There have, in general, been more investigations of pesticide degradation by soil isolates than by aquatic isolates. However, since there are at least qualitative similarities between aquatic microorganisms and those inhabiting soil, there is reason to assume that pesticide degradative mechanisms would be similar even if the gross contributions in the two environments are not. Reactions by which microorganisms degrade representatives of the major classes of pesticides have been extensively surveyed by Kaufman (1974) and Hill (in press). Microbial oxidative reactions on pesticides include, β-oxidation, N-dealkylation, o-ether cleavage, epoxidation, aromatic ring hydroxylation and cleavage, oxidative dehalogenation, and co-metabolic processes. Amide and ester bonds are hydrolysed and halogen substituents can be hydrolytically removed. The reductive reactions include dehalogenation and nitro-group reduction. Other reactions are dehydrochlorination and condensation. Typical pesticide-degrading microbial genera of aquatic environments are listed in Table 1. All of the algae included were isolated from aquatic situations. Although that is not necessarily so in the case of all of the other organisms listed, these genera are nonetheless commonly found in natural waters.

Table 1

Examples of pesticide-degrading microbial genera in aquatic environments

Bacteria and Actinomycetes	Fungi and Yeasts	Algae
Achromobacter	Aspergillus	Agmenellum
Aerobacter (Enterobacter)	Fusarium	Ankistrodesmus
Alkaligenes	Lipomyces	Chlamydomonas
Arthrobacter	Mucor	Chlorella
Azotobacter	Penicillium	Chlorosarcina
Bacillus	Saccharomyces	Cladophora
Clostridium	Torulopsis	Cylindrotheca
Corynebacterium	Trichoderma	Dunaliella
Escherichia		Scenedesmus
Flavobacterium		Synechococcus
Nocardia		Vaucheria
Proteus		
Pseudomonas		
Streptomyces		

It is not intended here to describe pesticide degradation mechanisms and metabolic pathways. These aspects, particularly in relation to soil microorganisms, have been reviewed for herbicides (see Kearney & Kaufman, 1969; Wright, 1971, 1974; Kaufman, 1974; Cripps & Roberts, in press), insecticides (Matsumura & Boush, 1971; Kaufman, 1974; Matsumura & Benezet, in press), nematocides and fungicides (Woodcock, 1971; Woodcock, in press). Rather, attention will be focussed on two spheres of biological importance, either or both of which are typical of most aquatic systems, for which there are specific data regarding pesticide degradation. These are (a) the algal and phytoplankton populations and (b) the microorganisms of the oxygen-deplete phases represented by mud, sediments and submerged soil.

The metabolism of pesticides, especially herbicides, in higher plants is widely reported. It therefore seems possible that the micro-algae, with cellular affinities to those of higher plants, should also be able to metabolize such compounds. Examination of the literature reveals several reports on algal metabolism of insecticides and surprisingly few on herbicide or algicide degradation by these organisms. The apparent emphasis on metabolism of insecticides, especially the organochlorines, is undoubtedly related to the concern for their high degree of environmental persistence and the tendency to accumulate in organisms at the base of the food chain, with subsequent biological magnification in predators. Many pesticides

contain aromatic or heterocyclic moieties, and reports that eukaryotic algae were capable of fission of the aromatic ring (Craigie, McLachlan & Towers, 1965; Vose, Cheng, Antia & Towers, 1971) and the heterocyclic pyrimidine ring (Knutsen, 1972) have indicated that this is not the restricted province of heterotrophic microbes. Although far less attention has been given to algal degradation than bacterial and fungal degradation of pesticides, the fact that several algal genera can be listed in Table 1 is surely significant.

Evidence points to a wide ditribution amongst micro-algae of the dehydrochlorination mechanism to form DDE, as the principal degradative reaction on DDT. The formation of the less toxic DDE from DDT was reported in marine diatoms (Keil & Priester, 1969; Bowes, 1972) and in freshwater diatoms isolated from a mosquito breeding site (Miyazaki & Thorsteinson, 1972). A small proportion of DDT was converted to DDE by the blue-green alga Synechococcus elongatus (Worthen, 1973). The freshwater green alga Ankistrodesmus amalloides (Neudorf & Khan, 1975) and several species of marine algae (Rice & Sikka, 1973a) also carried out this reaction. In the latter case DDE was the only DDT metabolite, whereas Neudorf & Khan (1975) also detected small amounts of the dechlorination product,DDD (TDE). Patil, Matsumura & Boush (1972) reported the formation of DDD in marine algal and plankton samples, whilst in pure cultures of Dunaliella sp. and Agmenellum sp. the principal metabolite was DDOH. Although Wheeler (1970) and Rice & Sikka (1973b) did not detect any algal metabolites of dieldrin, the toxic 'terminal residue' photodieldrin was found in marine algal samples collected by Patil et al. (1972). It is significant that aldrin was converted to dieldrin and transaldrindiol, and endrin to ketoendrin, in marine samples containing algae and other microorganisms, but not in plain sea-water (Patil et al., 1972). Sweeney (1969), who reported uptake and metabolic detoxication of gamma-BHC (as lindane) by the green algae Chlorella vulgaris and Chlamydomonas reinhardtii, considered that algal metabolism could account for the low levels of lindane detected in the Great Lakes.

Ahmed & Casida (1958) reported metabolism of some organophosphorus compounds by Chlorella. One of the organophosphorus insecticides, parathion, was rapidly degraded in rice paddy water, and the presence of algae hastened the degradation in vitro (Sato & Kubo, 1964). The major product of parathion degradation by Chlorella vulgaris was the reduced non-insecticidal compound aminoparathion (Zuckerman, Deubert, Mackiewicz & Gunner, 1970).

Ring-hydroxylation metabolites of the phenoxy-acid herbicide 2,4-D were formed by Scenedesmus quadricauda (Valentine & Bingham, 1974). Other herbicides degraded by algae include the urea compounds preforan and fluometuron (Tweedy, Loeppky & Ross, 1969); the s-triazine, simazine (Kruglov & Paromenskaya, 1970); and the acylanilide herbicide propanil (Wright, in press), the latter being converted to 3,4-dichloroaniline. Teal (1974) described the degradation of the fungicide ethirimol by green algae, and Fitzgerald (1975) gave evidence for algal degradation of some algicides.

Whilst the anaerobic conditions of sediments are probably unsuitable for biodegradation of some pesticides, there is evidence that for others, especially some organochlorines, such conditions are conducive to microbial degradation. Aly & Faust (1964) reported that whereas 2,4-D persisted in aerobically incubated lake water, rapid biodegradation occurred in lake mud suspensions pre-treated with 2,4-D, or in the presence of mud from a lake which had previously been treated with 2,4-D. These results indicated that lake mud contained microorganisms capable of adapting to degrade 2,4-D. Okey & Bogan (1965) reported considerable biodegradation of 2,4-D in activated sludge.

Other workers have also demonstrated pesticide degradation in aquatic systems of high biological activity and relative anaerobiosis. Hill & McCarty (1967) reported that all insecticides tested underwent at least some anaerobic degradation in digested waste-water sludge, which, with the exception of dieldrin and heptachlor

epoxide, occurred more rapidly than under aerobic conditions. DDT was the most striking example, being unchanged during aerobic incubation and rapidly converted to DDD (TDE) anaerobically. DDD was also formed from DDT in marine sediments (Patil et al., 1972) and in flooded soil (Castro & Yoshida, 1971). DDT, methoxychlor, DDD and heptachlor were degraded more rapidly by microbial action in flooded soil than in upland soil (Castro & Yoshida, 1971). Gamma-BHC persisted longer in sterilized flooded soil than in non-sterilized flooded soil, suggesting microbial degradation in the latter (Raghu & MacRae, 1966). Microbial isolates from sea-water (Patil, et al., 1972) and from lake water and silt (Matsumura, Patil & Boush, 1971) metabolized DDT to DDD and minor metabolites (DDE, DDNS), whilst dieldrin was converted to the toxic photodieldrin (Matsumura et al., 1970).

The organophosphorus insecticides are more soluble in water than organochlorines, and since they are likely to enter natural waters both indirectly and in deliberate applications, their degradation in these environments is important. Graetz et al. (1970) studied the degradation of aqueous parathion incubated at 23^{o} with lake sediments and found that the insecticide was both chemically hydrolysed and microbiologically degraded. Microbiological reduction of parathion to aminoparathion in the sediment system was substantiated under both anaerobic and aerobic conditions for lake sediment microbial isolates in culture. Under aerobic conditions aminoparathion was degraded further and it was concluded that microbial activity would markedly influence parathion persistence in the natural aquatic environment (Graetz et al., 1970). Sethunathan (1973) has considered that in addition to nitro-group reduction, biochemical hydrolysis of parathion occurs in flooded soil.

Microbial involvement in the degradation of the organophosphorus insecticide diazinon in submerged tropical soil was indicated by Sethunathan & MacRae (1969). Following the use of diazinon in rice paddy fields, Sethunathan & Pathak (1971) reported the development of a diazinon-degrading microbial agent in the paddy water. Diazinon degradation was not attributable to chemical hydrolysis, and was insignificant in paddy water which had not been previously treated with diazinon. Sethunathan & Pathak (1971) further established that aerobic microbial degradation of the insecticide in paddy water was far more rapid than the degradation rates observed in flooded soil by Sethunathan & MacRae (1969). The aerobic nature of the diazinon-degrading microflora (Sethunathan & Pathak, 1971) in this situation was considered significant in view of the aerobic status of rice field waters maintained by oxygen diffusion from the atmosphere and release by photosynthesizing algae. Microorganisms isolated from submerged soils metabolized diazinon in cultures provided with an additional carbon source (Sethunathan & MacRae, 1969; Sethunathan & Pathak, 1971).

Conclusions.

With locallized exceptions, pesticides in air and water are usually very dilute. Nonetheless it is possible for chemical, photolytic and biological forces, acting individually in combination or sequence, to effect structural changes in pesticides. Laboratory studies suggest the likelihood of photochemical reactions occurring in the vapour, particulate or surface-exposed phases in the air. In aquatic environments the additional biotic factors assume particular importance in pesticide degradation. Biological systems scavenge pesticides, with the result that metabolism and transfer of the pesticide and metabolites to other organisms in the food chain may occur.

To consider pesticide persistence solely from the aspect of loss of activity or even destruction of the parent compound is to ignore the possibility that some degradative agencies may elicit only subtle structural alterations in the pesticides. Thus, compounds of unknown toxicity may exist, if only transiently, and more recalcitrant toxic products of minor chemical alteration (e.g. photodieldrin) are also known. Other reactions, e.g. animal metabolic conjugations, 'microbial' condensations, and some photochemical processes may generate compounds structurally more complex than the pesticide itself. It is not easy to determine the degradative events of

pesticides in the air and water under natural conditions. However, laboratory experiments, usually with 'one member' reactant systems, are useful in providing fundamental data, even if limited in the extent to which they can be used to predict environmental events.

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