WHAT PESTICIDES DO TO SOILS

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Partly by design, partly as a side effect of other activities, pesticide chemicals in increasing quantities are finding their way into the soil. Numerous insecticides, herbicides, fungicides, and fumigants have proved their worth in the control of soil-borne pests; their commercial use in this way continues to grow. In addition, residues of pesticides applied above ground often arrive, by one route or another, upon or beneath the soil surface. What happens to these chemicals in the soil, and what happens to soil properties as a result of their presence, are matters of importance to agriculturists and to the agricultural chemicals industry. The articles that follow summarize the growing body of knowledge on soil-pesticide interrelationships

1. *Fumigants, Fungicides, and the Soil*

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FUMIGANTS AND FUNGICIDES are applied to the soil to kill or reduce the numbers of root-infecting organisms. The action of the chemicals, however, is not limited to parasitic forms. Saprophytic and autotrophic organisms may also be killed or reduced in numbers. The nature of the microbial population of the soil may be altered for relatively long periods of time, and chemical and physical changes may occur in the soil.

Influence on Soil Population

When a chemical is applied to the soil in sufficient concentration to kill plant root parasites, all or most types of soil microbes are either killed or, more commonly, reduced in numbers. The actual percentage of kill depends on such factors as soil type, moisture content, temperature, and physical condition, kind of chemical applied, and method of application. After the initial kill or reduction in numbers, certain types return very quickly and reach numbers far in excess of those in untreated soils, while others return at various times and may or may not exceed numbers in the original soil. With time, which may be a year or longer, total numbers tend to approach those of the untreated soil.

Bacteria multiply rapidly after fumigation or fungicidal treatment and within a few days are usually much more numerous than in the untreated soil. In general, the greater the initial kill the higher the subsequent peak in numbers.

Little is known concerning the influence of fumigants and fungicides on soil actinomycetes. Observations with over 200 chemicals indicate that generally the actinomycetes are affected in a manner similar to bacteria. Occasionally, however, they appear to be more resistant than bacteria are. Waksman and Starkey noted that actinomycetes are more tolerant of low dosages of toluene than are most bacteria, but when bacterial numbers increase after treatment, relative numbers of actinomycetes decrease. We have noted similar effects and so has Wensley.

Soil fungi are usually more readily killed by soil fumigants and fungicides than are some bacteria. However, some chemicals, such as 5-nitrobenzotriazole, *tris* (hydroxymethyl) nitromethane, and ethyl chloroacetate, exert a greater lethal effect on bacteria than on fungi. Following initial kill or reduction in numbers, fungi return to the soil. They may return soon after the bacteria and attain higher numbers than in the original soil, or they may remain at low numbers for relatively long periods of time. Warcup found that 18 months after treatment of a field soil with formalin, the numbers of fungi were still lower than in untreated soil. Field studies in southern California have indicated that following field applications of D-D or other fumigants to some soils, numbers of fungi may still be very low even three years after treatment, while in other soils they return within one to three months and may attain relatively high numbers.

In a laboratory study the numbers of molds reached a very high peak shortly after fumigation of acid soils, whereas in alkaline soils they reestablished slower and did not attain as high numbers.

Very little is known concerning specific effects of common soil fumigants and fungicides on numbers of protozoa, algae, bacteriophage, yeasts, earthworms, and other saprophytic soil forms. Early work on protozoa indicated that they are initially reduced in number and later may greatly increase. Studies on the parasitic nematodes show that they, too, are initially destroyed or reduced in numbers and later may attain greater numbers than in untreated soil. In our studies large numbers of yeast colonies have developed on dilution plates made from field and greenhouse soils previously fumigated, but this was rare.

In general, then, microbial numbers are initially decreased by fumigation, but certain forms quickly reinhabit or develop in the soil, and shortly after treatment over-all numbers are usually in excess of those in untreated soil.

Several factors contribute to the greater numbers. The cell material of the organisms killed by the chemical offers a ready source of energy and carbon material for the organisms which survive or which first become

established. In addition, the pesticide or a chemically altered form of it remaining in the soil or adsorbed by soil colloids, may be utilized as an energy source by certain organisms. Probably the main factor involved, however, is reduced competition. Many organisms, and even all organisms belonging to certain species, may be killed. Those surviving, or which establish first, have relatively little competition and therefore reach high levels of activity and high numbers.

Qualitative Effects

Probably of more significance than quantitative effects of fumigants and fungicides on the soil population are the qualitative effects, although studies of this type are meager for certain groups of organisms. Little is known, for example, about the effects of soil chemical treatment on the qualitative nature of the general bacterial and actinomycete population of the soil—probably because of the difficulty of identifying these organisms, and the tremendous amount of work involved in differentially culturing the large numbers of colonies which develop on various isolation media.

Several investigators have studied the influence of volatile fumigants on specific kinds of soil organisms. Nitrifying bacteria appear to be relatively sensitive, and may be inactive in the soil for several weeks to several months following treatment. Wensley noted that nitrifiers and certain cellulose-decomposing bacteria are more susceptible to methyl bromide than are other bacterial forms. Clark and Allison observed that spore-forming bacteria are relatively resistant to ethylene oxide fumigation of soil, and McKeen noted that this group is relatively resistant to methyl bromide. This does not necessarily imply, however, that spore-forming bacteria account for the large numbers of bacteria which quickly develop in fumigated soil. We have noted that spore-forming bacteria may be the only bacterial forms developing on plates from soil immediately after fumigation, but after numbers have increased most of the colonies consist of fluorescent or other types of bacteria.

Several investigators have noted that fumigants initially reduce or kill soil fungi, and that the molds which later develop represent relatively few species in comparison with those found in untreated soil. In rather extensive field and greenhouse tests in southern California, numerous fungus species developed as dominant species in soil following treatment with D-D, ethylene dibromide, ethylene dichloride, methyl bromide, Dithane, Vapam, chloropicrin, carbon disulfide, and other chemicals.

Some chemicals may not kill many of the soil molds but will stimulate growth of certain kinds. In one field test, for example, ethylene dibromide had little effect on numbers of fungi, but with time several species appeared to be stimulated.

Trichoderma viride most frequently is the first fungus species to recolonize fumigated or partially sterilized soils. Several factors may be responsible for its ability to do this. It appears to be relatively resistant to fungicidal chemicals; it may, therefore, survive treatment and develop quickly in an environment which is less competitive than that in untreated soil. If it is completely killed by the treatment, it may become re-established while sufficient chemical remains to prevent other species from developing. It may also, in a less competitive environment, grow faster and more vigorously than many other types and, therefore, quickly become dominant after the toxic action of the chemical has dissipated.

Significance of Qualitative Effects

It is well known that most plant root parasites will cause greater damage in a sterile soil than in a normal soil in which the parasite has to compete or grow in association with other microorganisms. Some soil populations exert a greater antagonistic or competitive action against root parasites than others. The changes in the microbial population of the soil following treatment with fumigants or fungicides may exert a biological control effect on root parasites. *Trichoderma viride,* which most commonly becomes dominant following partial soil sterilization with chemicals, is a well known antagonistic species. It has been shown to exert an antagonistic influence on *Phytophthora, Pythium, Armillaria, Rhizoctonia,* and other parasitic forms. Richardson noted that thiram treatment protected seedlings from damping-off after the material was decomposed in the soil. The treatment made the soil more resistant to artificial infestation with *Pythium ultimum* and prevented the natural increase in damping-off organisms that usually results from repeated cropping. It was also noted that this fungicide stimulated growth of *Trichoderma viride.* It was suggested that the protection of the seedlings was associated with the increased numbers and activity of *Trichoderma* in the soil. Bliss, and Darley and Wilbur observed that soil fumigation with carbon disulfide usually gave good control of *Armillaria,* a fungus which attacks the roots of citrus trees and other plants. Control was obtained even though the parasite was not killed by the chemical. After fumigation it was found that *Trichoderma* increased in abundance and parasitized and destroyed the *Armillaria.*

While treatment of soil with fumigants or fungicides usually aids in the control of plant root parasites, it may at times actually increase root damage. The parasite may be more tolerant of the chemical than are other organisms. If insufficient material is applied to kill the parasite, it may then be the first to recolonize the soil and will become more active than in untreated soil. Kenknight, for example, found that soil treatment with mercury chloride increased potato scab injury.

It is also possible that the population which develops after fumigation will be less antagonistic than the normal population. If the soil becomes recontaminated with the parasite, it will then do more damage than in untreated soil. Anyone who has worked extensively with soil fumigants knows that occasionally the activity of certain plant root parasites is increased following treatment.

In addition to antagonistic action, soil organisms carry out many important functions in the soil. These include decomposition of plant and animal residues, release of plant nutrients from soil minerals, improvement in soil physical condition, and decomposition of toxic organic substances. Some individuals have expressed concern over the possibility that soil fumigants and fungicides may interfere with the beneficial functions of the saprophytic soil organisms. Actually, there is no cause for alarm. The sterilizing effect is temporary. The population developing following treatment will decompose organic residues just as

readily as the original population. Special groups of organisms, such as the nitrifying bacteria, will return with time.

Soil Chemical Properties

Fumigant treatment may cause chemical changes in the soil. Several investigators have found that fumigants temporarily increase the concentration of water soluble macronutrient elements. In 1909 Russell and Hutchinson reported that fumigation of soil with carbon disulfide increased the phosphorus content of plants. Recently, ethylene oxide treatment was found to increase the soluble phosphorus content of the soil.

In another study D-D, chloropicrin, and carbon disulfide appreciably increased the calcium in the saturation extract in both field and laboratory soils. Soluble magnesium and potassium were increased to a lesser extent. Ethylene dibromide and propylene oxide, on the other hand, exerted only a slight effect on the solubilities of these cations. In field soil and in pots in the greenhouse, the greater amount of soluble calcium in the soil following fumigation was reflected in higher leaf calcium of citrus plants growing in the treated soil.

Soluble Micronutrient Elements

Soluble and exchangeable manganese, and to a lesser extent copper and zinc, are increased in some soils treated with fumigants. Changes in the availability of these nutrients can be detected by both soil and plant analyses. In a few high manganese soils, sufficient amounts of this element may be solubilized so that it becomes toxic to plants. In soils low in available micronutrient elements, on the other hand, fumigation may stimulate plant growth by increasing the available supply. Solubility is at a maximum immediately after treatment; it then gradually decreases.

Ammonium and Nitrate Nitrogen

The organisms which oxidize ammonia to nitrites and nitrates appear to be relatively sensitive to soil fumigants. Whereas organisms which release ammonium from organic nitrogenous complexes quickly return to soil following treatment, the nitrifiers are slow to develop. Their activity may be reduced for several weeks to several months. During this time ammonium accumulates from the decomposing organic fraction of the soil, and any ammonia added in fertilizer will remain as ammonium. This phenomenon may or may not affect plant growth. If concentrations are too high, ammonium sensitive plants may be injured.

Ammonium does not move as freely in the soil as does nitrate during rain or irrigation. In some soils distribution of the available nitrogen may be influenced. Most plants can readily utilize ammonium nitrogen, and some may even prefer this form. Tam and Clark found, for example, that pineapple plants at a certain stage of growth grew better, produced more dry weight, and had a higher nitrogen content when placed under ammonium nutrition by destroying the nitrifying bacteria with a fumigant and applying additional nitrogen in the ammonium form. If a plant absorbs its nitrogen largely in this form, then absorption of other cations, such as those of potassium, may be reduced.

Fumigant and Fungicide Residues

When fumigants or fungicides are applied to the soil, a portion, if volatile, will be dissipated into the air. The remainder will be adsorbed by soil particles. Organic chemicals will slowly or quickly decompose in the soil by chemical or microbial action. Materials composed of carbon, hydrogen, and oxygen will ultimately be decomposed to carbon dioxide and water. If other elements, such as nitrogen, sulfur, chlorine, bromine, copper, and mercury, are present in the molecule, residual products containing these will be formed.

Residual nitrogen will be utilized by plants or will leach out of the soil. It does not constitute a residue problem. Following soil fumigation with carbon disulfide, soluble sulfates may greatly increase. Ordinarily, the increase will not adversely affect plant growth. In a soil which is high in salts, however, it may cause additional trouble.

Soluble chlorides increase when soils are treated with chloride-containing fumigants. The chloride may be released quickly or slowly from the chemical. If soluble salts constitute a problem, the chloride residue from a material such as D-D or chloropicrin may accentuate the difficulty. Chloride-sensitive plants may be injured when planted in soil previously fumigated with chloride-containing chemicals. At the Citrus Experiment Station, residual chlorides following chloropicrin fumigation have caused leaf burn of avocados.

Some crops are sensitive to bromide ion or to chemicals containing bromide. In one study, comparable citrus leaf bromide concentrations, originating either from applications of calcium bromide or from pretreatment of the soil with ethylene dibromide, were associated with comparable growth retardation. Williamson reported injury to carnations growing in soil previously fumigated with methyl bromide. Addition of sodium bromide to the soil produced similar injury symptoms. Onions, garlic, sweet potatoes, potatoes, and stocks often grow poorly following soil fumigation with a bromide-containing fumigant. In addition, chrysanthemums, violas, and salvia are apparently sensitive to bromide.

The common soil fumigants and fungicides now in use do not contain iodine or fluorine. Some organic chemicals containing these elements are highly pesticidal, however, and, although relatively expensive, they may be considered in the future for control of soil pests. Should this be done, iodide residues in the soil may adversely affect more plant species than do bromide residues. Soluble fluorides apparently change rapidly to relatively insoluble forms in most soils. In one study, up to 3000 pounds of fluorine, as calcium fluoride, did not adversely affect germination or growth of sudan grass, rye grass, or alfalfa. Relatively large amounts of fluorides are added to soil with phosphatic fertilizers with no apparent detrimental effect on plants. The small amounts which may be incorporated with pesticides will probably prove inconsequential.

Copper and mercury fungicides have been used for many years in greenhouse or nursery beds and for local treatment in field soils. These elements react in most soils to form relatively insoluble compounds, and usually do not cause plant damage. In some soils or under certain conditions, however, they may be harmful. In Florida, copper toxicity on several crops has been reported in old vegetable fields. For many years vegetables growing in the soils had been frequently sprayed with Bordeaux for control of fungus diseases. Plants affected included celery, corn, beans, beets, cabbage, cauliflower, peppers, turnips, squash, strawberries, snapdragons, certain grasses, and ragweed. Whereas virgin soils contained about 10 p.p.m. copper, the affected soils contained up to 300 p.p.m. Liming the soil reduced toxicity symptoms.

Anne and Dupuis found that the copper content of some acid vineyard soils of France was as high as 400 p.p.m. The vineyards had been sprayed for many years with copper compounds for fungus control. Some plants were injured by half this amount of copper.

In the acid sandy soils of Florida, repeated fertilization of the soil with copper has caused toxicity symptoms on citrus. The excess copper causes twig dieback, leaf chlorosis, and a marked reduction in tree vigor and yield. Reuther and Smith found that toxicity was greatest in acid soils with a low exchange capacity. Liming the soil tended to reduce or overcome the toxic condition.

Under greenhouse conditions, treatment of soil with mercury chloride may cause plant injury. Zimmerman and Crocker found that after treating one bed of roses with mercury chloride all the roses of a certain variety in the house showed injury. It was found that the mercury is reduced in the soil and then vaporizes, causing damage to susceptible plants. Plants of 65 genera were found to be susceptible. Thirteen additional mercury compounds, both organic and inorganic, cause similar injury when added to soil.

Soluble residues, such as the bromides and chlorides, may cause plant damage. They will or can be leached out of the soil, however, so their effects are only temporary. Further, only certain species would ordinarily be influenced adversely.

If a crop is planted in the soil before the adsorbed fumigant has had time to decompose, the fumigant itself may adversely affect plant growth. At common dosage rates and with most crops, a waiting period of three to six weeks after treatment is sufficient. At high dosage rates, it may be necessary to wait three months or longer before planting a crop. For citrus replanting, a six-month or longer waiting period is recommended.

In summary, treatment of soil with a fumigant or fungicide may cause rather marked chemical and biological changes in the soil. Some of the changes may be beneficial, some may be detrimental, but in most soils they will not significantly influence plant growth. The changes induced by the chemicals are temporary. They may last from just a few days to several years, depending on numerous factors. But generally speaking, it is doubtful that increased use of soil fumigants will adversely affect soil properties.

2. *Insecticides and the Soil*

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Probably the greatest amount of work in soil-insecticide relationships has been done on the effect of DDT on biological processes in the soil and on plant growth. Appleman and Sears using 10% DDT reduced the height of legumes grown in sand with 100 pounds per acre. With 1000 pounds per acre nodulation was reduced. Plants grown in soil were injured less than those grown in sand. Amounts below 100 pounds caused no unfavorable results.

Bollen and others found that carbon dioxide evolution and dextrose decomposition in soil field-treated with 137.5 pounds of actual DDT per acre did not vary from levels observed in untreated soil. They believed that the stimulations and inhibitions observed would not materially influence soil fertility. Bollen and his group also made field applications of DDT at rates up to 20 pounds per acre in several loams and observed that it caused no immediate harmful effects on soil microorganisms.

Foster found in a greenhouse study that species differ markedly in their sensitivity to DDT in soil. Abruzzi and Rosen rye and stringless black valentine beans were among the most sensitive observed. Their growth was consistently and significantly depressed by 100 or more pounds of DDT per acre in mineral soils; but DDT was much less toxic on acid muck than on the mineral soils. Effects upon such very sensitive species were produced by as little as 25 to 50 pounds of DDT.

In contrast, no growth reduction was observed in two varieties of sweet corn grown on soil containing 1000 pounds of DDT per acre. In general, DDT had only a slight effect upon germination and stand, even among species that are sensitive after emergence. At concentrations of 400 and 1000 pounds per acre, however, stands were significantly depressed. The *o,p'* isomer of DDT was about four times as toxic as the *p,p'* isomer. Foster found the toxic effects of DDT on plants to be persistent, with no measurable decrease in toxicity after four years.

The gram stain reaction and rod length of *Rhizobium leguminosarum* Frank in the root nodules of the common bean were affected by DDT, according to Fultz and Payne. At a rate of 103 pounds, DDT resulted in 15.7% gram positive fields, compared to 3.3% for the water checks. DDT also increased the percentage of microscopic fields with predominantly long and medium length rods and decreased the percentage of those with short rods. Bacterial populations in nodule smears from the common bean were unaffected by DDT.

Horn found that DDT up to 120 p.p.m. in Arredondo fine sand resulted in significant increases in numbers of bacteria, actinomycetes, and fungi, but increases were not directly proportional to the amount of DDT added.

DDT in concentrations of 0.01 to 0.001% was not toxic to nitrifiers, ammonifiers, and sulfur-oxidizing microorganisms of the soil, according to Jones. Concentrations of DDT ordinarily applied to soil showed no evidence of toxicity to any important microbial process. Abnormally high concentrations, however, resulted in injury. Greater injury occurred in soils low in organic matter, and nitrifiers were damaged more than ammonifiers. There seemed to be no correlation between the numbers of microorganisms as determined by plate count and the injury to specific groups of soil microorganisms such as sulfur-oxidizing, ammonifying, and nitrifying bacteria. At the higher concentrations, numbers of microorganisms increased. For example, at the end of six months in soils containing 0.25% DDT, the count was approximately five times as great as that in untreated soil.

Morrison and others found that 137.5 pounds of DDT per acre caused severe stunting to bush and pole beans. Tomato transplants were slightly stunted and had small leaves and fruit.

Overman and others evaluated DDT for a period of three years during which recommended protective schedules resulted in the application of up to 48 pounds of DDT per acre. Neither yield nor quality of vegetable crops showed any significant differences due to treatment. Nitrate production and kinds and numbers of fungi indicated no toxic accumulations of the material or its breakdown products in Leon fine sand.

Payne and Fultz showed that 103 pounds of DDT per acre applied to the soil significantly depressed the number of nodules per plant on common bean.

DDT up to 120 p.p.m. applied to Arredondo fine sand had no significant effect on nitrification but stimulated ammonification, according to Ross.

Sheals found that the amounts of DDT commonly used in commercial practice induced marked and persistent quantitative changes in the microarthropod population. He stated that the response of the soil population to insecticides emphasizes the need for an ecological approach to pest control.

Smith added 2% of DDT to acid and alkaline soils and 18 months later found normal seed germination and root growth.

Early work on insecticides by Smith and Wenzel showed no definite injury to soil microbes by DDT up to 400 pounds per acre. They concluded, however, that care should be taken in applying new insecticides in massive dosages until shown to be harmless.

Wilson and Choudhri found no detrimental effects on nitrate production, ammonia production, and numbers of organisms from 0.5% DDT in Dunkirk silty clay loam. As much as 2% of DDT in Dunkirk fine sandy loam showed no detrimental effect on the nodulation of alfalfa, red clover, soybean, and vetch. Legume bacteria and certain fungi and algae grew well on agar slants covered with DDT prior to inoculation. They concluded that the quantity of DDT which they had mixed with the soil or spread on the surface of agar slants was much in excess of that which will ever be applied for the control of insects and, since no effect was noted from its application, additional work with DDT seemed useless.

Allen and associates found that cotton did not seem to be affected by as much as 100 pounds of DDT per acre; but this dosage caused some chlorine injury to tobacco and affected its yield and burning quality. Three annual applications of 10 or 20 pounds of DDT per acre reduced the stand and growth of cowpeas. One hundred pounds per acre seemed to retard growth of oats and Austrian winter peas. Rye growth was reduced from a total of 30 pounds applied over a period of three years.

Benzene Hexachloride

Allen and others, in experiments with technical benzene hexachloride, containing 12% gamma isomer, showed that as little as 50 pounds per acre reduced the stand of tobacco transplanted shortly after the insecticide application. In one instance, 16.7 pounds of BHC per acre reduced the stand of cotton, but in subsequent trials up to 83.3 pounds per acre was harmless. Benzene hexachloride did not seem to injure rye so much as did DDT, and for some unknown reason it increased the yield of peas. BHC at 83.3 pounds per acre imparted a reddish color to rye and oat plants.

Bollen and others found that BHC isomers added to a clay adobe soil at 1000 p.p.m. varied in their effects on the numbers of bacteria and molds which developed during incubation. The isomers also differed in their effects on ammonification and nitrification. The gamma isomer increased bacterial population, but decreased *Streptomyces*. Other isomers gave smaller increases. The delta and gamma isomers increased the numbers of molds in soils to which dextrose had been added, whereas the alpha and beta forms depressed them. In contrast, in the absence of dextrose, where mold growth was less, all isomers except alpha were inhibiting. Delta and gamma isomers increased ammonification of peptone; other isomers had no effect. Beta and gamma isomers increased nitrification of ammonium sulfate; however, 275 pounds per acre of BHC applied in the field subsequently decreased the production of nitrate in the laboratory.

Bollen and others also made field applications of gamma BHC at 20 pounds per acre on several loams, and found no immediate harmful effects on soil microorganisms.

Plant response to BHC on a loam in a greenhouse was studied by Foster, who found technical BHC at 400 pounds per acre generally harmful to germination and stand of all crops tested; only the more sensitive crops were harmed at 100 and 200 pounds per acre. Technical BHC at 200 pounds per acre was highly toxic to subsequent growth of all crops tested, more so to some than others. Most crops tested were harmed by 100 pounds. Although gamma BHC affected germination and stand less than the technical grade, it appeared to depress growth of most crops tested as seriously as did the technical grade. Foster found BHC to be less persistent than DDT, but persistent enough to accumulate temporarily to a harmful degree in soil under some conditions of use.

Gould and Hamstead found that BHC, at rates as high as 2400 pounds per acre, not only was a good material for controlling weeds in an apple orchard but also resulted in increased tree vigor. They believed lack of a cover crop gave the trees an added advantage in growth compared to checks, although many other factors could have been involved.

Gray found that 0.02% BHC in soil extract depressed the action of the urea-hydrolyzing bacteria; results with cultures in tap water were similar to those in soil extract except that a concentration of 0.01% was also effective. BHC at 0.02% in a 2% urea solution reduced the activity of urease about 50%. When the gamma isomer was added to the urea solution, urease was not affected. It appears, therefore, that another isomer, or material associated with the hexachlorocyclohexane, is toxic in this reaction.

Gray also found BHC and its gamma isomer at a concentration of 0.01% toxic against bacteria that oxidize ammonia to nitrite, and those that oxidize nitrite to nitrate, in solution media inoculated with soils. They were not toxic against the nitrifying bacteria in soils at concentrations up to 0.04%. They were also toxic against bacteria that oxidize thiosulfate in solution cultures of mineral soils; this experiment was conducted in a solution medium inoculated with soil suspension and containing either 0.05% BHC or 0.003% gamma isomer. The toxic component was in the BHC and not in the "filler" materials. The gamma isomer was less effective than some other component or combination of components of BHC. Neither BHC nor its gamma isomer stimulated nitrification.

Gray's study of heterotrophic bacteria showed that 13 strains of various species of saprophytic bacteria grew on plates of nutrient agar in the presence of BHC. Thirty-five strains did not grow in the presence of BHC, but these were not affected by the gamma isomer. BHC inhibited the growth of five species of phenol-decomposing bacteria; it did not affect the growth of an unnamed species isolated from soil under the influence of BHC. It prevented starch hydrolysis by four species of amylolytic bacteria and reduced that of three others; the gamma isomer also reduced enzyme action of these bacteria. BHC in soils did not appear to affect the cellulolytic bacteria. However, when in close contact, it prevented the growth of *Cytophaga* but had no effect on some other species. BHC prevented growth and nitrate reduction by *Bacillus mesentericus* and prevented nitrate reduction but not growth by *Micrococcus pyogenes* var. *aureus*. BHC and the gamma isomer prevented the reduction of sulfate by mixed soil microflora in Elion's medium.

Sheals stated that rates of BHC commonly used in commercial practice induce marked and persistent quantitative changes in the microarthropod population. The action of BHC is sufficient to warrant some concern about the adverse long-term effects on soil fertility which might occur as a result of a general decimation of saprophagous species by this widely used soil insecticide.

Simkover and Shenefelt found that crude BHC sprinkled over agar slants of *Rhizoctonia* greatly inhibited mycelial growth. *Rhizoctonia*-infested Plainfield sand treated with crude BHC at one pound of gamma isomer per acre and planted to Norway pine seedlings showed that BHC inhibited damping-off. They also tested the effect of BHC on mycorrhizal fungi and found that dosages of 5, 2.5, 1, 0.5, 0.25 pounds of gamma per acre decreased the number of mycorrhizal rootlets in direct proportion to the dosage. At 2.5 and 5.0 pounds per acre root clubbing was so severe that inspection for mycorrhizae was impossible. Root nodulation on black locust was not affected by BHC at 1 pound of the gamma isomer per acre.

Smith treated acid and alkaline soils with 2% of BHC (mixed isomer containing 10% of the gamma isomer) and found that these soils, 18 months after treatment, prevented root growth of germinating seeds. This harmful effect was still apparent when one part of the BHC-treated soil was mixed with 99 parts of the control soil.

Wilson and Choudhri studied the effect of BHC on soil organisms and found 0.15% of 20% crude BHC in Dunkirk fine sandy loam had no effect on ammonification or the population of fungi and bacteria. This amount is approximately 100 times as much per acre as is ordinarily recommended to eradicate wireworms. Soil plaque counts of azotobacter showed that as little as 4 pounds per acre of 20% BHC reduced the numbers of azotobacter-like colonies; generally, the heavier the application the greater the injurious effect. Nodulation on red clover, soybeans, alfalfa, and hairy vetch was seriously injured by 30 p.p.m. BHC and even the effect of 3 p.p.m. could be noted; the heavier the application the more serious the injury. Hardly any growth occurred with 500 and 1000 p.p.m. BHC present. It was observed, however, that where lateral roots developed nodules were invariably present. Apparently the bacteria for these species of legumes tolerated a heavier application of the BHC than did the green plants.

According to Wilson and Choudhri, much of the toxic action of BHC that contains a total of 20% of the isomers should be attributed either to the gamma isomer or to the delta isomer. Heptachlorocyclohexane, equally injurious and present in almost all crude mixtures of BHC, may also be responsible for some of the toxic effects.

Chlordan

Bollen and associates made field applications of chlordan at rates up to 20 pounds per acre on several loams and found no immediate harmful effects on soil microorganisms.

Plant response to chlordan was investigated by Foster in a greenhouse study. Limited tests soon after putting it in the soil indicated that chlordan in amounts of 100 pounds per acre or more was even more harmful to germination and stand than was BHC. Most vegetable crops tested were significantly depressed in stand by as little as 25 pounds per acre. Corn appeared tolerant, but honeydew melon was especially sensitive. In subsequent growth, 100 pounds per acre or less appeared to be without consistent effect, but 400 pounds markedly reduced growth of most cucurbits, tomato, and beet. Beans, members of the cabbage family, sweet corn, and cotton appeared somewhat tolerant. Chlordan is said to be less persistent than DDT, but it is persistent enough to accumulate to some extent in the soil.

Horn found that up to 50 p.p.m. of chlordan in Arredondo fine sand increased the number of bacteria, reduced the number of fungi, and had no significant effect on the actinomycete population.

With amounts up to 200 p.p.m. on the same soil type, Ross produced no significant effect on nitrification or ammonification.

Overman, in a three-year evaluation of chlordan applied at recommended rates (a total of 5 pounds per acre), found no significant differences in either crop yield or quality. Nitrate production and kinds and numbers of fungi gave no indication of toxic accumulations of the material or its breakdown products.

Although a 20-pound soil application of chlordan per acre was made each year for three years by Stone and co-workers, none of a variety of vegetables tested showed any detrimental effects from the treatment.

Parathion

Bollen and his associates made field applications of parathion at the rate of 10 pounds per acre on several loams, and found no immediate harmful effects on soil microorganisms.

Foster found that relatively heavy doses of parathion appeared to have a slight but temporarily depressing effect on germination and stand. In a few tests run soon after application, tomato, muskmelon, and snap bean were depressed in growth by 50 or 100 pounds per acre. Crops planted some months after soil treatment were unharmed. He also stated that parathion is evidently unstable, and is used in such small amounts per acre that it is not now an object of concern as a potentially harmful residue in the soil.

Kasting and Woodward found that parathion persisted in all treated soils on the fifth day after treatment but was not detected after 16 days at the 2-pound level or after 79 days at the 12-pound level. The content in soil from two 100-pound treatments dropped to 1.2 p.p.m. (2.4 pounds per acre) in 165 days. A final check after 325 days showed only traces in any of the soils.

The effect of parathion in the soil on the total number of bacteria, actinomyces, and fungi was determined. There was a slight reduction in numbers at the 100-pound level five days after treatment; this effect was not apparent at other concentrations or at later sampling dates. Parathion had no apparent effect on the numbers of nitrifying, denitrifying, cellulose-decomposing, manganese-oxidizing, or spore-forming bacteria at any of the sampling dates. Similarly, the treatments had no effect on the quantity of nitrate in the soil.

There was a tendency for the 12- and 100-pound treatments to delay germination of lettuce; however, after 16 days all seeds from treated and untreated soil had germinated. These two also delayed vetch germination but had no effect on oats. There was a general trend toward increased phosphorus content in plants with increases in parathion treatments.

Overman and coworkers evaluated parathion during a three-year period in which recommended protective schedules were followed (a total of 5.8 pounds of parathion per acre). Neither crop yield nor quality showed any significant differences due to treatment. Nitrate production and kinds and numbers of fungi gave no indication of toxic accumulations of the material or its breakdown products.

Aldrin

Bollen and others found no immediate harmful effects on soil microorganisms from field applications of aldrin at 10 pounds per acre.

According to Fletcher and Bollen, aldrin at 200 and 1000 p.p.m. in several types of soil had a stimulating influence upon the total number of soil microorganisms. Concentrations as low as 25 p.p.m. depressed the overall nitrogen transformations by soil microorganisms; this was not great and appeared to be of short duration. Ammonification was enhanced at an early stage, became slightly inhibited upon further incubation, and then returned to control levels. Nitrosofication showed slight stimulation at each concentration while nitrifiers were moderately depressed. Carbon dioxide production from treated soils and soil extracts was slightly increased following an initial temporary inhibition. No adverse effects on the development of *Azotobacter* on soil plaques were observed.

In another report Fletcher and Bollen stated that in a laboratory study of 10 Oregon soils aldrin applied at 200 and 1000 p.p.m. increased bacterial populations; however, mold and *Streptomyces* counts showed stimulation as well as depressive effects not consistent with incubation time, treatment, or soil type. Only minor and irregular effects on ammonification and nitrification occurred. The absence of any marked effect is considered significant. Slightly larger amounts of carbon dioxide were produced in a clay loam treated with 200 and 1000 p.p.m. aldrin. These workers concluded that concentrations of aldrin recommended for insect control will not affect soil microorganisms enough to produce significant changes in fertility.

Horn found that, on Arredondo fine sand, aldrin up to 25 p.p.m. had no effect on the bacterial numbers. But 1, 2, 4 and 25 p.p.m. significantly increased the numbers of actinomycetes. Aldrin had little effect on the number of fungi.

Stone *et al.* found no detrimental effects on the growth and yield of vegetable crops from three annual soil applications of aldrin at 4 pounds per acre. Nor could they find residual aldrin in the soil after a 4-pound application.

Toxaphene

Bollen and others reported no immediate harmful effects on soil microorganisms from field applications of toxaphene at 10 pounds per acre. None of the treatments resulted in either an approach to sterility or a many fold increase in molds, bacteria, or *Streptomyces;* no marked changes in the proportions of these microbes were produced.

Limited plant response tests with toxaphene by Foster indicated that amounts of 100 pounds or more per acre depressed somewhat the germination of all vegetable crops tested except sweet corn. Only tomatoes and watermelon were affected significantly. In subsequent growth, cucurbits and tomato were significantly depressed while corn and beans were not at 400 pounds of toxaphene per acre. Toxaphene is susceptible to breakdown by soil organisms, and is believed to be relatively unstable in the soil; therefore, it is less likely than some other insecticides to accumulate harmful residues.

However, Stone *et al.* found that, following the second and third application of toxaphene at an annual rate of 20 pounds per acre, there was a trend toward lower yields of Fordhook lima beans, celery, and carrots. After three annual applications of this insecticide, the yield of potatoes was reduced substantially below that of the check plots. Chemical analyses of the soil indicated that approximately 45% of the toxaphene remained in the soil a year after the second application.

Dieldrin

Bollen and associates found no immediate harmful effect on soil microorganisms from field applications of dieldrin at 10 pounds per acre.

Overman and her coworkers evaluated dieldrin over a three-year period in which recommended protective schedules were followed and a total of 2.5 pounds of the material was applied. Neither crop yield nor quality showed any significant differences due to treatment. Nitrate production and kinds and numbers of fungi gave no indication of toxic accumulations of the material or its breakdown products in Leon fine sand.

EPN

Bollen and others made field applications of EPN (ethyl *p*-nitrophenyl thionobenzene phosphonate) at 10 pounds per acre, and concluded that no immediate harmful effects on soil microorganisms were caused. None of the treatments resulted in either an approach to sterility or a many fold increase in molds, bacteria, or *Streptomyces;* no marked changes in proportions of these microbes were produced.

Demeton and Heptachlor

Overman *et al.* evaluated demeton and heptachlor during a three-year period in which recommended protective schedules were followed. In each case a total of 5.0 pounds of insecticide was applied. They found no significant differences in crop yield or quality due to either treatment. Nitrate production and kinds and numbers of fungi gave no indication of toxic accumulations of the materials or their breakdown products in Leon fine sand.

Colorado 9

Fultz and Payne found that Colorado 9, 1-trichloro 2,2-*bis*-(*p*-bromophenyl) ethane, effects the gram stain reaction and rod length of *Rhizobium leguminosarum* Frank in the root nodules of the common bean. One hundred three pounds per acre mixed with soil resulted in 30% dominantly gram positive fields as compared to 3.3% for water checks; the data were significant at about the 0.10% level. Colorado 9 increased the percentage of fields with dominantly medium length rods and decreased the percentage with short rods. It also increased the bacterial population in nodule smears.

Payne and Fultz also showed that the same amount of Colorado 9 applied to soil did not affect the number of nodules on the common bean.

3. *Herbicides and the Soil*

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Each year in the United States, about 35 million acres are sprayed with herbicides, 30 million of them with substituted phenoxyacetic acids. Approximately 1 million acres of crops, including 350,000 acres of cotton, are treated with pre-emergence herbicides. Over 30 million pounds of substituted phenoxyacetic acids are consumed each year.

The compounds may be applied to plant foliage at rates as low as 0.25 pounds per acre. In pre-emergence treatments, herbicides are applied in general at rates of 0.5 to 12 pounds per acre, the rate depending upon the compound, crop, and soil. Organic soil sterilants are applied at 10 to 100 pounds per acre with most applications being at 25 to 30 pounds. A large percentage of it ends up in the soil, whether directly applied or not.

In the use of all herbicides we are concerned that they will not have a detrimental effect on soil microorganisms or soil microbial processes. We are also concerned about the effects of soil properties on herbicides.

With pre-emergence herbicides and soil sterilants, persistence and leachability are extremely important. They are influenced by soil texture, chemical composition, organic matter, pH, moisture, and temperature.

Microorganisms and Microbial Processes

Of the many studies conducted on effects of herbicides on soil microorganisms and microbial processes, most have been concerned with 2,4-D and related phenoxyacetic herbicides. The general conclusion of these investigations is that normal rates of treatment are noninjurious to soil microorganisms.

It has been shown that various phenoxyacetic acid herbicides are more inhibitory to microorganisms under acid conditions than under neutral or alkaline conditions. For example, in Thornton's medium 125 p.p.m. of 2,4-D and other phenoxyacetic acids inhibited soil bacteria at pH 5.6, but not at pH 6.4 or higher. The normal concentration of 2,4-D in soil would rarely exceed 10 p.p.m. A concentration of 100 p.p.m. of 2,4-D or 2,4,5-T in soil has been shown to increase plate counts of fungi.

There is considerable variation in the susceptibility of microorganisms to 2,4-D. As little as 2 p.p.m. inhibits growth of certain *Rhizobium* species, while 40,000 p.p.m. is required to inhibit certain fungi. Gram positive bacteria are inhibited at lower concentration than gram negative; aerobic bacteria are inhibited at lower concentration than facultative anaerobes.

Trichloroacetic acid, used as a grass herbicide, is no more inhibitory to soil fungi than is 2,4-D—some species resisting 40,000 p.p.m. In contrast, 100 p.p.m. of dinitro-*o*-sec-butylphenol is inhibitory to certain fungi. However, this still is higher concentration than would normally be employed.

Concentrations of 18,000 and 36,000 p.p.m. of maleic hydrazide were required to inhibit two species of soil bacteria. Dalapon stimulated bacterial growth slightly when applied at 68 pounds per acre.

It has been reported that nodulation of legumes was inhibited by a rate of 2,4-D as low as 0.009 pounds per acre; other reports indicate normal nodulation with a rate of 6 pounds per acre. Consensus is that 2,4-D is more inhibitory to legumes than to the nodule bacteria. *Rhizobium* is among the more sensitive species. In culture some species are inhibited by 2 p.p.m. 2,4-D; others require 2000 p.p.m.

Normal rates of treatment of soil with 2,4-D, 2,4,5-T, 2-methyl-4-chlorophenoxyacetic acid, dinitro-*o*-*sec*-butylphenol, dalapon, and maleic hydrazide do not injure *Azotobacter.* In fact, an adapted culture could grow in the presence of 5000 p.p.m. 2,4-D. Maleic hydrazide at 1000 p.p.m. is only slightly inhibitory.

Normal rates of various herbicides also are noninjurious or only slightly injurious to nitrification. Most investigators have found that very high rates of 2,4-D are required for inhibition of nitrification, but in one study, 4 pounds per acre decreased nitrification slightly for the first 12 days of incubation followed by enhanced nitrification.

Extremely high amounts of 2,4-D are required to inhibit ammonification.

Evolution of carbon dioxide from soils in the presence of herbicides may be used as a criterion of influence on the microbial population as a whole. Some workers have found normal applications of various herbicides to be inhibitory to respiration; others have noted no effect or at the most a temporary inhibition. In one study 200 p.p.m. of 2,4-D slightly stimulated carbon dioxide evolution, while 500 p.p.m. slightly depressed it.

Herbicides applied to soils may be decomposed by microorganisms, decomposed chemically or photochemically, leached out of the root zone by rain, adsorbed by soil colloids in active or inactive form, and volatilized. The relative importance of these factors will be determined by the nature of the herbicide, the composition of the soil, and environmental conditions. In many instances it is difficult to separate the various factors involved in the loss of herbicidal effectiveness in soils.

With many herbicides decomposition by microorganisms appears to be the single most important factor in their disappearance; with others, leaching or adsorption by soil constituents appears to be the most important. Frequently a combination of factors is responsible for loss of herbicidal effectiveness.

Great variations in the persistence of 2,4-D have been reported—from less than 10 days to more than 7 weeks. Rates as high as 40 pounds per acre had no effect on corn planted 3 weeks later in a Nebraska study. In contrast, Crafts in California reported many losses of spring vegetables resulting from spraying the previous fall.

Slight changes in the ring structure may change persistence appreciably. Thus 2,4,5-trichlorophenoxyacetic acid is markedly more persistent than 2-methyl-4-chlorophenoxyacetic acid, which in turn is more persistent than 2-4-dichlorophenoxyacetic acid.

Phenoxyacetic acids disappear more rapidly from soils under conditions favorable for microbial development. In autoclaved soils there is no disappearance. 2,4-D disappears more rapidly from soils which have been treated with it previously, but this is not the case for 2,4,5-T.

Six groups of investigators have isolated bacteria capable of decomposing 2,4-D and MCPA. No organisms able to decompose 2,4,5-T have been isolated. Yet it is apparently decomposed by soil microorganisms.

The phytotoxicity of phenoxyacetic acids may also be decreased by adsorption on soil colloids, and by removal through leaching. These factors in general are less important than microbial decomposition.

Adsorption of the esters of 2,4-D is greater than that of the amine salt. Adsorption is greater in high organic matter soils and mucks than in low organic matter soils.

Sodium 2-(2,4-dichlorophenoxy)-ethyl sulfate is unique in that it is nonphytotoxic or essentially so when applied in aqueous solution to plant foliage or germinating seeds, but is highly herbicidal in soil. It is converted in soil by either acid or enzymatic hydrolysis to 2,4-dichlorophenoxyethanol, which in turn is oxidized to 2,4-D. Conversion proceeds in sterile soil at pH values below 5.5 and in nonsterile soils at pH 3 to 7, but not at pH 8 after 5 days' incubation.

Phenyl Carbamates

Isopropyl N-phenyl carbamate (IPC) and its 3-chlorophenyl derivative (CIPC) are employed as pre-emergence herbicides on grasses and certain broadleaf species. With both compounds, factors favoring microbial development favor their disappearance. These compounds in general are less persistent than 2,4-D.

Some investigators have suggested that volatilization is a major factor in the disappearance of these compounds. This conclusion was based primarily on the loss of these compounds from glass slides, metal foil, and filter papers. But in studies with radioactively labeled IPC and CIPC, it was demonstrated that microbial action was much more important than volatilization in the loss of these compounds from Duffield silt loam. From dry soils there is slight or no loss at temperatures to 60° C; from sterile moist soil there is appreciable loss, and much greater loss from nonsterile soil.

Both IPC and CIPC are adsorbed quite strongly by soil colloids. Hence they are not readily leached from soils.

TCA, Dalapon, and Substituted Phenyl Ureas

Both trichloroacetic acid (TCA) and dalapon, employed in controlling grasses, are leached extremely readily from soils. Both compounds disappear more rapidly under conditions favorable for microbial development. Jensen isolated a group of bacteria, apparently belonging to the *Agrobacterium,* which decomposed dalapon. A nonsporeforming bacterium which decomposed TCA has also been isolated. It thus appears that the disappearance of TCA and dalapon results from removal by leaching and microbial decomposition. The relative importance of these two means depends on soil and environment.

Substituted phenyl ureas are finding extensive use as pre-emergence herbicides and as soil sterilants. The most commonly used ones are 3-(*p*-chlorophenyl)-1,1-dimethylurea, known as monuron, CMU, and Karmex W; and 3-(3,4-dichlorophenyl)-1,1-dimethylurea, called diuron and Karmex DL.

These compounds are among the most persistent herbicides now in use. At many locations 1 and 2 pounds per acre have persisted in phytotoxic amounts for four to eight months.

It has been demonstrated that microorganisms play an important role in the disappearance of these compounds from soil. Conditions favorable for microbial growth favor their disappearance.

Monuron is strongly adsorbed by soil colloids. Plant toxicity is also less in organic and fine textured soils than in sandy soils.

Both monuron and diuron are highly resistant to leaching. In the field most of these compounds remains in the upper 1 or 2 inches with small amounts leached below 8 inches. Naturally greater leaching occurs in sandy soils. Some loss of monuron may occur from photodecomposition, especially in dry areas where lack of rain may confine it to a surface film.

Aminotriazole and Dinitro Compounds

3-Amino-1,2,4-triazole, used primarily in foliage treatments, is strongly adsorbed by soils. In one study 40% was adsorbed in a nonrecoverable form by a sand after two days' incubation, while 85% was adsorbed by a muck. The adsorbed compound does not affect plant growth.

Aminotriazole persists longer in sterilized soil. It also persists longer with increasing temperature from 8° to 100° C. Thus it appears doubtful that microorganisms play an important role in the disappearance of aminotriazole. At normal rates of treatment it persists as little as seven days.

4, 6 - Dinitro - *o* - *sec* - butylphenol (DNBP) and its alkanolamine salts have been widely employed as pre-emergence herbicides. These compounds are moderately to highly persistent, but there is no direct information on their microbial decomposition.

DNBP is strongly adsorbed by soil constituents, as much as 50% not being recoverable. The water soluble amine salt is more readily leached than the phenol itself.

During 1952 considerable acreages of cotton were seriously injured by pre-emergence applications of formulations of DNBP. It was demonstrated that plant injury was caused by volatilization of the phenol. Only slight amounts of DNBP are lost from air dry soils, but much larger amounts are lost from moist soils, primarily by water vapor distillation. Presence of lime decreases the loss by shifting the equilibrium toward the calcium salt which is not volatile.

Limited information is available on such compounds as pentachlorophenol, N-1-naphthyl phthalamic acid, maleic hydrazide, and phenyl mercuric acetate. Most of these apparently are subject to microbial attack.

Comparisons of Herbicides

Warren, at Purdue University, has made a number of comparisons of various herbicides in different soils.

The least persistent herbicides in a silt loam soil were dalapon, 2-4-D amine, 2,4-D ester, sodium 2-(2,4-dichlorophenoxy) ethyl sulfate, and isopropyl N-(3-chlorophenyl) carbamate. The most persistent compounds included 4,6-dinitro-*o*-*sec*-butylphenol, monuron, and diuron. Persistence was somewhat less for some compounds in muck, and somewhat greater for some in a fine sand. TCA and dalapon leached readily in all soils, while diuron and CIPC were highly resistant to leaching. Others showed intermediate leachability.

The adsorption of herbicides was determined by ascertaining the amount of compound required to cause 90% inhibition of crabgrass growth in silica sand, a fine sandy soil, a silt loam, a new muck, and an old muck. There was little adsorption of TCA, dalapon, or 2,3,6-trichlorobenzoic acid by any of the soils. In contrast monuron, diuron, DNBP, CIPC, and pentachlorophenol were strongly adsorbed. It required 24 to 90 times as much of these to cause 90% inhibition in old muck as in silica sand.

With the presently employed herbicides there is no indication that normal applications will seriously injure soil microorganisms or microbial processes. In general, extremely high rates are required to cause significant effects on the soil population. Higher plants are much more sensitive to herbicides than are the soil microflora. In some instances normal rates of treatment may be injurious to organisms in a thin layer of soil, but rapid recovery of these organisms can be expected upon disappearance of the herbicide.

The principal cause of the disappearance of many herbicides from soils is microbial decomposition. Removal by leaching, adsorption by soil colloids, and volatilization are other important causes.

In the development of new herbicides it would be desirable to ascertain the mechanisms of disappearance and to evaluate each in representative soils. Only when such information is available can intelligent recommendations on the use of herbicides in soil applications be made. Soil scientists could make major contributions in the development of new herbicides.

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