I. Introduction

The only criterion by which to judge an agricultural fungicide is its success, but this is composed of many things. To protect plant surfaces, the fungicide must be deposited uniformly and adhere well. It must withstand weathering by sunlight, air, and water, and if used in the soil, it must survive attack by microorganisms and spontaneous reactions with metabolic debris until it has halted the advance of the fungi. Some-
how it must do all this inexpensively without injuring the host plants. Therefore it should be no surprise that few out of many candidate compounds succeed. Yet from each failure there is a lesson to be learned if we look closely enough.

Sometimes failure may result from a defect in formulation, or then again it may arise from an intrinsic weakness in the compound that can be remedied only by the synthesis of a new derivative with improved properties. Often the case is hopeless. Whatever the cause, an understanding of the basic scientific principle involved will help clear the way for future successes. Good fungicides may still be discovered by accident, but at least these should be planned accidents based on what plant pathologists and chemists have learned about their interactions with their environments during the past 75 years. This chapter summarizes some of these lessons.

II. PROTECTION OF PLANT SURFACES

A. Physical Factors Influencing Deposition and Distribution

1. Mechanics of Deposition and Spreading

Protectant fungicides are applied to fruit and foliage as dusts or sprays. To be able to settle on the plants the particles must have enough momentum to overcome repulsive forces which exist near surfaces. These may be electrostatic in nature or they may arise from convection currents caused by temperature differentials between the surfaces and the surrounding atmosphere. Furthermore, the high velocity air streams used to propel dusts and concentrate sprays tend to glide around plant surfaces. Consequently the particles carried by them must have enough momentum to strike the plant surfaces, instead of being carried away by the deflected air current. Momentum is the product of mass and velocity; hence when the particles are extremely minute, they must be projected at high speeds to penetrate these barriers. However, direct impingement of the particles on the surfaces accounts for only part of the fungicide deposited. Much of it must miss the main targets and eventually settle on the plants by gravity. Consequently particle size cannot be too small, for the limiting velocity a spherical object can attain on falling through still air is given by Stokes' law as

\[ v = \frac{2r^2g(d - d_0)}{9\eta} \]  

(1)

where \( d \) is the density of the fungicide, \( d_0 \) the density of air, \( r \) the particle radius, \( g \) the acceleration of gravity, and \( \eta \) the viscosity of air. Calculations made from this equation show that a particle with a radius
of 10\(\mu\) and a density of 2 gm. per cm.\(^3\) would reach a limiting velocity of 2.3 cm. per second and have a momentum of \(1.9 \times 10^{-8}\) gm. cm. per second. This is about the minimum value that would enable it to penetrate the barriers created by repulsive forces at the plant surfaces. Thus dust particles would have to be about 20\(\mu\) in diameter or form aggregates of about this size to obtain satisfactory deposit build-up. Unfortunately particles or aggregates of particles in this size range are easily dislodged by wind and rain, so dusting has never been a highly satisfactory method for protecting crops.

Overcoming the repulsive forces at surfaces is not the only problem in the deposition of small particles, for calculations from Stokes' law (equation 1) show that a particle 100\(\mu\) in diameter with a density of 1 will fall at a rate of 30 cm. per second in still air, while a 1\(\mu\) particle has a limiting velocity of only 10 cm. per hour. Thus, air currents may tend to carry the dust away from the area of application faster than it settles.

Occasionally it has been suggested that the deposition of dusts may be promoted by the presence of positive electrostatic charges on the individual particles induced by friction in the blowing apparatus, which would cause them to be attracted to negatively charged surfaces of leaves by electrostatic forces. However, the charges induced on dusts during blowing are weak, and they vary in sign, so it is unlikely that they improve deposition significantly (Gill, 1948). Recently, Bowen et al. (1952) have described an electrostatic duster which is said to impart very high charges to particles by application of a 12,000 volt potential difference in the same manner used for the electrification of dusts in industrial precipitators. The authors state that a particle 5\(\mu\) in radius, bearing a high charge, would be attracted to a surface by an image force about equal to gravity at a distance of 100\(\mu\). This calculation is based on the assumption that plant surfaces are perfect conductors, which is probably untrue. Interestingly enough, good deposition was obtained when the particles were negatively charged. This shows that the image charge induced on the surfaces of the plants by the dust cloud was positive in sign even though it is generally assumed that leaves are negatively charged. Deposition was superior to that of uncharged dusts, but the particle size range of the preparation used was not given.

Many of the disadvantages of dusts are eliminated in sprays. Here the small primary particles of fungicide are encapsulated in larger liquid droplets that can be given sufficient momentum to penetrate the barrier immediately surrounding the foliage. The droplets spread on impact, and when the liquid carrier evaporates, the fungicide particles
are left on the fruit and leaves. Coverage is never as uniform as that obtained with a dust distributed randomly, but smaller particles can be deposited and the tenacity of the residue is greater.

In conventional high volume sprays applied at rates of 75 to 300 gallons per acre, drop size is likely to be of the order of 0.5 to 3 mm. If properly formulated, these large drops easily acquire enough momentum to drench the leaves thoroughly. However, in concentrate spraying, as little as 1 to 15 gallons of liquid per acre may be used to distribute the same amount of chemical. Drop size must therefore be reduced drastically to achieve adequate coverage of the foliage. For application of concentrate sprays from the ground with air blast equipment, optimum radius is 15 to 40μ, while for aircraft application it is about 35 to 70μ (Potts, 1958). While this size range is considerably above the minimum required to overcome the repulsive forces at the surfaces, it is sufficiently small so that high velocities must be imparted to the particles to carry them to their destinations. Yeomans and Rogers (1953) state that the maximum distance a particle can move in a direction parallel to the ground is directly proportional to its initial velocity and to the square of its radius. Consequently, very small particles will be stopped much more readily than large ones. For example, a droplet with a radius of 50μ and an initial velocity of 112 m.p.h. will travel 150 cm., while a 5μ droplet ejected at the same speed will be stopped after penetrating only 1.5 cm. of air. Therefore small drops must be carried by air currents moving at high velocities to obtain good deposition of concentrate sprays.

However, delivery of droplets to plant surfaces may not always be enough to insure good deposition. Thus, Burchfield and Goenaga (1957b) found that deposit build-up of 10-10-100 Bordeaux mixture on young banana leaves was very slow when the leaves were kept in motion during spraying. Careful inspection revealed that the spray droplets were bouncing off the surface as if they were minute rubber balls. Evidently the contact angles between the leaves and droplets were too high to permit retention of the spray under these conditions.

Contact angle (θ) is defined by

$$\cos \theta = \frac{W_a - \pi_e}{\gamma_L} - 1 \quad (2)$$

where \(\gamma_L\) is the surface tension of the liquid, \(W_a\) the work of adhesion, and \(\pi_e\) a quantity that can be determined from the Gibbs adsorption isotherm. The contact angle is critical in determining whether a spray suspension will spread uniformly on the surface of a plant. A contact angle approaching zero indicates that the liquid is attracted to the
surface by forces as high as the internal forces of cohesion, so that the spray droplets tend to flatten and form thin films. Conversely, a contact angle approaching 180° indicates that wettability is so poor that the droplets do not adhere to the surfaces. Actually these extreme values are never reached, the contact angle of water on paraffin being only about 100°. Evidently a similar situation occurred when the young banana leaves were sprayed with Bordeaux. When a nonionic surfactant was added to the formulation to reduce interfacial tension, the leaves were wet uniformly and the amount of copper deposited under the same conditions increased fivefold. Deposit build-up with ordinary Bordeaux was faster on older leaves, but in all cases it was improved by the surfactant. However, caution must be used in generalizing on the effects of spreaders, since Somers (1957) found that some anionic surfactants decreased deposit build-up severely on easily wettable leaves although he also found that nonionic adjuvants were beneficial.

Somers (1957) states that the advancing contact angles of waterdrops on the upper surfaces of leaves of potato, bean, and laurel were 35°, 49°, and 81°, respectively, and that their wettability decreased in that order. Generally, deposit build-up is poorest on plants with smooth waxy surfaces and best on rough or moderately hirsute leaves. Thus, peppers, crucifers, and tropical plants such as banana accumulate less chemical under equivalent conditions of spraying than crops such as beans, potatoes, and eggplant. Usually deposition can be improved by the incorporation of suitable surfactants, but the value of this is governed in each individual case by the crop and the spray volume. This latter factor is particularly important, since the amount of fungicide deposited on leaf surfaces at equal total doses tends to decrease as the volume of carrier liquid is increased. This is because run-off of the spray occurs earlier at high volumes and some of the fungicide is carried away with the water. Adding surfactant to such mixtures decreases the volume of spray required to obtain run-off still further, and consequently decreases deposit. For example, Cupples (1941) found that improved wetting properties led to lower fungicide deposits on apples. Presumably at intermediate and low gallonage applications runoff would not occur, so that only the beneficial effect of the spreader would be retained. Thus, Swales and Williams (1956) report that inclusion of nonionic surfactants in lime-sulfur, sulfur, and ferbam (ferric dimethylthiocarbamate) concentrate spray mixtures improved their effectiveness for the control of apple scab. While this may have resulted in part from improved distribution of the fungicide, it appears that over-all deposition could not have been reduced seriously by the adjuvants.

Other things being equal, the amount of fungicides deposited on
plant surfaces should be directly proportional to its concentration in the spray suspension. Factors which might tend to obscure this simple relationship include changes in the droplet size of the spray and deposition after runoff. Most fungicide formulations contain surfactants. Consequently the surface tensions of sprays should be somewhat less at high concentrations than at low. Low surface tension is known to cause the formation of small drops, which might reduce deposition through greater drift of the spray with wind. However, indirect proportionalities have been reported between concentration and deposit where this could not be a factor. Thus, Rich (1954) found that the amount of Bordeaux deposited on leaves of beans and celery tended to reach a limiting value as the concentration in the spray tank was increased, while zineb (zinc ethylenebis[dithiocarbamate]) deposits increased linearly with concentration in the range studied. He pointed out that Bordeaux particles are positively charged—a fact which might cause them to be attracted to negatively charged leaf surfaces by electrokinetic forces. As the unoccupied sites on the foliage surfaces became reduced in number, rate of deposition would tend to decrease. These results seem inconsistent, since zineb particles are negatively charged and thus should be deposited with less rather than greater efficiency than Bordeaux. However, the concentration range studied was not the same for the two fungicides, so more evidence is required. The most reasonable explanation for this phenomenon is that deposit was directly proportional to concentration up to the point of runoff. When this condition was finally exceeded, Bordeaux continued to be deposited at a slower rate, the runoff water being slightly poorer in copper than the impinging spray droplets. Thus, deposition might not cease abruptly when runoff is reached, but continue awhile beyond it until the capacity of the leaves for retaining fungicide is exhausted. This could not occur when runoff is very rapid and insufficient time is allowed for the fungicide to become attached to the leaves. It has not been established whether electrokinetic effects are involved in this process. However, in view of the finding by Somers (1957) that negatively charged surfactants such as sodium dioctyl sulfosuccinate decrease deposit build-up a reinvestigation of this problem would be of great interest.

2. Role of Particle Size and Redistribution in Disease Control

Deposition of a fungicide on a plant surface is not by itself sufficient to insure the utmost utilization of its capacity for controlling disease. It must be distributed so that the maximum number of potential loci of infection is protected. Wilcoxon and McCallan (1931) found that there were significant differences in toxicity between sulfur dusts having
different particle sizes when they were compared on an equal weight basis, the more finely divided dusts being able to inhibit spore germination at lower doses. When the dusts were compared on the basis of an equal number of particles per unit area, there was no major difference in toxicity. This illustrates the importance of good coverage in protecting surfaces and stresses that the number of particles used is most critical when they are distributed randomly in the infection court. However, the sizes of the individual particles cannot be neglected entirely, for this would imply that small particles containing minute amounts of fungicide would be as effective as large ones for preventing infection by the parasite. This supposition may be approximately correct within a limited range, but must be invalid when the particles become extremely small. This is shown by the findings of Burchfield and McNew (1950), who measured the capacity of different particle size fractions of dichlone (2,3-dichloro-1,4-naphthoquinone) to control early blight of tomatoes in greenhouse tests. When particle size was reduced from a mean radius of 24.5μ to 0.45μ, only one-fortieth as much dichlone was required to maintain disease control. Fungicidal efficiency was not directly proportional to the number of particles on the surface. Instead, a limiting value was approached at small particle sizes, indicating that capacity for controlling disease was proportional to the logarithm of the number of particles per unit area of surface, or

$$1/G = m \log_e \frac{3G}{4\pi r^2 d} + q$$  (3)

where $G$ is the weight of fungicide per unit area required to control the disease, $d$ its density, $r$ the mean particle radius, and $m$ and $q$ are empirical constants.

This equation suggests that two basic factors are involved in the protection of surfaces by fungicides. These are: first, that the number of particles necessary to insure that each potential locus of infection is given nominal protection is constant and independent of the dose; and second, that on subdivision of a constant weight of material the rate of change of fungicidal effectiveness is inversely proportional to the number of particles present at the time of the change. The first of these assumptions is based on the supposition that the fungicide is randomly distributed in the infection court. If this occurs, a small number of large particles will lead to superabundance of chemical in some localities and little or none in others, while subdividing the material will tend to equalize coverage at various loci of potential infection.

Equation (3), as well as the practical results of many workers, shows that improvement in efficiency of utilization by reducing particle size
soon reaches a limiting value beyond which it is uneconomical to go. Thus the effectiveness of dichlone in protecting tomatoes from early blight was increased by only 25% on decreasing mean radius from 0.81 to 0.45 $\mu$, while the specific surface of the powder, which is related to the work required for comminution, was almost doubled.

Furthermore, it suggests that weak fungicides which can be used at high doses because of low cost are not likely to be improved as much by extreme subdivision as compounds with high intrinsic toxicity. A material with very low toxicity would have to be applied at such high doses to obtain any disease control at all that the surface would be saturated with respect to coverage at comparatively large particle sizes. Conversely, when intrinsic toxicity is very high, great care must be taken to distribute the smaller amount of material in such a way that all the potential infection loci are protected. For example, compounds which must be used at relative doses of 100, 10, and 1 units because of differences in intrinsic toxicity would give equivalent coverage at mean particle radii of 3.2, 1.6, and 0.7 $\mu$, respectively.

Even in greenhouse tests coverage is never so complete as would be predicted from particle size alone, since sprays are deposited unevenly. Often the droplets coalesce and runoff occurs, leaving different amounts of fungicide on the tips and mid-veins of leaves than found on the edges and interiors of the blades. Field applications are even more spotty, and this condition is likely to be aggravated in deposits formed from low gallonage concentrate sprays where as little as 15% of the plant surfaces may be coated with fungicide. In these cases, disease control in unprotected areas may be achieved through redistribution by dew and rain, so that physical factors other than particle size become important (Rich, 1954). Thus, Björling and Sellgren (1957) found that rain treatments improved the protection of potato foliage by Bordeaux mixture against infection by Phytophthora infestans when the fungicide was applied as small droplets in small volumes, while deposits formed from large drops applied at high volumes were not affected significantly. They ascribed this improvement to the local redistribution of the fungicide by weathering. However, they found that the effect of rain on zineb deposits was irregular. Improvements in disease control were recorded in a few tests, but more often deterioration of the protective power of the residue occurred. Perhaps this difference arose in part from the fact that Bordeaux mixture is much more tenacious than particulate fungicides and that the effects of redistribution were not overshadowed by a high over-all loss in residue (Burchfield and Goenaga, 1957a). Furthermore, the dosage-response curve of Bordeaux mixture is exceedingly flat, so that disease control would not be seriously reduced in
protected areas by the removal of sizable amounts of fungicide. The redistribution of comparatively small amounts of copper in previously unprotected spots might result in more effective disease control in these locations. Thus the over-all result might be favorable despite a net loss of fungicide. However, this behavior would not be expected from compounds having very steep dosage-response curves and poor tenacity, since control in protected areas might be decreased sharply without commensurate improvements in other localities owing to the relatively small amount of toxicant redistributed.

Butt (1955) investigated the movement of captan \([N-(\text{trichloromethylthio})-4\text{-cyclohexene-1,2-dicarboximide}]\) deposits on pear leaves and obtained no evidence to show that it was translocated in leaf tissue. He assumed that its fungicidal action was exerted through water layers linking the captan to the spores. Photomicrographs of captan deposits in waterdrops suggested that particles of the fungicide may become detached from the leaves and be redeposited near the periphery of the original residue, thus resulting in an expansion of the protected area. Presumably this process would be carried out more efficiently by gentle dews than by driving rain, since the latter would be expected to result in an over-all loss of the spray deposit with negligible opportunities for redeposition of dislodged particles and aggregates.

Contrary to the finding of Butt, Napier, et al. (1957) present evidence which they interpret to mean that captan exerts systemic action in the protection of broad beans against \textit{Botrytis fabae}. They found that sprays applied to the dorsal surfaces of leaves resulted in significant reductions in the number of lesions found on the ventral surfaces, although complete disease control was never achieved. Furthermore, treatment of the first leaves of bean resulted in reduction of the infection incidence of the second and third leaves. While diffusion of captan through leaves \textit{via} dorsal and ventral stomata and the loosely organized structure of the spongy parenchyma is possible, translocation through greater distances in the vascular tissue of the plant is unlikely, owing to the extremely high instability of captan in aqueous media (Burchfield and Schechtman, 1958). It should be noted that the bean plants used in these experiments were incubated in a moist chamber for 18 hours to provide conditions suitable for infection by the pathogen. Thus the fungicide may have been redistributed in small moisture droplets or conveyed to the spores \textit{via} the vapor phase by convection currents. It must be considered that some metals have high enough vapor pressures to kill spores by fumigant action in enclosed spaces. Examples from the history of plant pathology show that similar cases of “action at a distance” have been misinterpreted. Therefore, experiments which show
that protectant fungicides can be redistributed by translocation within the plant must be re-evaluated critically before final acceptance.

B. Interactions of Fungicides with Their Environments

1. Extrinsic Factors in the Persistence of Fungicides

Particles may be bound to surfaces by London-van der Waals' forces, electrostatic attraction, capillarity, or some combination of these effects (Burchfield, 1959). Most physical studies on the adhesion of small particles have been made on smooth homogeneous surfaces, such as those of glass or quartz. Even so, there is disagreement among physicists as to the relative importance of these forces and the distances over which they are effective. Plants are grounded semi-conductors with rough surfaces. Moreover, the leaves of many of them excrete waxy blooms in uneven patterns, so that some particle surfaces may be in contact with wax and others with cell walls. Consequently, areas of close contact between particles and leaves are likely to be small and heterogeneous. Furthermore, changes in the moisture content of the air might shift the balance of forces responsible for adhesion. At high humidities electrostatic potentials between particles and leaves might be discharged because of the high conductivity of the air, while capillary attraction through the formation of films of water connecting the particles to the surface would tend to increase. As a result of the instability of the environment, the heterogeneity of the surfaces, and the multiplicity of forces involved, it is unlikely that the mechanism of adhesion of pesticides to plants will be clarified for some years to come, except in general terms.

The attachment of pesticide particles to plants is weak compared to the strengths of bonds created by adhesives. Thus, Somers and Thomas (1956) found that wind alone reduced cuprous oxide deposits by more than 50% after 27 days' exposure, while Byrdy et al. (1957) report significant reductions in the toxicity of DDT residues after exposing them for 5 minutes to air currents with a velocity of 3.5 meters per second. Rain removes spray deposits considerably faster than wind, but in the field the action of wind is more prolonged. Burchfield and Goenaga (1957a) found that 43% of the cuprous oxide deposited on banana leaves was removed by the first quarter inch of rain. However, the next quarter inch removed only 4%, and succeeding treatments removed only about 1 to 2% per 0.5 inch of rain. Similar results were obtained with cuprous oxide on artificial surfaces (Somers and Thomas, 1956) and with captan and maneb (manganous ethylenebis[dithiocarbamate]) on tomato foliage (Burchfield and Goenaga, 1957a), sug-
gesting that 30 to 80% of most fungicides is deposited in forms that have very poor residual properties. Pond and Chisholm (1958) recently reported that 26 to 63% of the amount of DDT on potatoes was lost during 24 hours weathering in the field, so it appears that as much as one-half of the value of the chemicals used for plant protection is expended with small return. Reduction of this figure should be one of the chief goals of formulation research, since it may represent an annual loss of the order of $100,000,000 in the United States alone.

One reason for this high initial disappearance of fungicide may be unfavorable particle size distribution. Many workers have shown that the tenacities of fungicides increase with decreasing particle size, probably owing to higher specific surface. This allows for a greater total area of contact between the fungicide deposit and the leaves. Since the total force of adhesion is the product of the contact area and the force per unit area, it is evident that increasing the former automatically results in an increase in total force of adhesion. Furthermore, small particles should resist dislodgement better since they are lighter in weight. Thus it is possible that the high initial losses experienced on weathering arise from a rapid and complete loss of large particles, while the tenacious part of the residue consists of small particles. Ground powders contain many more small particles than large ones, but the large ones usually contribute most to the weight. Thus one particle with a radius of $10\mu$ would weigh as much as 1000 particles with radii of $1\mu$. Therefore, if particle size is a predominating factor in regulating tenacity, a high initial rate of loss should occur as large particles are removed, followed by a slower rate of loss of the remainder of the fungicide as is found in practice. In other words, the spray deposit is heterogeneous with respect to particle size and consequently tenacity, so that plots of the logarithm of the deposit retained against inches of rain are usually curvilinear (Burchfield and Goenaga, 1957b).

Primary particle size of the fungicide alone probably does not account for all of this effect, because aggregates of small particles can be formed which might behave like large particles in weathering tests. Thus Gullstrom and Burchfield (1948) found it necessary to use a 0.25% solution of dispersing agent to deflocculate dichlone to the point where the particles would sediment individually rather than in groups. This is far in excess of the amounts of these agents that would be included in commercial fungicide formulations, so it is likely that most materials are aggregated to a greater or lesser extent in the spray tank and that these agglomerates are carried over onto the leaves. Further evidence for the occurrence of interactions between particles can be adduced from the finding of Somers and Thomas (1956) that the tenacities of copper
fungicides increased with decreasing initial deposit. This agrees with the earlier observation of Turner and Woodruff (1948) who suggested that particle-surface adhesion governs the tenacity of sparse spray deposits while particle-particle cohesion becomes important with increasing deposit. This is equivalent to saying that aggregates have lower tenacity than discrete particles. Assuming ideal (random) distribution of the fungicide on the plant surface, lateral associations between particles would be negligible since scale drawings have shown that dichlone can control tomato early blight when most of the surface is unoccupied by particles (Burchfield and McNew, 1950). However, in practice, distribution of primary fungicide particles is probably far from random, owing to the presence of aggregates in the spray tank.

Tenacity can be influenced by the spreading properties of the spray on foliage. Thus Bordeaux mixture applied to the waxy leaves of bananas collects as discrete droplets at the leaf veins (Burchfield and Goenaga, 1957b). On drying, these form small friable pellets of Bordeaux which are easily dislodged mechanically by the first rain. The addition of a nonionic surfactant to the mixture reduces interfacial tension so that the droplets spread. The deposit that is formed is exceedingly tenacious, even in the presence of 3 times the amount of surfactant required for good spreading. Similar results were obtained with copper oxide deposits on banana leaves, so evidently these observations hold for particulate fungicides as well. Presumably, good spreading results in the formation of smaller and fewer aggregates during drying. However, the use of large amounts of surfactants may lead to premature runoff in high gallonage applications, and the foliage may be more easily rewet by rain. Spreaders could probably be used most advantageously in medium and low gallonage applications, providing they do not accentuate phytotoxicity.

It might be possible to minimize some of the undesirable residual properties of spreaders by creating compounds with labile bonds that will hydrolyze within a few hours after they are dissolved in water. Thus a nonionic material such as

\[(CH_2)_n CH_2 O M \overset{\text{O}}{\longrightarrow} CH_2 CH_2(\text{CH}_3\text{CH}_2\text{O})_m \overset{\text{CH}_2}{\longrightarrow} CH_2 \text{OH}\]

might be synthesized, where M is a substituent which forms easily hydrolyzable bonds. Conceivably, the intact molecule could be a good spreader, while the fragments formed on cleavage at the O—M or C—O bonds would be inert. Thus, advantage could be taken of the beneficial effects of spreaders without encountering residual detergent properties.

Stickers have also been used in attempts to improve performance.
Unfortunately much of the early work was done with proteins such as casein. Evidently such materials are not successful stickers in agricultural applications possibly in part because they tend to decrease the toxicities of copper fungicides, owing to the formation of metal complexes (Heuberger and Horsfall, 1942). Recently, Somers (1956) evaluated forty-seven materials for their abilities to improve the retentiveness of cupric oxide to cellulose acetate surfaces. Encouraging results were obtained with agar, linseed oil, lime-casein, polyvinyl acetate, coumerone resin, rubber latex, and polyvinyl chloride. However, with the exception of polyvinyl acetate and chloride, all of these materials decreased the toxicity of the CuO to Alternaria tenuis in vitro tests, and none of them improved control of potato blight in field tests. This is typical of experience with stickers. They sometimes improve tenacity, but usually at the expense of fungitoxicity.

The tenacity of Bordeaux mixture is outstanding, compared to that of most other fungicides (Burchfield and Goenaga, 1957b). When freshly prepared or suitably preserved with adjuvants, it has the properties of a deformable hydrogel, and spreads over the plant surface to form more or less continuous films. The first 0.5 inch of rain removes only 10% of the deposit, and 70% of the initial residue remains after 8 inches of rain. Furthermore, the logarithm of the tenacity is directly proportional to inches of rain. This suggests that all components of the spray deposit adhere equally and that the amount of fungicide removed with each rainfall treatment is a constant percentage of the amount present at its beginning. This shows that the deposit is essentially homogeneous. On aging, 10-10-100 Bordeaux forms spherulites about 5 to 6μ in diameter which have almost no resistance to weathering. However, 10-3.2-100 Bordeaux and similar preparations retain absorbed water and good tenacity indefinitely, even though X-ray diffraction data show that small crystallites are formed very rapidly after mixing (Magdoff et al., 1958). The superior tenacity of Bordeaux hydrogels suggests that tank mix preparations of ziram (zinc dimethyldithiocarbamate) made by adding zinc sulfate to an aqueous solution of the sodium salt might be superior to the wettable powder for similar reasons (Wilson, 1953). The iron, zinc, manganese and copper salts of dithiocarbamic acid and of 8-hydroxyquinoline could also be prepared as hydrated gels which might adhere to surfaces better than the corresponding wettable powders if sprayed before sizable crystallites had a chance to form.

No matter how good the tenacity, spray deposits will be attenuated by plant growth during the early and middle parts of the growing season. Usually the grand period of growth for foliage occurs earlier than for
fruit, thus lengthening the period during which frequent sprays must be applied. Frear and Worthley (1937) found that apple leaves on trees grown in southern Pennsylvania attained 28% of their full size at the first cover spray on May 28, while development was 98% complete by June 6. By contrast, the surface area of the top fruit doubled between July 1 and July 26. At the time of the last cover spray there were 10 to 16 times more chemical (lead arsenate) on the fruit than on the foliage. This must have been caused in part by the earlier growth of the former. Thus the limiting factor in the efficiency with which plant protectants can be used is the time and rate of expansion of the surfaces which must be protected.

2. Intrinsic Properties Influencing Performance

a. Physical Considerations. Intrinsic properties of fungicides, such as water solubility, volatility, and chemical reactivity may often play major roles in their performance in the infection court. Compounds such as copper sulfate and quaternary ammonium salts give good control of diseases in greenhouse tests but are ineffective in the field because they are easily washed from plant surfaces by rain. Consequently, successful foliage fungicides, with the potential exception of systemics, should usually have low water solubility. This property may also govern the rates at which chemical changes take place in the infection court, because reactions such as hydrolysis are probably confined to the dissolved portion of the fungicide in the moisture films at plant surfaces.

The rate at which a solid will dissolve in water under continuous agitation is given by:

\[
\frac{dx}{dt} = kA(S - x)
\]  

(4)

where \(x\) is the concentration of solute in the aqueous phase at time \(t\), \(S\) its solubility, \(A\) the surface area of the solid and \(k\) a proportionality constant. The rate of solution therefore depends on water solubility as well as specific surface.

Although most fungicides are generally regarded as being insoluble, this is only true in a relative sense. If a compound were truly insoluble it would be unlikely to be fungitoxic because of its inability to reach and permeate the protoplasm of spores and mycelia. From the standpoint of toxic dose, commercial fungicides have appreciable solubility in water, that of Dyrene being about 10 p.p.m. and that of dichlone about 7 p.p.m.\(^1\) Compounds with solubilities greatly exceeding these values would probably have poor residual properties when exposed to rain,

\(^1\) Burchfield, H. P. Unpublished data.
while compounds which are insoluble compared to dichlone might be unable to reach vital sites in the fungi.

Fungicides can also disappear from the infection court by sublimation. The air in direct contact with small spherical particles of volatile compounds is saturated with vapor, and the rate of exchange of molecules between the solid and its surrounding shell of vapor is very rapid, compared to the rate at which the vapor can diffuse away into the air. Consequently, rate of evaporation is determined in part by rate of diffusion through the surrounding air, and is given by

$$\begin{align*}
- \frac{dm}{dt} &= \frac{4\pi r D M p}{RT} \\
\end{align*}$$

where $-\frac{dm}{dt}$ is the rate of weight loss of a single particle, $r$ the radius of the particle, $D$ the diffusion coefficient of the compound, $M$ its molecular weight, $p$ its vapor pressure, $R$ the gas constant, and $T$ the absolute temperature. Thus the molecular weight of the compound and its diffusion coefficient, as well as vapor pressure, influence rate of dissipation by sublimation. It is also noteworthy that the weight loss of small particles is proportional to their radii and not to their surfaces.

Thatcher and Streeter (1925) have shown that sulfur deposits are attenuated by sublimation. More recently Miller and Stoddard (1957) found that o-chloronitrobenzene had strong fumigant action, pentachloronitrobenzene moderate fumigant action, and captan and chloranil (tetrachloro-p-benzoquinone) weak fumigant action when tested against 4 species of fungi in closed containers. Thiram (tetramethylthiuram disulfide) and other related compounds were ineffective. This suggests that sublimation might be an important factor in the disappearance of some of these compounds from the infection court and be negligible in others. Decker (1957) regards sublimation to be highly important in determining the rate of residue loss of insecticides. He points out that persistence is directly proportional to the logarithm of the time of exposure under conditions where losses caused by wind, rain, and plant growth are negligible. Furthermore persistence of insecticides on foliage decreases in the order: DDT > methoxychlor > toxaphene > dieldrin > chlordane > heptachlor > aldrin > lindane, which is the order of increasing volatility. Since most of these compounds are stable chemically, sublimation appears to be the only reasonable way to account for their disappearance.

As shown earlier, fungicides must be ground to small particle size to obtain adequate coverage of plant surfaces. However, extreme subdivision may lead to poor persistence when the compound is volatile.
or can react chemically in the infection court. The total surface of fungicide per unit area of plant or fruit is

\[ A = \frac{3G}{rd} \]  

(6)

where \( A \) is the surface, \( G \) the weight of fungicide per unit area, \( d \) its density, and \( r \) the particle radius. Thus the surface of fungicide exposed to weathering is 10 times greater at a particle radius of 0.5\( \mu \) than at 5\( \mu \). Burchfield and McNew (1950) suggest that a compromise between coverage and surface exposed might be reached by selecting a particle radius near where disease control is achieved at minimum total surface of fungicide. Theoretical calculations based on data obtained on dichlone show this to be

\[ r = \left[ \frac{3}{8mdc^{2-\varphi/m}} \right]^{1/3} = 4.9\mu \]  

(7)

where the constants are the same as those of equation (3). This relation is based on the fact that when particle size is large, specific surface is small. However, so much material is required to give disease control that the total surface of the fungicide per unit area of plant is large, showing that it is not being used efficiently. As particle radius is reduced, coverage improves faster than specific surface increases, so that the total surface of fungicide required for control of the disease decreases. Finally, when the surface nears saturation with particles, the effect of increased specific surface predominates, and the total surface of fungicide per unit plant area required for disease control increases. The radius of 4.9\( \mu \) given by equation (7) is at the minimum of this curve.

When dichlone preparations having mean particle radii of 1.5 and 3.6\( \mu \) were evaluated for capacity to control tomato early blight, fungicidal efficiency diminished by only 30\% when the plants were held in the greenhouse for one week between spraying and inoculation. At radii less than 1\( \mu \), 80\% of the protective value of the fungicide was lost, and at radii of 8.4\( \mu \) and above it disappeared altogether. Presumably the total failure of the larger particle size preparations to control the disease arose from poor tenacity even in the absence of rain. Sulfur has also been shown to have impaired residual properties at very small particle size, but fixed coppers do not, possibly because they are chemically stable and have negligibly low vapor pressures (Horsfall, 1956). Thus the optimum size distribution for good persistence is regulated by the intrinsic chemical and physical properties of the fungicide.

b. Chemical Reactions. Plant protectant fungicides are labile chemicals that can react within spores or in the external environment. Typical reactions which can take place at foliage surfaces include oxidation,
carbonation, photolysis, and hydrolysis. In some cases metal ions can
be chelated by components of guttation fluids or substances excreted by
fungus spores.

Many compounds such as dihydric phenols and mercaptans are
susceptible to oxidation. Thus aqueous solutions of hydroquinone and
1,4-dihydroxynaphthalene become orange-red on exposure to air, par­
ticularly at high pH values. This results from oxidation to quinones
which can react further to yield colored polymeric materials called
humic acids. In the case of hydroquinone, the following reactions
probably take place at pH 8:

\[
\begin{align*}
  \text{OH} & + \text{O}_2 \rightarrow \text{OH} \\
  \text{OH} & + \text{H}_2\text{O}_2 \rightarrow \text{OH} \\
  \text{O} & + \text{H}_2\text{O} \rightarrow \text{humic acids}
\end{align*}
\]

When all of the hydrogen atoms adjacent to the carbonyl groups of the
quinones are replaced with chlorine atoms, as in chloranil and dichlone,
secondary reactions with hydrogen peroxide cannot occur. The reduction
products of these toxicants, tetrachlorohydroquinone and 2,3-dichloro­
1,4-dihydroxynaphthalene, respectively, are as good plant protectants
as the parent quinones. This observation has no practical significance
from the standpoint of disease control, since it is more convenient to
use these compounds in their oxidized states. However, it serves to point
out that many fungicides can exist in oxidized and reduced forms, and
that these may be interconvertible on plant surfaces.

The best authenticated example of the oxidative activation of a
fungicide in the infection court is represented by nabam (disodium
ethylenebis[dithiocarbamate]. Nabam is a water soluble compound
that is fungistatic but not fungicidal. Spores immersed in a 10% solution
of it are able to germinate after they are removed and washed with
water. Even though water soluble, it often gives good persistence and
disease control on foliage, suggesting that it is converted \textit{in situ}
to water insoluble compounds with high fungitoxicity. Ludwig \textit{et al.}
(1954) demonstrated that it can be oxidized to ethylene thiuram mono­
sulfide and polymers and that these materials appear to be toxic to
fungus spores. Sijpesteyn and van der Kerk (1954) confirmed these
findings but suggested that the toxic principle is ethylene diisothio­
cyanate, generated either directly from nabam or its oxidation products.
This conclusion was later supported by Thorn and Ludwig (1954).
Thus satisfactory evidence is available that nabam is oxidized on plant
surfaces to a material with good residual properties and that this deposit then generates a nascent toxaphore.

Aside from oxygen, carbon dioxide is the only component of dry air known to react with fungicides. It converts the excess lime of Bordeaux mixture to calcium carbonate within a few hours after spraying. The copper components of Bordeaux mixtures containing more than 2.5 lb. of lime per 10 lb. of cupric sulfate have average compositions of \( \text{Cu}_4\text{Ca}_{n}\text{SO}_4(\text{OH})_{8+2n} \cdot x \text{H}_2\text{O} \) (Magdoff et al., 1958). Carbonic acid may react with some of these highly basic materials to form products with different physicochemical properties. On prolonged washing of Bordeaux deposits with water, calcium and sulfate ions are removed, and the amount of soluble copper increases. Reckendorfer (1936) suggests that the copper in Bordeaux mixture is solubilized by the formation of copper bicarbonate. However, Wilcoxen and McCallan (1938) point out that basic copper carbonate, rather than \( \text{CuCO}_3 \), is obtained by ordinary methods of preparation, and they state that it is unlikely that an acid carbonate could be formed under as low pressures of \( \text{CO}_2 \) as exist in the atmosphere. Free (1908) found that \( \text{CO}_2 \) increased the amount of soluble copper in equilibrium with insoluble basic copper carbonate by a factor of 5. The additional copper thus dissolved is insignificant stoichiometrically, but could have a pronounced influence on preventing germination of fungus spores. The exact role of carbon dioxide is regulating the properties of Bordeaux is uncertain. Similarly there is very little information available on its effects on lime-sulfur deposits, where it could play a dominating part in regulating the properties of the residues.

The decomposition of some groups of pesticides can be initiated by light. Thus, \( p \)-benzoquinone yields hydroquinone and a product believed to be a dimer when exposed to light of wavelength less than 5770 Å. The quantum yield is 0.505. The efficiency of the photochemical process decreases as chlorine atoms are substituted into the molecule, so that the quantum yield for chloranil is only 0.095. Despite this low efficiency, aqueous solutions of it are very unstable unless stored in the dark.

The threshold wavelength region for the photolysis of quinones decreases with decreasing oxidation potential. Thus, chloranil with a potential of 0.73 volt and a threshold region in the neighborhood of 5770 Å, should decompose more readily when exposed to light than dichlone, which has an oxidation potential of only 0.42 volt. Measurements of the decomposition rates of the two compounds in dioxane-water solutions exposed to sunlight show that dichlone is the more stable
Many fungicides containing reactive halogen atoms can hydrolyze in solution. These include captan, Phaltan \([N-(\text{trichloromethylthio})\text{ phthalimide}]\), Dyrene \([2,4\text{-dichloro-6-(o-chloroanilino)}\text{-s-triazine}]\), dichlone, and chloranil. Generally the reactions proceed by replacement of a halogen by a hydroxyl ion, so that they take place more rapidly in alkaline than in acid media. Thus, Daines \textit{et al.} (1957) found that captan decomposes slowly at pH 7 and instantaneously in the presence of sodium hydroxide. Actually, decomposition is rapid even in neutral solution, as shown by the finding that captan has a half-life of only 2.5 hours in aqueous buffer at pH 7 (Burchfield and Schechtman, 1958). However, it persists much longer than this on foliage because of its low solubility in water and the fact that only material in true solution can hydrolyze. Nevertheless it is an unstable compound in this respect, compared to Dyrene, which has a half-life of about 22 days under similar conditions (Burchfield and Storrs, 1956). This shows that hydrolysis might be an important factor in the depletion of captan residues, and inconsequential in the case of Dyrene.

Some fungicides containing copper and perhaps other metals can be chelated by amino acids, hydroxy acids, and other compounds found in the guttation fluids of higher plants and excretions of fungus spores (Horsfall, 1956). Thus glycine, aspartic acid, and sodium malate will sequester copper from Bordeaux mixture, and even sucrose will complex it at high pH values. This has led to a wealth of work and speculation on whether the copper in Bordeaux deposits is mobilized by the action of the host plants or by the spores themselves. McCallan and Wilcoxon (1936) found that water extracts from 100,000,000 fungus spores dissolved from 0.013 to 1.01 mg. of copper from Bordeaux mixture, depending on the species. In the case of \textit{Neurospora sitophila}, the amount of copper solubilized was about 3500 \(\mu g\) per gram of spores, exclusive of the amount that might have been taken up by them. Determination of the total solids excreted by the spores showed that the species excreting the most were also most active in dissolving copper from Bordeaux mixture. Furthermore, the five fungi tested differed little in susceptibility to copper poisoning when it was administered as cupric sulfate, but in general the species capable of solubilizing the greatest amount of copper from Bordeaux mixture was most sensitive to it. Malic acid was identified as one of the excretion products of \textit{N. sitophila}. Its copper complex had
about the same toxicity to spores as copper sulfate, suggesting that at least part of the copper dissolved by the action of the spores may be present in a form readily assimilable by them. This is not always true. Glutamine, asparagine, and some proteins are known to reduce the toxicities of copper fungicides (Horsfall, 1956). Probably each copper chelate has its own unique bioactivity depending on its stability constant, diffusion coefficient, and capacity to permeate spores.

The nature of the host leaves and invading fungus also influences the toxicity of Bordeaux mixture. Yarwood (1943) found cupric sulfate to be 100 times more toxic than Bordeaux to rust spores in vitro, but only one-tenth as effective for preventing infection of bean plants by the fungus. This seems to have arisen from a synergistic interaction between the Bordeaux deposit and bean leaves rather than from secondary effects such as poor weathering of the cupric sulfate residue, for the protective action of Bordeaux deposits was not potentiated when used for the control of downy mildew of cucumber. Thus, organic copper chelates may have been formed by chemical reactions on the bean foliage that were more toxic than the original spray residue.

3. Physicochemical Basis of Phytotoxicity

Injury to the host plant is often a limiting factor in the use of fungicides. This must be expected, since most chemicals used as protectants can react with components of protoplasm, chelate essential metals, or accumulate at vital biological interfaces. They are less specific in their action than antimetabolites such as the sulfanilimides, and are likely to be phytotoxic if they can penetrate the cuticularized tissue protecting the host. Thus compounds such as dichlone, which otherwise can be used safely on many plants, will cause severe burning when mixed with oils. Presumably, the fungicide dissolves in the hydrocarbon, which enables it to permeate the leaf tissues more efficiently.

Sometimes the difference between a safe fungicide and a phytotoxic compound is determined by the length or nature of a side chain. In a study of imidazoline derivatives Wellman and McCallan (1946) found that optimum fungitoxicity was obtained when the alkyl side chain substituted in the 2-position of the heterocyclic ring contained 17 carbon atoms, but when it contained 11 carbons the compound was phytotoxic. Similarly, Schuldt and Wolf (1956) showed that derivatives of 2,4-dichloro-6-anilino-s-triazine are good protectant fungicides, while Koopman and Daams (1958) found that similar triazines containing alkyl in place of aryl groups are herbicides.

Some of these differences in specificity of action may arise from changes in solubility relationships:
Thus, Compound (I) is not accumulated rapidly by fungus spores, and is ineffective for the control of early and late blights of tomato. Its solubility in water is about 100 p.p.m., and it injures the test plants. Substitution of a methyl group in the ortho position of the benzene ring (II) reduces solubility to 60 p.p.m. and results in improved fungitoxicity, while a chlorine atom in this position (III) enhances its properties still further. The solubility of Dyrene (III) in water is only 10 p.p.m. and it is a far better fungicide than (I). Furthermore, it is not phytotoxic to the test plants under conditions where (I) produces severe injury. Since both compounds react with the same metabolites and compete for the same sites within fungus spores, it is likely that they have the same mode of action (Burchfield and Storrs, 1957a). Therefore the difference in phytotoxicity between these compounds may arise from a difference in solubility, and hence in rate of movement. Compound (I), being 10 times more soluble in water than (III), might dissolve faster in moisture films and move into the host plants through the stomata. Water seems to be implicated in the movement of these compounds, since Dyrene causes necrotic flecking and defoliation of pepper plants when they are incubated in a moist chamber for 24 hours before being placed in a greenhouse. Plants sprayed with Dyrene and transferred directly to the greenhouse bench are unaffected. The leaves are dropped while still turgid by disintegration of the abscission layer, so evidently this compound can be translocated to some extent under extreme conditions of humidity.
However, solubility cannot be the only factor governing phytotoxicity, since captan is at least as soluble as Dyrene in water, and it is considerably safer for use on apples for the control of scab. An explanation might be sought in the fact that the half-life of captan in buffer at pH 7 is only about 2.5 hours, compared to about 22 days for Dyrene, so that their longevities in the aqueous phase differ by a factor of more than 200. While captan might diffuse far enough to reach fungus spores or localized regions within the plant tissues, it would not have the range of penetration of Dyrene because of its shorter life. Thus the intermeshed effects of water solubility, diffusion coefficient, and hydrolysis rate, in combination with intrinsic biological activity, might help to explain why some compounds are phytotoxic and others are not.

It is interesting that the injury caused by both captan and Dyrene can be reduced by formulation with calcium carbonate. Both compounds produce hydrochloric acid on hydrolysis, and in the case of captan the acidity might become high enough to burn the plants (Daines et al., 1957). The presence of the carbonate would tend to minimize this through neutralization of the acid with the formation of CaCl₂ and CO₂. Daines et al. (1957) showed that kaolinite, which has a low capacity for disposing of acids, aggravates injury. However, Dyrene decomposes so slowly that the concentration of HCl at the plant surface is never likely to be very high. It is possible that calcium carbonate safens it by accelerating its decomposition rate in the aqueous phase so that the range over which it can diffuse is limited.

Evidently the hydrolysis products of Dyrene are harmless, but in some cases the breakdown products of fungicides are more injurious than the original compounds. Thus, aqueous suspensions of dichlone formulated with some attapulgite clays slowly become deep red in color and are phytotoxic to higher plants. Presumably the red compound is 2-hydroxy-3-chloro-1,4-naphthoquinone. Although it is a weak fungicide compared to dichlone, it can probably permeate leaf tissues more rapidly because of the higher water solubility conferred on it by the hydroxyl group.

Examples where fungicides have conjugates with a basically different type of biological activity are not uncommon. Thus, 1-fluoro-2,4-dinitrobenzene is probably toxic to spores because it can participate in substitution reactions with metabolites such as amino acids and proteins, while its hydrolysis product, 2,4-dinitrophenol, uncouples phosphorylation from oxidation. Similarly, pentachloronitrobenzene produces pentachlorophenol on hydrolysis. Both these compounds are good fungicides but have different areas of application, the former being used in soil and the latter for the protection of wood. These observations suggest that
the margin of safety which separates a fungitoxic dose of chemical from a phytotoxic dose might be narrowed perilously if interactions in the infection court convert a compound that is predominantly fungicidal to one with herbicidal properties.

III. Treatment of Soils and Seed

A. Chemical and Biological Interactions

1. Microbial Conversions

The large and diversified population of microflora and microfauna inhabiting soils leads to many complications in the control of plant afflictions of subterranean origin that are not encountered above ground. Indiscriminate uptake and dissimilation of pesticides by a variety of parasites, saprophytes, and symbionts is one of these. Thus phenol, which is used as a standard in testing bactericides, can serve as a sole source of carbon for many soil-inhabiting organisms. It is first hydroxylated in the ortho position of the benzene ring to yield catechol, which is subsequently oxidized to o-benzoquinone. The latter compound then undergoes ring cleavage with the formation of ketonic and aldehydic acids (Evans, 1947).

\[
\begin{align*}
\text{OH} & \rightarrow \text{OH} \\
\text{aliphatic compounds}
\end{align*}
\]

One of the intermediates is degradation, o-benzoquinone, is a highly effective but unstable fungicide (McNew and Burchfield, 1951). Benzoic acid is metabolized similarly, with the probable formation of 3,4-dihydroxybenzoic acid and the corresponding quinone as intermediates. Other aromatic compounds oxidizable by soil microorganisms include p-hydroxybenzaldehyde, syringaldehyde, vanillin, and ferulic acid (Henderson and Farmer, 1955). Of 61 fungal isolates from soil that could use these compounds as sole sources of carbon, 2 were Mucor species and the remainder, Deuteromycetes.

Even hydrocarbons can be metabolized, as demonstrated by the finding of Murphy and Stone (1955) that naphthalene was destroyed by Pseudomonas sp. with the sequential formation of salicylic acid, catechol, and \(\beta\)-adipic acid. Corynebacterium italicum degrades hexadecane, tetradecane, and decane completely (Ladd, 1956). This species also oxidizes fatty acids and alcohols containing 1 to 11 carbon atoms as well as several aliphatic aldehydes and higher methyl ketones. Other chemical reactions that can be catalyzed by the enzymes of microorgan-
isms include cleavage of aromatic ethers to yield phenols and decarboxylation of aromatic acids (Henderson, 1957).

Microorganisms isolated from soil can metabolize pesticides containing nitro groups. Thus, Gundersen and Jensen (1956) isolated a strain of Corynebacterium simplex that could use 2,4-dinitro-o-cresol as a sole source of nitrogen and carbon when cultured in agar or liquid media. Degradation was probably initiated by an attack on the para nitro group followed by hydrolysis of the group ortho to the hydroxyl, resulting in the elimination of inorganic nitrite and the formation of dihydric and trihydric phenols. One of the nitro groups must be para to a hydroxyl group for dissimilation by this particular organism, for p-nitrobenzoic acid was not attacked, although it can serve as a sole energy source for the aerobic growth of a strain of Pseudomonas fluorescens. Intermediates in the metabolism of this latter compound include p-aminobenzoic acid, p-hydroxybenzoic acid, and protocatechuic acid (Durham, 1957). This last compound is a naturally occurring fungicide responsible for the resistance of red onions to smudge (Angell et al., 1930). The nitro group of p-nitrobenzoic acid is reduced to an amino group, which is then split off by ammonolysis, a reaction that would not occur under physiological conditions unless catalyzed by enzymes.

Other nitro compounds degraded by Corynebacterium simplex include p-nitrophenol, 2,4-dinitrophenol, and picric acid, all of which have some measure of bioactivity. As might be expected, the bacteria must be adapted to the substrate before they can commence their attack, but this takes place with remarkable rapidity in the case of dinitro-o-cresol. Continued treatment of soil with this chemical results in its enrichment in microorganisms active in dissimilation. Thus the toxic effect of dinitro-o-cresol to higher plants persists for a long time on the first addition of the compound to soil, but repeated applications result in a gradual shortening of the time required for detoxication. Presumably this treatment kills off highly susceptible organisms and results in the multiplication of species able to use the toxicant for a substrate. Thus continuous use of some pesticides in soils may result in reduced efficiency owing to shifts in the microbial population.

However, changes in microbiological balance might be advantageous when fungicides are selective enough in action to suppress the growth of plant pathogens and at the same time permit multiplication of species naturally antagonistic to them. Thus, Moje et al. (1957) found that acetylenedicarboxylic acid treatments stimulated the production of an almost pure culture of Trichoderma viride in soil, while crotonic acid resulted in a preponderance of Fusarium solani. These authors suggest this might be an indirect method for controlling disease, since T. viride
12. PERFORMANCE OF FUNGICIDES

is known to be antagonistic towards root rot and damping-off organisms such as Phytophthora and Rhizoctonia spp. Similarly, Richardson (1954) found that thiram protected pea seedlings for a longer time than it persisted in soil. He suggested that thiram-resistant species such as T. viride became dominant, and this suppressed the pathogens through competition or direct antagonism. He pointed out that T. viride is known to produce two antibiotics, gliotoxin and viridin, and can protect seedlings of several species of plants from damping-off organisms.

Biologically active compounds might also be generated from inert precursors in soils. Well-attested cases of the in situ activation of fungicides in this medium have not been described, but the conversion of 2,4-dichlorophenoxyethyl sulfate to 2,4-D provides a good illustration of this process from the related field of plant growth regulation. The former compound is nontoxic when sprayed on plants, but is a pre-emergence herbicide when mixed in soil. Vlitos (1952) showed that it was hydrolyzed to 2-(2,4-dichlorophenoxy)ethanol by Bacillus cereus var. mycoides under conditions where acid catalyzed hydrolysis would not be expected to take place. The intermediate alcohol was then oxidized to the active principle 2,4-D. Organisms capable of this latter conversion were not isolated. Thus microbial action, possibly in combination with spontaneous chemical reactions, can create toxicants from biologically inert compounds. This possibility should be kept in mind in designing new organic molecules and in interpreting the results of bioassay. Cases where candidate compounds are highly active in some soil environments and fail miserably in others occur much too frequently to be ascribed entirely to experimental shortcomings.

2. Spontaneous Reactions with Metabolic Debris

Fertile soils are rich in organic matter resulting from the decay of plant and animal debris. Segments of the carbon and nitrogen cycles operate continuously in them and generate a host of metabolites and their degradation products. Many of these contain amino, phenolic, and other nucleophilic groups which can react spontaneously with some fungicides. Thus, Stevenson (1956) isolated 29 ninhydrin-positive compounds from the hydrolyzate of an extract from silt loam soil. The total weight of amino acids averaged 5.7 mg. per gram. Undoubtedly many of these were present originally as components of proteins or polypeptides, since free amino acids are deaminated in 26 to 36 hours when added to soil (Greenwood and Lees, 1956). However, some peptides and proteins are more reactive than their component amino acids with toxicants containing reactive halogen (Burchfield and Storrs, 1956).

Many of the reactions of pesticides with metabolic debris take place
through addition or substitution mechanisms. Fungicides that can undergo addition reactions include some quinones, N-arylmaleimides, and compounds with double bonds α-β to carbonyl groups. These chemicals can react with free amino and sulphydryl groups as follows, using a maleimide as an example:

\[
\begin{align*}
\text{HC} & \text{C} \quad \text{N} \quad \text{O} \\
\text{HC} & \text{C} \quad \text{N} \quad \text{O}
\end{align*}
\]

Sometimes compounds which appear to undergo substitution reactions actually combine by addition. Thus bis(β-chloroethyl)sulfone reacts with amines in a way that ostensibly suggests substitution of a chlorine atom by nitrogen. Yet it has been shown that dehydrochlorination first occurs with the formation of vinyl sulfones as intermediates (Price, 1958). The over-all course of the reaction is therefore:

\[
(\text{ClCH}_2\text{CH}_2\text{SO}_2 + 4\text{RNH}_2 \rightarrow [(\text{CH}_2=\text{CH})_2\text{SO}_2] \rightarrow (\text{RNHCH}_2\text{CH}_2\text{SO}_2 + 2\text{RNH}_2\text{Cl}).
\]

Fungicides that can participate in true substitution reactions include dichlone, chloranil, Dyrene, pentachloronitrobenzene, captan, phaltan, 1-fluoro-2,4-dinitrobenzene (FDNB), nitrochlorobenzenes and naphtalenes, and compounds with allylic halogen (Burchfield and Schuldt, 1958). They differ enormously in stability towards hydrolysis and reactivity with various metabolites. Yet their over-all reactions are very similar, as exemplified by the combination of a para-substituted nitrobenzene with an amine:

\[
\text{O}_2\text{N} + \text{Y} + \text{R} + \text{NH}_2 \rightarrow \text{O}_2\text{N} - \text{NH} - \text{R} + \text{HY} \text{ or } \text{H}^+\text{Y}^-
\]

In this example, NO₂ is the activating group and Y the reactive group. Usually it is customary to think of Y as a halogen atom as in FDNB, Dyrene, and similar compounds. This shortsightedness may result in many missed opportunities in the field of pesticides, for purely chemical studies have shown that Y can be groups such as —NO₂, —SO₃H, —N(CH₃)₃⁺, —S(CH₃)₂⁺, —O₂⁺NO₂, and —SO₂⁺. Thus the reactive group in the fungicide pentachloronitrobenzene (PCNB) and some related compounds is not one of the chlorine atoms as would commonly be supposed, but the nitro group (Betts et al., 1955).

Most of these compounds probably react with metabolic debris by one or the other of two basic mechanisms. These are: first order nucleo-
philic substitution ($S_{N_1}$) and second order nucleophilic substitution ($S_{N_2}$). In $S_{N_1}$ reactions the rate-controlling step is the ionization of a halogen atom or equivalent group to form a carbonium ion which then reacts with any nucleophile that happens to be handy. The kinetics are therefore first order, so that the rate of disappearance of the toxicant is independent of the concentration of metabolite. Thus a compound reacting by an $S_{N_1}$ mechanism will disappear from soil at constant rate under the same moisture, pH, and temperature conditions regardless of organic matter content. In $S_{N_2}$ reactions a transition complex is formed between the toxicant and metabolite, and the reaction is bimolecular. Therefore the persistence of toxicants which react by this mechanism will be dependent on the concentrations of nucleophilic compounds in soils, assuming of course that losses due to hydrolysis and microbial interactions are not rate-determining. The fungicides Dyrene and FDNB have been shown to react with metabolites by the $S_{N_1}$ mechanism (Burchfield and Storrs, 1956, 1957b). Often these reactions take place more rapidly than hydrolysis, so that theoretically at least they could play important roles in the depletion of some fungicides in soils. Thus the half-life of Dyrene in aqueous phosphate buffer at pH 7 is about 22 days, compared to 1 hour when 0.1% of the amino acid hydroxyproline is added. Other metabolites known to react rapidly with Dyrene and related $s$-triazines include tyrosine, nicotinic acid, $p$-aminobenzoic acid, and glutathione. Burchfield and Storrs (1956, 1957b) studied the reactions of $s$-triazine derivatives and FDNB with more than 60 metabolites, and found that apparent velocity coefficients varied by more than one-thousandfold, depending on the functional groups involved and their positions in the molecules.

Only the ionized groups of metabolites ($R—NH_3^+$, $R—S_2^-$, etc.) are known to participate in these reactions. The $R—NH_3^+$ and $RSH$ groups are either inert or react extremely slowly. Consequently, apparent reactivity depends on the ionization constants of the functional groups ($K$) and the hydrogen ion activity of the medium ($a_{H^+}$). Therefore the second order velocity constant for the reaction of a fungicide at initial molar concentration $a$ with the functional group of a metabolite at concentration $b$ is

$$k = \frac{2.303(K + a_{H^+})}{t(a - b)K} \cdot \log \frac{b(a - x)}{a(b - x)}$$

where $x$ is the amount of fungicide reacted at time $t$. The reactivities of metabolites with high pK values are therefore dependent on hydrogen ion activity, so that each unit increase in pH represents a tenfold increment in apparent reactivity up to about pH 8 to 10, depending on the
substrate. However, the reactivities of molecules with very low pK values, such as p-aminobenzoic acid and pyridine derivatives, are almost completely independent of pH increases above 6. Consequently in alkaline soils \( S_N \) and \( S_N^+ \) toxicants might react preferentially with aliphatic amines and phenols because of the high intrinsic reactivities of the \( R—NH_2 \) and \( \phi—O^- \) groups, whereas in soils at pH 5 to 6 they might react preferentially with aromatic amines and compounds related to the pyridine nucleotides because of the greater ionization of these groups under acid conditions. Therefore reaction specificity as well as over-all rate of disappearance of fungicide may be regulated by the pH of the soil.

3. Persistence in Soils

Pesticide residues in soils can be depleted by microbial dissimilation, hydrolysis, and chemical reactions with organic matter as well as by purely physical processes such as evaporation and leaching by water. Therefore, measurements of residual pesticide made by chemical or bio-assay methods indicate over-all rate of disappearance only, without providing any information on the fate of the toxicant. Nevertheless, it is possible to gain some insight into the various processes involved by storing treated soils in closed containers at constant temperature and moisture content to minimize some of the physical variables.

Under these conditions the half-life of captan at an initial concentration of 100 \( \mu \)g. of fungicide per gram of composted loam soil was about 3.5 days at 25° C., compared to a stability of only 2 to 3 hours when it was dissolved in aqueous phosphate buffer at pH 7.\(^2\) The greater stability\(^3\) of captan in soil than in water may arise from the fact that it was mixed with soil as solid particles which must dissolve in soil moisture before hydrolysis, uptake by soil microorganisms, or reactions with metabolic debris can take place. The solubility of captan in water is between 8 and 70 p.p.m., so that rates of solution and diffusion might be limiting factors in controlling breakdown rate. This speculation is given some support by the finding that all pesticides containing reactive halogen so far examined are more stable in dry than in moist soil.

In contrast to the behavior of captan, the half-life of Dyrene in moist soil is less than one day, compared to a half-life in aqueous buffer of about 22 days. Since it is about as soluble in water as captan (10 p.p.m. compared to 8–70 p.p.m.), factors other than hydrolysis and solution rate must play important roles in its depletion, for based on the

\(^2\) Burchfield, H. P. Unpublished data.

\(^3\) Hereafter the word "stability" refers to the time required for one half the pesticide to disappear.
soil stability—hydrolysis rate ratio established for captan—it should survive for a minimum of 2 years in soil. FDNB is more soluble in water (about 400 p.p.m.) than captan, and hydrolyzes in aqueous buffer at about the same rate as Dyrene. Yet its stability in moist loam soil is also less than a day. Therefore FDNB and Dyrene must be depleted by soil interactions other than hydrolysis, for they are much more stable than captan with respect to this property, but do not last as long in soil.

The higher stability of captan in soil may result from the fact that it does not react rapidly with compounds containing amino groups although it combines with thiols much faster than either Dyrene or FDNB. However, these latter groups are probably not found in soils in appreciable amounts, while amino groups are (Burchfield and Storrs, 1957b). Thus the selectivity of action of toxicants, their reaction mechanisms ($S_N$ or $S_{N\cdot}$), as well as their hydrolysis rates, may influence the length of time residues of fungicides will persist in soil.

The effects of environmental conditions on the stability of PRD (3,4-dichlorotetrahydrothiophene-1,1-dioxide) and related compounds were studied by Schuldt et al. (1957) using a colorimetric method which measures both PRD and its dehydrochlorination product 3-chloro-1,2-dihydrothiophene-1,1-dioxide (Burchfield and Schuldt, 1958). Persistence of residues as measured by total color developed was dependent on the initial concentration of nematocide and temperature. In moist soil in a closed jar at an initial concentration of 100 $\mu$g. of PRD per gram of soil the time required for one half the color-forming capacity of the residue to disappear was 20 days at 32° C., 45 days at 22° C. and 115 days at 10° C. This indicates a temperature coefficient ($Q_{10}$) greater than 2. PRD persisted in dry soil 3 times as long as in moist soil. After 53 days in moist soil at 22° C. the total residue was 2% at pH 8.3, 10% at pH 7.4, and 38% at pH 6.6. Therefore temperature, soil pH, and moisture content were all shown to be influential in governing the longevity of the residue.

Soil type is another important factor. Thus, Sund (1956) found that only 31% of the amount of aminotriazole added to muck soil could be recovered by immediate extraction, while 93% could be recovered from Duke sand. After 21 days the recovery from Duke sand dropped to 54%, while the amount extractable from muck was negligible. Sund pointed out that the base exchange capacity of the muck was 99 milliequivalents per 100 grams of soil, compared to only 3.6 milliequivalents for the sand, and suggested that poorer recovery from muck was caused by stronger sorption of the triazole by soil particles. This may be true in part, but it is also likely that chemical and microbiological degradation occurs more rapidly in soils with high organic matter, as witnessed by the finding that DDT had a residue of 25% after 8 years in muck, compared to 74% in
sandy soil (Thomas, 1957). Similar findings are reported by Young and Carroll (1951) who applied PCP (pentachlorophenol) formulated in a petroleum oil to soil at a rate of 15 lbs. active ingredient per acre. The half-life was about 10 to 20 days, with breakdown occurring fastest when the organic matter was high and the water content was close to the moisture equivalent of the soil.

Compounds containing sulfur, as well as those in which the principal substituent is halogen, undergo changes in aqueous solution and in soil. For example Vapam (sodium N-methyldithiocarbamate) is a water soluble fungicide and nematocide that becomes immobile in soils within 24 hours after application, either through sorption or chemical decomposition (Baines et al., 1957). However, it retains its toxicity to nematode larvae for 96 hours after application. In aqueous solution it yields methylisothiocyanate, which is volatile and only slightly soluble. Similarly, Torgeson et al. (1957) found that Mylone (3,5-dimethyltetrahydro-1,3,5,2H-thiadiazine-2-thione) hydrolyzed soon after it was applied to warm moist soil. Among the materials identified were methylisothiocyanate, formaldehyde, hydrogen sulfide, and methylamine. None of these materials when used alone at concentrations that might have evolved from the complete decomposition of Mylone was sufficiently fungicidal to inhibit Pythium sp. in soil. Either uptake of Mylone by fungi prior to hydrolysis or a recombination of its decomposition products into an active fungicide is indicated. Evidently methylisothiocyanate is not by itself sufficiently toxic to control soil-borne organisms.

About 90% of the amount of thiram (tetramethylthiuramdisulfide) added to sandy soil at a rate of 50 p.p.m. disappeared within 5 days as indicated by bioassay with Glomerella cingulata (Richardson, 1954). Only a little over 20% remained after 1 day. Yet it was effective in preventing infection of seedlings in the treated soil for much longer times, probably by encouraging the growth of saprophytes antagonistic to the damping-off organisms, as mentioned previously. Thus for practical purposes the residual power of a pesticide may not always be directly proportional to the time it remains in soil. A truer measure is the time required for the parasite population to reestablish itself at its former level of inoculum potential. In some instances this may be related to the stability of the chemical in soil, but in others not.

In summary, pesticide residues in soils can be depleted by microbial action, hydrolysis, and chemical reaction, but in certain specific cases activation of biologically inert compounds can occur as well. The time required for toxicants to disappear from soils differs from a few days for captan and thiram to a number of years for chlorinated hydrocarbon insecticides. Breakdown occurs most rapidly at high temperatures and
pH values and in wet soils rich in organic matter. It may occur through enzyme action or spontaneous reactions with the environment, including hydrolysis, oxidation, addition reactions, and substitution reactions of the $S_n^1$ and $S_n^2$ types. In some instances beneficial effects may persist after the toxicant has disappeared, a fact that may be very important in the pre-planting application of phytotoxic chemicals for the control of soil-infesting parasites of higher plants.

B. Physical Interactions

1. Distribution of Solids

Pesticides with low water solubilities and vapor pressures must be disced or plowed into soil to secure effective results below the surface level. However, compounds with higher water solubility can be broadcast or raked into the top few inches of soil in the expectation that they will be carried to greater depths by the infiltration of irrigation or rain water. The relation of solubility to penetration is shown by the finding that the herbicide monuron is carried to greater depths by an equivalent amount of rain than diuron, while fenuron is more mobile than either (Abel, 1957).

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} \\
\text{NH} & \quad \text{NH} \\
\text{CON(CH}_3\text{)}_2 & \quad \text{CON(CH}_3\text{)}_2 \\
\text{Diuron (40 p.p.m.)} & \quad \text{Monuron (230 p.p.m.)} \\
\end{align*}
\]

These compounds decrease in water solubility with increasing chlorine substitution in the benzene ring in the order: fenuron > monuron > diuron so that penetration improves with increasing solubility. This is not the only factor involved since diuron is more strongly sorbed by soils than monuron, a fact which would also impede its movement. Thus these two properties reinforce each other, high solubility being coupled with low sorptivity, and low solubility with high sorptivity.

If a compound is soluble enough in water and not too highly sorbed by soil, it can be carried to considerable depths by rain, irrigation, or water used during application. Often very large amounts of water are required. Thus Baines et al. (1957) found it necessary to apply Vapam in basins of water 6 to 12 inches deep to control nematodes and fungi to a depth of 4 ft. Other procedures such as injection, injection followed
by row treatment, or row application of Vapam dissolved in water were ineffectual at this depth.

Schuldt et al. (1957) found that the experimental nematocide PRD (3,4-dichlorotetrahydrothiophene-1,1-dioxide) initially moved downward in soil with rain in a zone 3 to 4 inches thick, resembling the distribution of chemical compounds on chromatographic columns. Continued rain drove it still deeper. However, when the soil dried out, the chemical moved upward and was concentrated in the top inch. Presumably, as surface moisture evaporated, water in the lower levels of the soil was drawn to the surface by capillarity, carrying the chemical with it. This is somewhat analogous to the upward movement of chemicals in ascending chromatography. Renewed exposure to rain drove the chemical downward again. Thus, alternating periods of wet and dry weather moved the zone of maximum PRD concentration up and down in the soil. However, the zone gradually widened, so eventually the PRD was distributed more uniformly vertically. In field applications made in the fall, PRD followed this pattern, irrespective of whether it was broadcast or worked into the top 3 to 6 inches. The chemical penetrated to a depth of 15 inches after a total of 6 inches of rain, and about 50% of it was recovered after 178 days in soil at pH 5.

Mobility by means of soil moisture movement is important in the distribution of some compounds, but it seems to occur comparatively rarely. Thus, Newhall (1958) found that only 4 fungicides out of 36 tested were effective against *Fusarium oxysporum cubense* at a depth of 7 inches when they were applied to the surface and attempts made to move them downward by drenching with water. Presumably, this is because most organic fungicides are relatively insoluble in this medium. However, since one-ninth of the materials tested could move through soil to this extent, the search for solid fungicides and nematocides that can be applied by broadcasting should not be abandoned.

2. Diffusion of Fumigants

Nematodes and soil-inhabiting fungi can be killed with compounds having fumigant action, such as EDB (ethylene dibromide) and Nemagon (1,2-dibromo-3-chloropropane). These materials are injected into soils at depths of 6 to 15 in. and spread considerable distances, both vertically and laterally, by diffusion. Some fumigants, such as methyl bromide and carbon disulfide, boil near room temperature, while others are much less volatile. Nemagon, for example, has a vapor pressure of only 0.8 mm. of Hg at 21° C. (Ichikawa et al., 1955). The behavior of such materials must differ somewhat from what would be expected of an ideal gas. Nevertheless their steady-state movement through soils...
in the vapor phase can be described by Fick's first law, which states that

\[ \frac{dm}{dt} = -D_0 \frac{dc}{dx} \]  

(9)

where \( D_0 \) is the diffusion coefficient of the vapor and \( dm/dt \) is the rate at which it diffuses through a plane of unit area against a concentration gradient of \( dc/dx \). The movement of vapors through soils is complicated by many factors not associated with free diffusion, one of the most important of these being sorption by soil. However, by considering only steady-state diffusion this factor can be minimized, since the ratio of the concentration of chemical in the vapor phase to that bound by the soil will be constant. Nevertheless, diffusion takes place much more slowly in soils than in air.

Call (1957b) proposes that the apparent diffusion coefficient of a compound in soil is related to its value in air by

\[ D = (S - S') \frac{D_0}{k} \]  

(10)

where \( S \) is the total porosity of the soil, \( S' \) is the fraction of pores that are blocked, and \( k \) is the average tortuosity of the pores.

The tortuosity factor takes into account the fact that the pores in soils through which vapors diffuse are unlikely to be straight, so that a gas must travel a longer distance to reach any given destination than it would in air.

Call (1957b) studied the steady-state diffusion of EBD in various soils having different porosities, and confirmed that the relation between \( D/D_0 \) and \( S \) was linear. This led directly to values of 0.1 for \( S' \) and 1.5 for \( k \). Thus, the distance the vapor had to travel appeared to be about 50% longer than in air, and about 10% of the pores in the soils were blocked off, so that the vapor diffusing into them reached dead-ends. Observed diffusion coefficients in soils varied from 1 to 20% of the value found in air, the higher figure, of course, being for the most porous soil.

These findings support the earlier conclusion of Hanson and Nex (1953) that porosity, or total air space, is the most important single factor governing the movement of EDB in soil. They found that high moisture content increased packing, which in turn decreased diffusion rate. Also, movement of the chemical was slower in compact clay loams than in loose sandy loams. Biological control is also usually poorer in heavy soils than in light soils. This may arise in part from higher sorption of the chemical at soil interfaces, but it appears that failure to diffuse into regions of high inoculum potential may be the predominant reason.
The capacity of fumigants to diffuse rapidly through light sandy soils may be an important factor in achieving biological control, but high mobility may also be detrimental since the loss of chemicals by evaporation at soil surfaces may also be high. Several days after rain the porosities of soils down to 6 or 9 in. are 50 to 100% greater than below this depth, owing to evaporation from the surface and/or drainage to lower levels. Fumigants applied in such soils would move upward rather than downward and would be lost by evaporation into the atmosphere. Concentrations of fumigants near the surface layers of soils are always lower than in the interior for this reason. Consequently, biological control in the top few inches of soil is very poor. This might be improved by using nonvolatile toxicants such as PRD in combination with fumigants, since the former compound is known to move upward in soil and become concentrated in the top few inches during periods of dry weather (Schuldt et al., 1957).

Water seals are used to reduce the escape of volatile compounds such as methyl bromide and chloropicrin from soils. Baines et al. (1956) obtained increased kills of citrus nematodes with Nemagon (b.p. 196° C.) in loam soils at depths of 6 to 8 ft. by irrigating 5 to 9 days after treatment with enough water to penetrate to the 8- or 9-foot level. However, no benefit accrued by wetting the top 6 to 8 inches of soil, which should have been sufficient to block the upward movement of vapor. Thus it appears that the large amounts of water used in these experiments may have carried the fumigant down to great depths with it rather than functioning as a seal.

The movement and distribution of fumigants in soil under uniform conditions of moisture and bulk density has most recently been studied by Call (1957c). He treated soils at field capacity with 1 ml. of EDB at a depth of 6 inches, and measured fumigant concentration in the vapor phase at various times and distances from the point of injection. The compound diffused laterally so that a maximum concentration of approximately 20 μg. of EDB per milliliter of air was reached at the end of one day at a point 2 inches away from the site of application. Thereafter the concentration of toxicant at this point diminished. Four inches away from the injection point maximum concentration was reached in 2 days, but it was only 25% as great as was attained at 2 inches. Thus a peak concentration of fumigant traveled through the soil, but it was rapidly damped out by sorption and dispersion over an expanding spherical frontier.

The fumigant diffused vertically in the same manner at a slightly slower rate, but it appeared to travel upward further than downward. This result does not agree with earlier observations that heavy vapors
tend to move downward in soil because they are more dense than air. In field experiments the EDB distribution reported by Call (1957c) might be anticipated because of the lower porosity of soil at great depths, but in his experiments the free air space should have been the same throughout unless a porosity gradient developed in his soil through compaction by its own weight. In any event it appears that gravitational effects are negligible, compared with changes in soil porosities at various distances and directions from the site of application.

Thus fumigants can move away from an injection point in all directions by a modified diffusion process. However, horizontal diffusion takes place more rapidly than vertical diffusion. Consequently, the geometrical solid encompassing the maximum lethal range reached by the toxicant approximates an oblate spheroid with its shortest axis in a vertical position, but its bottom is slightly flattened.

3. Sorption of Fumigants

Chemicals can be bound to soils by adsorption at various interfaces, and to a smaller degree through dissolving in free water and organic matter. Hence the purposely vague term “sorption” is used to describe the over-all effect. The quantitative aspects of the binding of monomolecular films to solid surface are predicted adequately by the Langmuir equation. However, multimolecular films are often formed which cannot be treated in this way. In such cases skewed S-shaped isotherms are obtained when the amount of adsorbate bound to the solid is plotted against the equilibrium concentration of the compound in the vapor phase. These data are described mathematically by the Brunauer-Emmett-Teller isotherm, which states that the weight of fumigant adsorbed \( W \) at pressure \( P \) is

\[
W = \frac{W_m CP/P_o}{1 - P/P_o} \left[ 1 - (n + 1)(P/P_o)^n + n(P/P_o)^{n+1} \right] \tag{11}
\]

where \( W_m \) is the weight of a single monolayer, \( P_o \) is the saturation pressure, \( C \) is a constant related to the heat of adsorption and heat of liquefaction of the vapor, and \( n \) is the maximum number of layers that can be built up on the surface.

Jurinak (1957) fitted the data obtained during studies on the adsorption of Nemagon by a series of oven-dried montmorillonitic clays to this equation and found that the best straight line for each soil over the greatest \( P/P_o \) range was obtained when \( n = 4 \), indicating that the sorbed film of fumigant can reach a maximum thickness of 4 molecules. On soils containing predominantly kaolin or illite clay minerals the isotherms can be reproduced by the equation up to a \( P/P_o \) of 0.6, but \( n \) assumes
a value of infinity. This indicates adsorption on a free surface so that
at the saturation pressure of the gas an infinite number of layers can be
built up on the adsorbant. However, the physical significance of these
values is questionable since it is now generally agreed that the theo­
retical basis of the Brunauer-Emmett-Teller equation is unsound, even
though it is a convenient empirical method for the evaluation of sorption
data (Jacobs and Tompkins, 1955).

When the sorption isotherms for the montmorillonitic series were
corrected for the specific surface of each soil, all of the points fell on
the same line, showing total surface area to be the principal factor other
than those discussed above, such as chemical reaction, diffusion, etc.,
governing the binding of Nemagon by dry soils. Similar results were
obtained with the kaolinitic group, but the corrected isotherms for the
two clay types differed appreciably. The sorptive capacity of a dry soil
containing 35% organic matter was relatively low when compared to
most mineral soils. Jurinak (1957) pointed out that this is of special
interest since more fumigant is usually required to obtain control of
soil organisms in organic soils than in mineral soils. However, as will
be seen later, this picture changes entirely in soils at field capacity.

The mechanism of binding of fumigants to soils has been studied by
Call (1957d), who found that sorption of ethylene dibromide by most
soils was highest when the relative humidity of the air in equilibrium
with the soils was zero. The isotherms were skewed S-shaped curves,
indicating at least qualitative adherence to the Brunauer-Emmett-Teller
equation. However, when the relative humidity of the air in equilibrium
with the soil was increased to 5 or 10%, sorption of EDB decreased
sharply, showing that water molecules were competing with fumigant
molecules for sites on the surfaces of soil particles. About 6 to 40
molecules of water were required to displace each fumigant molecule,
depending on soil type. However, when the relative humidity of the air
was between 10 and 20%, and the soils contained just enough water to
form monolayers on all the particles, about 6 water molecules were
required to replace each fumigant molecule regardless of soil type.

Evidently, different mechanisms of sorption are possible, depending
on moisture relations in soil. In very dry soils multilayers of fumigant are
probably formed at the surfaces of clay particles. When water is intro­
duced into the system, fumigant molecules are displaced. However, all
of them do not escape into the vapor phase, since calculations made
from surface energy values using the Gibbs equation (Call, 1957d) show
that 1.6 $\mu$g. of EDB per square meter can be accumulated at air-water
interfaces at an equilibrium vapor phase concentration of 1 $\mu$g. of fumi­
gant per milliliter of air. Moreover, EDB and probably other fumigants
can be bound at soil-water interfaces, since soils completely covered by water can still sorb chemicals. True solution of EDB in soil water would not be important until the sorbed moisture films attained sufficient thickness to have the properties of bulk water. This probably occurs to some extent at field capacity. However, measurements made on such soils show that they bind from 2 to 3 times more EDB than can be accounted for by solution of the chemical in water, even assuming that all the moisture in the soil is present as free water. Thus, fumigants can be sorbed in a variety of ways depending on soil composition and moisture content.

The interactions of EDB with montmorillonites are of special interest since, unlike other clays, these minerals sorb more chemical in equilibrium with air at 5 to 20% relative humidity than when dry. This occurs because adjacent sheets of the dry mineral are spaced about 9.5 Å apart, which is sufficient to admit water molecules, but excludes EDB. When the surrounding air contains moisture, water molecules diffuse into the free spaces and expand the crystal lattices—or, in ordinary terminology, the clays swell. Molecules of EDB can then diffuse into the roomier lattices, and compete with water molecules for the newly exposed receptor sites. Thus, water leads the way and the EDB follows. This free ride does not last forever, for when the relative humidity of the air reaches 30%, competition by water molecules for sites in the soil becomes too strenuous and the amount of bound chemical decreases.

However, in all other cases studied, the presence of moisture decreased the amount of fumigant sorbed. Thus, it may seem paradoxical to find that the amount of EDB bound by a series of 20 soils at field capacity increased with increasing moisture content (Call, 1957a). For example, a sandy soil at 10% moisture had a sorption coefficient only one-tenth that of peat soil at 75% moisture. Although water desorbs EDB, the capacity of a soil to hold water is evidently a measure of its capacity for retaining EDB.

Sorptive capacity also increased with increases in specific surface, clay, and organic matter. Variance analysis showed that moisture content alone accounted for 91% of the information, while the 4 parameters taken together accounted for 96%. Correlation of sorption coefficients with clay content was poorest. A soil with a clay content of 46% and an organic content of 4.6% had a sorption coefficient of only 31, compared to a value of 103 obtained on a soil containing 42% clay and 36.5 organic matter. Thus, while clay content and specific surface are the principle factors regulating the sorptive capacities of dry soils (Jurinak, 1957), content of organic matter is critical at field capacity. Presumably soils rich in organic matter contain more extensive networks of water films
on which fumigants can be sorbed, for otherwise higher moisture content alone would decrease the amount of fumigant sorbed, as observed for all individual soils and clays with the exception of the montmorillonites.

The proportion of fumigant in the air space of soil is actually very small, varying from 0.28% of the total amount of EDB in peat soil to 3.4% in a sandy soil with a low content of clay and organic matter. Sorption is greater at low than at high temperatures, the ratio of the coefficient at 15°C to the coefficient at 20°C being about 1.32 for soils of all types (Call, 1957d).

It is clear that the sorption of fumigants by soils must play an important role in their performance by regulating distance and rate of diffusion, availability to the parasites, and the longevity of residues. More work on determining vapor pressures, diffusion coefficients, and sorptivities of individual chemical compounds, as well as on the physicochemical properties of various soil types, seems a promising goal for future research.

C. Treatment of Seed

1. Seed Protection

The protection of seed and seedlings from soil pathogens with chemicals is not complicated by the host of problems associated with other soil treatments for one overriding reason. The chemical is applied to the seed in massive doses and often stuck to it with stickers. Thus the fungicide occupies a strongly fortified position within a microenvironment of the soil rather than being dissipated throughout it. Furthermore it need not travel anywhere, either by diffusion or the haphazard movement of soil moisture. Consequently compounds such as thiram, captan, and dichlone, which are poor to fair soil fungicides, are among the best seed treatments available commercially. As shown previously, these compounds have very poor residual properties when distributed uniformly in organic soils. It is not known whether their comparatively high success as seed protectants results from their capacity to persist in soils for a longer time when concentrated at seed-soil interfaces or whether they kill most of the pathogens in the microsphere surrounding the seed very soon after application. In either event the use of organic compounds as seed treatments has met with far more rapid acceptance than their use as soil fungicides or as fumigants.

Particle size, which is very important in the protection of foliage surfaces, has only secondary influences on the performance of seed
treatments because of the comparatively large doses that are used (Burchfield and McNew, 1950). Thus, pea seed treated with 10 μ (radius) particles of dichlone at a rate of 0.12% by weight would contain $2.5 \times 10^4$ fungicide particles per cm.$^2$ of surface. By contrast only 600 particles of dichlone per cm.$^2$ of leaf area were required to obtain 95% control of tomato early blight when the particle radius was 8.4 μ. Since most, if not all, seed treatments are ground to powders with mean radii much less than 10 μ, it is evident that inadequate coverage of the seed surface should not be an important consideration in failure to control diseases. This surmise was confirmed by some experiments in which pea seed was treated with a series of 4 dichlone formulations having average radii of 2.3 to 9.5 μ (Burchfield and McNew, 1950). No significant differences in per cent emergence of seedlings could be detected 10 days after the seed were planted in infested soil. In a similar series of experiments with chloranil some lack of control was experienced with very large particles (35 μ), but this may have been caused by failure of the dust to adhere to the seed. It is probable that the particle size of seed protectants should be fairly small to secure good adhesion or good suspendibility, if a slurry method of application is used. However, if too small, the fungicide may be vulnerable to attack by deteriorating influences in the soil.

Seed treatment is not without its problems, however, for compounds must be formulated to give optimum performance in application equipment, while injury to seed or seedlings by the chemical may often be a factor limiting usefulness. Chemicals which are highly toxic to seed will usually be eliminated in screening. However, chemicals can perform satisfactorily in some locations and cause damage in others. Thus chloranil is an outstanding treatment for legume seed, particularly peas and beans. In addition to being effective against most soil-inhabiting fungi it is safe on many crop seed, and otherwise has some very desirable properties. It is nonirritating to humans and has a lubricating effect on seed somewhat like graphite. This latter property facilitates the flow of seed through the cups of grain drills, and thus eliminates much of the seed injury caused by other treatments. However, it is unsatisfactory for the treatment of spinach and beet seed when they are planted in alkaline soils of mineral origin, although excellent results were secured on peat soils. Presumably, chloranil hydrolyzes in alkaline media to yield water-soluble phytotoxic compounds such as chloranilic acid (McNew and Burchfield, 1951). Thus, interactions with the environment can lead to serious problems in the protection of seed with chemicals.
2. Seed Disinfection

Cereal seed are enclosed in husks or fruit coats. Some fungi which attack these crops can penetrate the husks and overwinter as mycelia inside them. When the seed are planted, the mycelia become active and attack the young seedlings. Seed protectants, such as thiram and captan, cannot permeate the husks, so volatile fumigants, such as organic mercury compounds, must be used for disinfection. Although they act as fumigants, their vapor pressures are very low, being of the order of $10^{-5}$ mm. of Hg. They are applied to seed as dusts or liquids. The amounts used are as small as 0.2 ml. per 100 grams of seed, so that uniform distribution is critical. Lindström (1958) recently studied the action of mercurials and concludes that coverage occurs in two steps: distribution on the seed in the treating equipment and redistribution by evaporation and resorption of the compound. In this latter process the chemical tends to leave locations where it is abundant and be resorbed where it is scarce, so that in time uniform coverage is achieved. Lindström (1958) believes that two kinetic processes are involved in the movement of mercurials, namely, evaporation rate and diffusion rate, and of the two he considers diffusion to be the slower or rate-controlling step. He found the distribution of Panogen [cyano(methylmercuri)guanidine] to be satisfactory 2 hours after mixing. There was a further small improvement at increased storage time, but the gain was of no practical importance.

Distribution of a nonvolatile placebo dressing labeled with Th$^{204}$ was surprisingly good when used at a rate of 0.2 ml. per gram of seed, but even so, Lindström concludes that redistribution of mercurial fungicides by evaporation and resorption improves the uniformity of the deposits obtained initially and may compensate in part for poor mixing. Even more important is his finding that the ratio of $\beta$ to $\gamma$ radiation emitted from Hg$^{203}$ labeled Panogen decreased from about 90 on a nonpermeable surface to about 30 to 50 on seed. This suggests that much of the weak $\beta$ radiation emitted by the mercury was not detected because the fungicide was located behind a barrier which absorbed the softer $\beta$ rays while the hard $\gamma$ rays were not absorbed. Lindström presents data which suggest that the reduction in $\beta/\gamma$ ratio is about what would be expected if the barrier were 100 $\mu$ thick. This corresponds roughly to the thickness of the fruit coats of wheat kernels. Additional evidence for this will be required, but it appears that one more of the important physical problems of plant pathology is near solution.

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