead to detoxication and increased water-solubility which aids excretion (Walker, 1975). The primary site of both types of reaction is the liver although other organs may also be involved. The first phase metabolic reactions include: hydrolyses (e.g. esterase, phosphatase and amidase); oxidations (e.g. by mixed-function oxidases); hydration, and reduction. Conjugation reactions include those with glucuronic acid (forming glucuronides), sulphates, and glutathione. These processes have generally been studied in target organisms and those high in the food chain.

Mixed-function oxidases (MFO) are responsible for epoxidation reactions of cyclodiene insecticides (e.g. conversion of aldrin to dieldrin) in fish and a variety of fresh-water invertebrates, and also for hydroxylation of certain cyclodienes in fish (Khan, Gassman & Ashrafi, 1975). Like epoxidation, the reduction of pesticides containing nitro (-NO₂) groups to the amino (-NH₂) compound, is a property shared by fish and microorganisms. Thus, both parathion and paraoxon are reduced in fish tissues to the amino derivative which may then be hydrolyzed to p-aminophenol and subsequently conjugated (Khan et al., 1975).

(c) Metabolism by microorganisms

Of the fact that in many aquatic environments there exist microorganisms with the ability, or adaptability, to transform or degrade most organic pesticides, there

seems to be little doubt. It is even possible to regard aquatic microorganisms as the active ingredients of a biological 'soup', which in certain cases may have considerable degradative potential. This idea can be related with some certainty to those situations where the microorganisms and pesticides are present at the same time in significant concentrations and under suitable conditions of, for example, pH and temperature. Such situations may be represented by the dense cell populations of algal blooms, by high numbers of heterotrophic bacteria in organically polluted water, in muds and sediments, and where submerged particles, plant and stone surfaces, decaying organisms or other underwater structures, are colonized by microorganisms.

Just as in the study of pesticide degradation by soil microorganisms, aquatic environments can be shown to yield isolates capable of pesticide degradation in vitro; but to what extent do such reactions relate to any which may occur in the natural water? Indeed, is it not possible that the reactions are artefacts of the controlled pure culture regime, which bears virtually no resemblance to the biologically and physico-chemically heterogeneous natural aquatic system? Whilst the pH of cultures usually relates somewhat to that in natural water, the temperatures selected rarely do. There are not many natural aquatic systems where the temperature ever reaches values of 25°-30°C (commonly used in pure culture pesticide degradation studies), let alone constantly maintained at such levels.

The pure culture approach to pesticide degradation by aquatic microorganisms can be justified in so far as data can be obtained on the degradative ability of such organisms and the mechanisms involved. It is desirable though that some attempt is made to relate experimental systems to the natural environment. To this end the use of mixed microbial cultures, possibly in the presence of other organisms such as invertebrates, under physico-chemical conditions and pesticide concentrations akin to those in the environment, may prove a useful starting point. Ideally, microbial degradation of pesticides should be studied in the natural aquatic systems, preferably in situ. There are, however, considerable experimental and analytical difficulties to overcome in this approach in order to characterize degradative sequences and attribute them with any degree of certainty solely to microbial activity. For evidence of microbial degradation of pesticides in aquatic environments reliance is largely placed either on data from pure cultures, or on experiments with incubated water and mud samples (often with sterilized controls) which indicate biodegradation and which, in the absence of other visible forms of life, is reasonably presumed to be microbiological.

Pesticides of low water-solubility may passively partition into microbial cellular lipids. However, although there is little specific information, many pesticide molecules also seem to be of types suited to active uptake by microbial cells both for metabolism as carbon, nitrogen, and energy sources, or even for incidental enzymic conversion (co-metabolism). Microorganisms are potentially efficient scavengers of pesticides in the diluted state of aquatic environments, and being generally active and resourceful metabolically it is likely that under suitable conditions they could constitute a significant pesticide degradation force in aquatic systems. By the release of pesticide metabolites and through their action upon the chemical and photolytic products of pesticides, microorganisms probably occupy an important position in what may be a composite network of abiotic and biotic factors determining the fate of a pesticide in water.

Some microorganisms found in freshwater and estuarine situations are closely related to the types found in soil, whilst others, especially marine types, are specialized for an aquatic existence. The numbers and types in aquatic microbial populations are determined by light penetration, salinity, pH, temperature, nutrient availability, and the activity of predators. The 'typical' aquatic microorganisms span much of the microbial kingdom from blue-green algae and bacteria to the eukaryotes, including yeasts, protozoa, algae, diatoms, dinoflagellates, desmids, and multi-cellular algae and fungi.