

Factors  
Affecting  
Pesticide  
Behavior  
and  
Breakdown

# Factors Affecting Pesticide Behavior and Breakdown

## FORMULATIONS

Pesticides, whether purchased for agricultural or homeowner use, contain two groups of chemicals. The first group is the active ingredient(s) and the second is the inert or inactive ingredients. The combination of active and inactive ingredients is known as the pesticide formulation.

The active ingredient(s) is that part of the formulation designed to control the target pest. Some “inert ingredients” are also poisonous but their purpose and function in the formulation is to enhance application and effectiveness of the active ingredient(s). They are chemicals such as petroleum solvents, emulsifiers which allow the active ingredient to be mixed in water, wetting agents that aid wettable powders to “wet” in the sprayer tank and the target pest, and ultraviolet (UV) light-blocking chemicals that increase persistence of the active ingredient.

The various formulations allow the pesticide chemical to be applied by different means (sprays, dusts, granules) to achieve specific results. Many active ingredients are used in a variety of formulations and at various concentrations.

■ Emulsifiable concentrate formulations have the active ingredient dissolved in an organic solvent because they have very low solubility in water. Emulsifying chemicals are added to enable mixing with water (resulting in the “milky” solution). Wetting agents, UV light blockers and various other chemicals may be added to perform specific functions. Similar kinds of formulations, from the standpoint that they are applied through a sprayer, are water soluble granules (WSG) or water dispersible granules (WDG), sprayable (S) and flowable (F) formulations. These are all mixed with water or some other carrier (e.g. special oils, diesel fuel, nitrogen fertilizer) and applied as sprays.

■ Microencapsulation is a technique whereby the active ingredient is encapsulated as microscopic droplets (about the size of pollen grains) in a nylon-like material. Microencapsulation reduces dermal toxicity and extends residual time because the amount of active ingredient is limited at any given time to that found on the surface of each droplet. The active ingredient moves through the capsule in response to a concentration gradient (lower at the surface). Microencapsulated products are formulated as emulsifiable concentrates in all other respects.

■ Wettable powders are formulations in which the active ingredient is not dissolved in petroleum solvents but rather is very finely ground and diluted with a powder such as talcum or other inert powders. Wetting agents are added to the formulation to aid in mixing the powder with water so it can be applied through a sprayer. Wettable powders must be continuously agitated in the spray tank because they are not in solution or emulsion, but rather are held in suspension through agitation.

■ Dust formulations are similar to wettable powders except they are applied as a dry dust. In Kansas commercial agriculture, dust for-

mulations are rarely used anymore. They are still used to some degree by the residential pest control industry and in an array of homeowner products (shaker cans).

■ Aerosols are usually in a pressurized container. By pushing the valve nozzle, a very fine-droplet mist or aerosol is shot into the surrounding air or onto a target surface.

■ Fumigants are chemicals that are highly volatile. Some fumigants are kept as liquids under pressure. When released they go directly into the true gaseous state. Other fumigants are formulated as dry tablets or pellets which, upon exposure to moisture in the air, chemically react to produce highly toxic gases. Fumigants are not fine droplets like an aerosol, but are, in fact, true gases.

■ Granular formulations are made by placing the active ingredient on a core material such as clay, sand or ground corncob. The core material imparts various qualities (e.g. flowability, dust, release rates) to the formulation. These granular formulations are applied as purchased, i.e. dry. In contrast, water dispersible granules have a granular form but they are mixed with water similarly to wettable powders. From the standpoint of the hazardous dust associated with dry formulations, granular formulations are generally safer for the applicator than dusts and wettable powders.

■ Baits are specialized formulations in which the active ingredient is placed on/in an attractant material (e.g. apple pomace, corncobs, bran) depending on the target pest. The material can be dried and ground, pelletized or extruded as appropriate for the pest and application method.

■ A unique formulation incorporates the active ingredient in plastic resin strips. Examples include the pest strip and livestock ear tag. The release rate of the active ingredient can be precisely controlled by the density (or hardness) of the resin strip or tag. The active ingredient moves to the surface of the strip/tag in response to the concentration gradient (lower on the surface).

In summary, pesticides are “formulated” in many ways, each with its own characteristics, to meet a wide array of pest control conditions/needs, application methods, applicator/environmental safety, handling/storage conditions, and actual pesticidal characteristics.

Pesticide behavior is important because all pesticides are poisons, deliberately introduced into the environment. To maintain minimal nontarget exposure, chemical and physical behavior of pesticides must be taken into account. The following terms and illustrations are meant to provoke thought and understanding of some aspects of pesticide behavior.

## TERMS, ILLUSTRATIONS

### HALF LIFE

Half life is an estimate of the time it takes for half of a known amount of pesticide active ingredient to break down. Half lives are determined under highly controlled laboratory conditions where factors such as temperature, moisture (humidity), light, and pH are held constant. The time it takes for the pesticide (by weight) to be broken down is called the "half life." For example, if a pesticide has a half life of 1 week, the amount remaining would be 50 percent 1 week after application; 25 percent after 2 weeks, and 12.5 percent after 3 weeks, etc.

In Figure 1, the amount of chemical remaining is shown on the vertical (Y) axis, with time increasing along the X axis. Chemical "A" has a laboratory half life of 4 weeks, chemical "B" has 2 weeks and "C" has 1 week.

In actual use conditions, half life is only useful as a reference point. In other words, half life, *in practical sense, is* variable depending on the interaction of such field factors as temperature, moisture, light, microorganisms, soil pH and others.

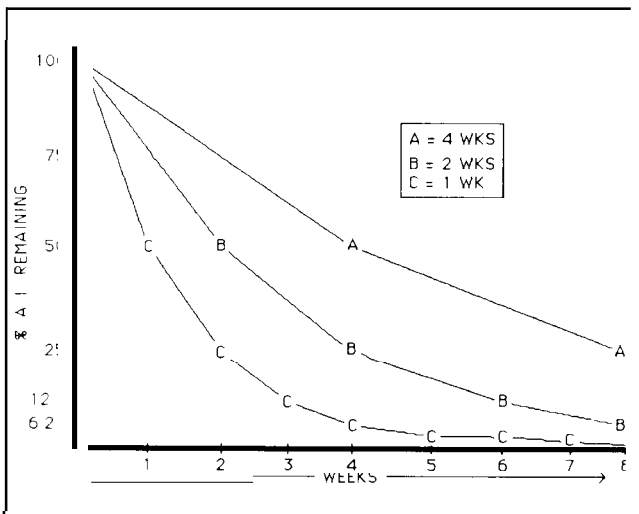


Figure 1

### PERSISTENCE

Persistence is the inherent stability of the chemical or pesticide. Another term for persistence is "residual time"—how long it effectively lasts. As represented in Figure 2, two pesticides are applied at the same time, at one pound AI per acre (100 percent) and, for example, say that at 0.25 pound per acre or less, they are no longer effective in controlling the pest. Based on this, it's obvious that chemical A was more persistent (residual) with 6 weeks of control, and chemical B persisted 3 weeks. This illustrates the persistence (or residual time) of these two chemicals under identical conditions of temperature, moisture and light.

Let's look at Figure 2 in a different vein. Let's say that both lines represent the *same chemical* applied under different light (Lt), moisture (Me) and temperature (To) conditions. Again, less than 0.25 pound per acre is ineffective for pest control. Under existing levels

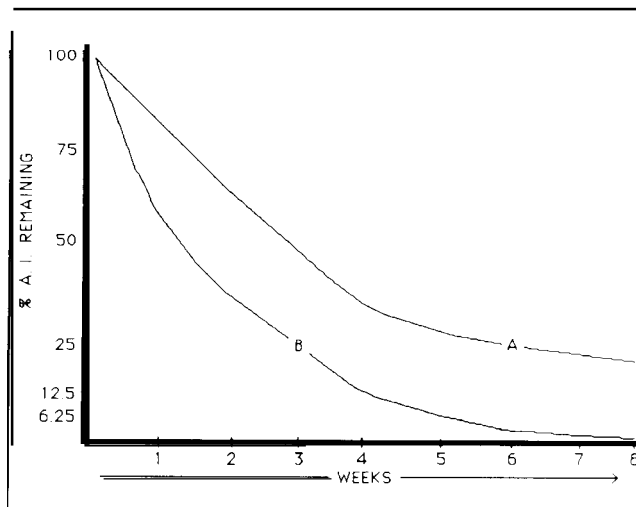


Figure 2

of Lt, Mo or T<sup>o</sup>, curve A represents a 6-week residual time. Now; consider that curve B represents a second application of the chemical later in the season when the factors of Lt, Mo or T<sup>o</sup> are even more favorable for breakdown. The result is only 3 weeks of residual time. Thus persistence, like half life, is variable under field-use conditions.

NOTE: There is a detectable amount of active ingredient that is less than the lowest level required for effective control. In the previous example, curve "B" provided 3 weeks of residual control. However, though declining, it is still detectable for at least 8 weeks (curve "A" lasts even longer). These "post-control residues" (e.g. weeks 4 and 5) may affect subsequent crops and are referred to as "carry over."

In the past, even lower residues, i.e., weeks 6 to 8, were often undetectable and so were of little or no concern. Today, analytical procedures allowing detection in parts per billion (ppb) are common and parts per trillion (ppt) are available for some chemicals.

At this time, nobody knows what effect, if any, these extremely tiny amounts exert on biological systems over long periods of time. In other words, the chemist's ability to detect a chemical has far outstripped the biologist's ability to determine the biological or environmental significance.

### DEGRADATION

Degradation is the active ingredient breakdown process. It is strictly a chemical breakdown as illustrated in Figure 3 by the diazinon, carbaryl and malathion molecules. In chemical degradation, for purposes of illustration, the methyl group (CH<sub>3</sub>) at the top of the diazinon molecule has been replaced, in the degraded state, by a hydrogen (H) atom (as seen to the right).

In the case of carbaryl, the oxygen (O) atom in the side chain has been replaced by a couple of hydrogen atoms and in the case of malathion, one of the oxygen atoms has been replaced by a sulfur (S) atom.

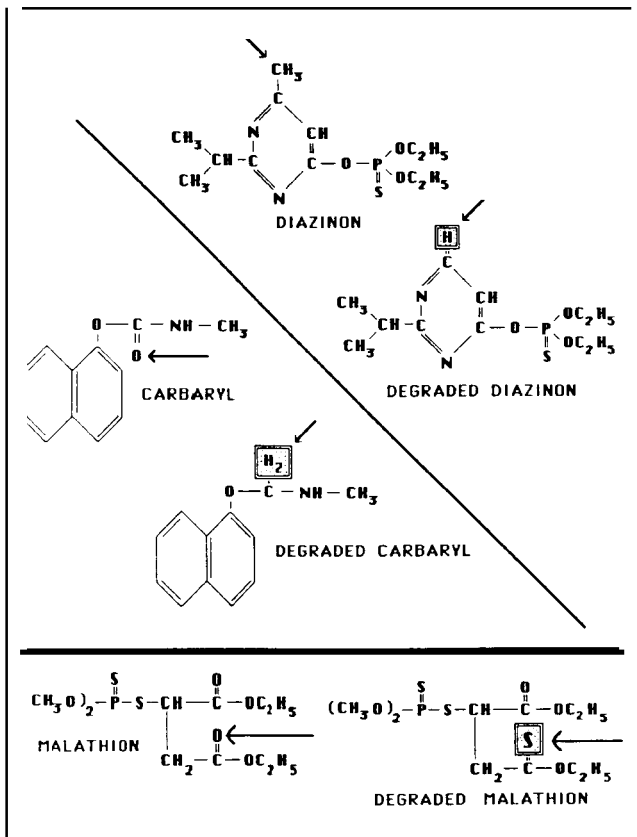


Figure 3

This form of degradation is strictly a chemical reaction between the pesticide active ingredient and the various chemicals in the soil or on the leaf surface or wherever the pesticide happens to be the time the degradation is taking place. The rate of chemical degradation is governed largely by temperature, that is, for every 10°C rise in temperature the chemical reaction rate will double.

The importance of chemical degradation is that the faster the pesticide compound degrades, the less time it is available for pest control, leaching, adverse environmental effects, etc. Note in some cases the breakdown product(s) can be more toxic than the original active ingredient. Therefore, when the U.S. Environmental Protection Agency registers any pesticide product, they must also be concerned about the degradation products of the active ingredient.

### DEACTIVATION

Some deactivation occurs when some of the pesticide adheres so tightly to a soil clay particle, organic matter in the soil, the leaf surface or some other compound in the environment that it is no longer biologically available. As illustrated in Figure 4, the benefin (*Balan*), glyphosate (*Roundup*), diazinon and carbofuran (*Furadan*) molecules remain intact but they are partially bound to clay particles or organic matter in the soil so that too little pesticide is available to kill or adversely affect the target pest. For example, a root hair growing in soil where the glyphosate is bound to the clay may not be affected by the glyphosate molecule. Similarly, diazinon may be bound extremely tightly to the organic matter and not kill a white grub or wireworm moving through the soil where the diazinon is located.

If a soil sample containing deactivated chemicals is taken into the laboratory for analysis, the amount of pesticide present, say four, five or ten parts per million, maybe *chemically detected* in the soil sample even though, from a *biological standpoint*, it does not control the target pest.

From the standpoint of leaching into the groundwater, it is apparent that if the pesticide is so tightly bound to the soil particles that it is biologically inactive, it will not be inclined to leach or otherwise move through the soil. On the other hand, should there be soil erosion, a deactivated chemical held to the soil particle will move off site with soil sediments. At any time, conditions may change, allowing the pesticide to be released from the soil particle. If it does not degrade upon release, it may exert its pesticidal activity. This example illustrates the difference between degradation and deactivation.

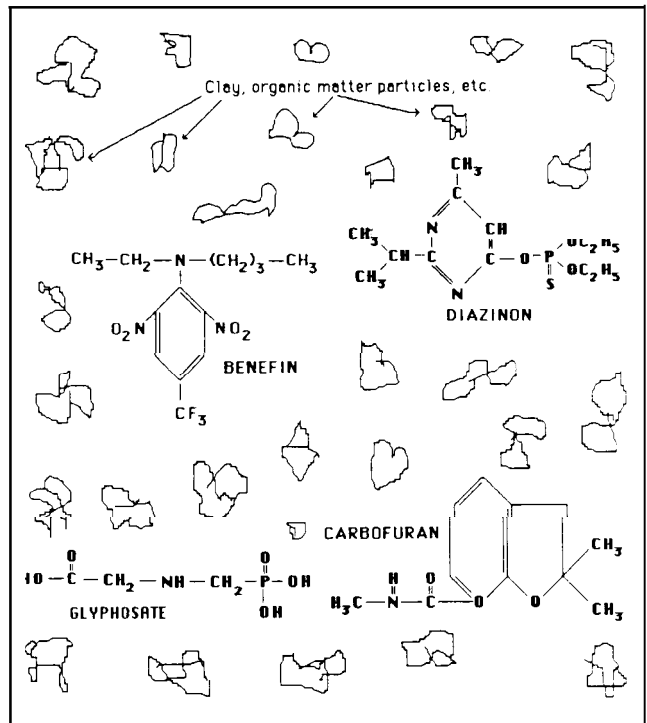


Figure 4

### VOLATILITY

Volatility is the ability of a chemical to form (change to) a true gas from a liquid or solid state. Fumigants are highly volatile pesticides that depend on volatility as the method of dispersal (in a confined area).

In many cases, when a pesticide volatilizes it breaks down into one or more decomposition products. Thus, these gases are not the active ingredient, but rather are the gaseous form of the chemical breakdown products. Thus, in a gaseous or volatilized form, the "pesticide" is no longer toxic. In other cases, however, as exemplified by 2,4-D, the gaseous or volatilized form remains toxic and injury symptoms may be seen downwind from the actual point of application.

As with the other types of chemical behavior (or breakdown), volatilization is important from the standpoint of the length of time the active ingredient is present in the environment in a toxic form. Volatilization can change the chemical into a non-toxic form or it can remain toxic. In either case, it has a great degree of mobility either in the air or through the soil.

## PHOTODECOMPOSITION

Ultraviolet (UV) light is a very high source of energy, and it promotes the breakdown of many chemicals. Most of the pesticides we use today are somewhat subject to photodecomposition. Some pesticide formulations contain UV light blockers that lessen the amount of photodecomposition of the pesticide active ingredient. Figure 5, using carbaryl to illustrate the concept, shows that the bond to the methyl group is broken by UV light, which results in the chemical being broken down into a non-toxic product. Using the example of diazinon, the phosphorous-to-oxygen bond may be broken, resulting in the breakdown of the diazinon active ingredient. Similarly, when permethrin, malathion, carbofuran and other pesticides are broken down by light it is principally due to UV light.

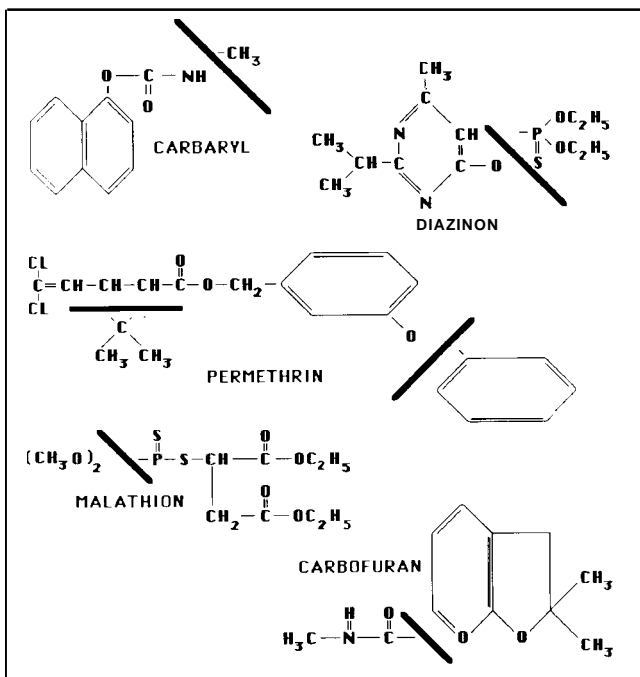


Figure 5

Obviously, chemicals applied to leaf surfaces or the soil surface are subject to rather intense UV light. One way to break down *excessive* amounts of certain pesticides in the soil (due to spills or over application) is to plow or disc the soil two or three times during the summer to allow new soil and chemical to be brought to the surface and exposed to the high temperatures and light conditions which can photodecompose it.

Ultraviolet light is an extremely destructive source of energy and plays a very important role in terms of the persistence of pesticides which are exposed to it. Some pesticides are packaged in brown-colored glass. This cuts out the light and thereby stops the photodecomposition of the pesticide ingredient while it is on the shelf.

## HYDROLYSIS

Hydrolysis is the combination of a water molecule with another molecule that results in the splitting of the larger molecule. Hydrolysis, in combination with photodecomposition, is often involved in the

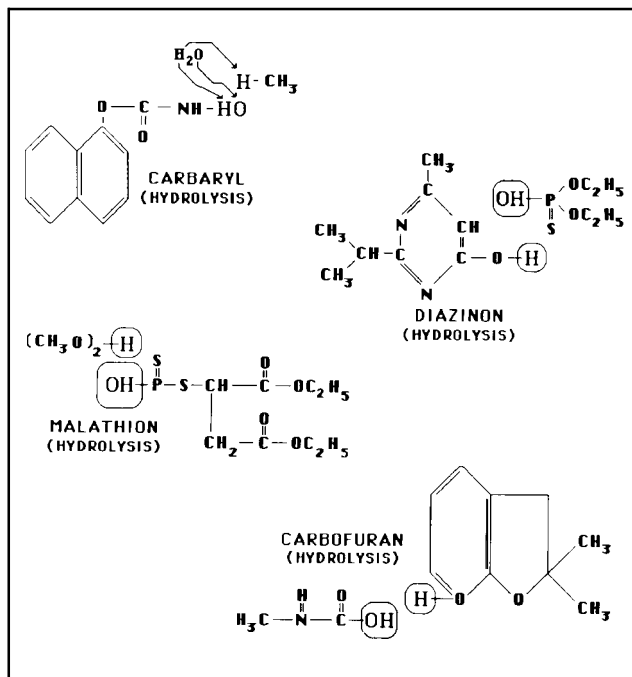


Figure 6

breakdown of various pesticide active ingredients. In Figure 6, the water molecule ( $H_2O$ ) provides one hydrogen atom that can be combined with the methyl group ( $CH_3$ ) and the hydroxyl ( $OH$ ) part of the water molecule combines with the nitrogen atom and carbaryl, in this example, has been hydrolyzed into an inactive chemical with the release of methane gas. Similar examples appear in Figure 6 for diazinon, malathion and carbofuran.

Hydrolysis can take place in the bottle, bucket, drum, paper bag, or other container before the pesticide is ever applied. Once the container seal is broken, moisture in the air moves in and out of the container with each atmospheric pressure change, and the small amount of moisture (water vapor) in the air combines with the active ingredients in the container. When this occurs, the shelf life of that particular product is reduced.

Hydrolysis is an important mechanism in pesticide breakdown. The faster the hydrolysis reaction takes place, the less time the pesticide is available in the environment for pesticidal activity, leaching or other movement.

## TEMPERATURE

Temperature is another very significant factor in the breakdown of pesticides. As Figure 7 shows, temperature can be divided into two categories: 1) above the soil surface and 2) below the soil surface. Above the soil surface, the air temperature is highly variable, fluctuating radically, but in general, it increases with height above the soil surface. For every  $10^\circ C$  rise in temperature, the chemical reaction rate doubles. Thus, if a pesticide is applied close to the soil surface vs. the top of a crop canopy, the rate of chemical breakdown may increase up through the canopy due to higher temperatures at the top.

Below the soil surface, the soil temperature drops at a rather steady rate. For every  $10^\circ C$  drop in temperature, the chemical reaction rate is cut in half. As the pesticide moves further below the soil surface,

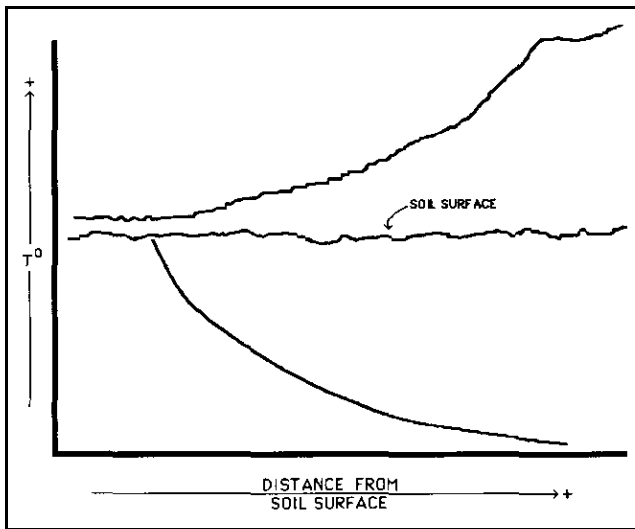


Figure 7

the temperature is cooler, slowing chemical breakdown reaction to the extent it is dependent on temperature.

Therefore, if a chemical gets below the root zone, the soil temperature (along with oxygen level and microbial activity) will often be such that breakdown will be relatively slow. This could lead to leaching to the groundwater. Leaching is more highly dependent on solubility in water and soil sorption than temperature.

### METABOLITES

Metabolites are the breakdown chemical products that result when a pesticide passes through a biological system. When a pesticide enters a bacterium, plant, horse, or person, stomach acids and enzymes break the pesticide down into decomposition products known as metabolites.

As Figure 8 shows, diazinon is broken down similarly to the chemical decomposition discussed earlier. In this case, the decomposition took place in a biological system, e.g. soil bacteria, and therefore the breakdown product is called a diazinon metabolize. The metabolites, in most cases, are non-toxic. It should be pointed out however, that in some cases the metabolites are more toxic than the parent compound. Similar examples are shown in the figure for carbaryl and malathion.

### pH

pH is a measure of the acidity of any substance, e.g. soil, leaf surface etc., where the pesticide may be applied, Indeed, pH of pesticide mixtures can be measured. pH affects pesticides in many ways. If a slightly acid pesticide is applied to a basic (alkaline) surface, for example a calcareous soil, the pesticide may break down more rapidly.

Similarly, slightly basic pesticides applied to an acidic soil or leaf surfaces will break down fairly quickly. A violent example of an acid/base reaction occurs by pouring vinegar (acid) into baking soda (base). Pesticide reactions in the soil or on the leaf surface are not so violent because the acids and bases are so weak, but the principle of breakdown or neutralization is the point. In some cases, buffering chemicals are included in pesticide formulations to help stabilize the pH and, in turn, reduce breakdown of the pesticide.

pH is also very important in solubility of some pesticide active ingredients. As illustrated in Figure 9, the soil pH is determined by a

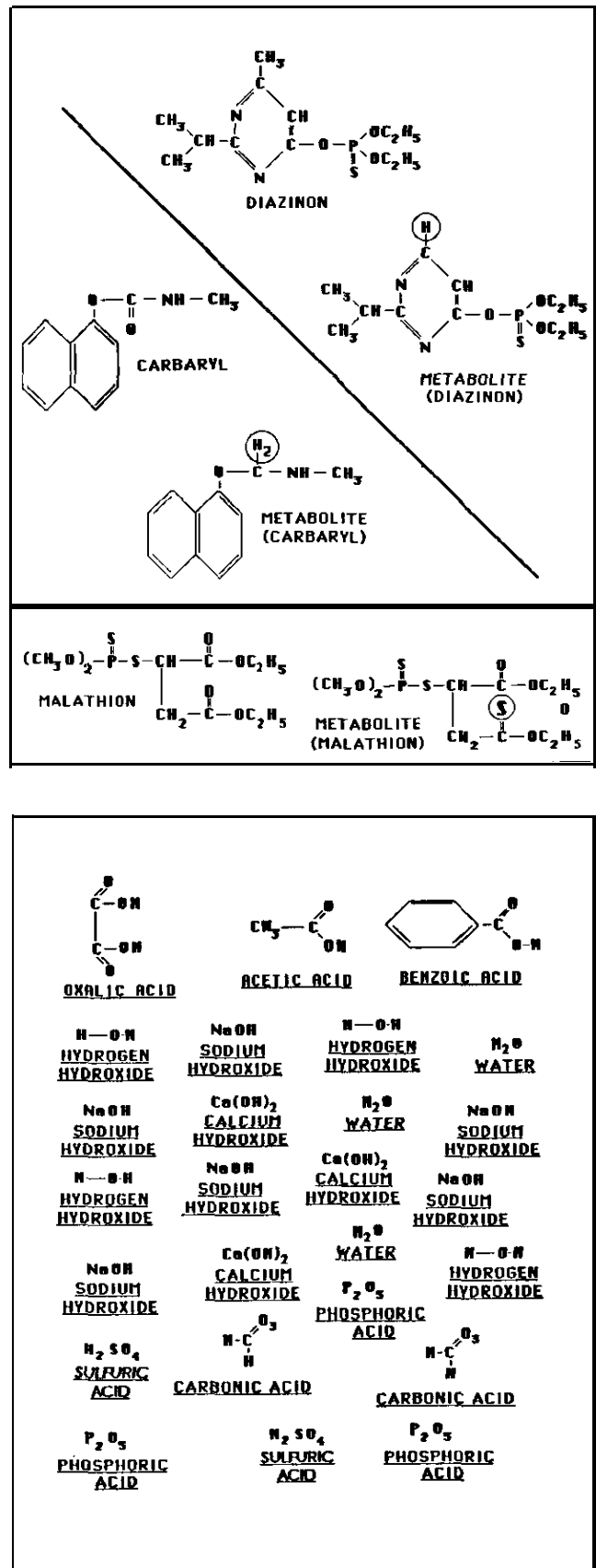


Figure 9

number of organic acids such as oxalic, acetic, benzoic and others. There are also various inorganic bases found in the soil as exemplified by sodium hydroxide, calcium hydroxide, hydrogen hydroxide (water), etc. In addition, there are various inorganic acids (shown at the bottom), e.g. sulfuric acid, phosphoric acid, and carbonic soil.

Soil is a mixture of all of these and many other chemicals, all of which react with each other to form a soil pH. If the pH of the soil is such that the pesticide is neutralized (broken down) relatively rapidly, the pesticide is unavailable for pesticidal activity or adverse environmental effects.

## SUMMARY

In many cases the designation of a half life is referred to in terms of how long a pesticide will last. As shown in Figure 10, one pesticide, A, is decomposing at the theoretical rate under controlled conditions. The other line indicates that pesticide B, under field conditions, decomposes rather rapidly, then levels out. It then breaks down rapidly again only to slow down and level out again. In fact, these two breakdown curves can indeed be the *same chemical* but under a different complex of factors.

Temperature, light, moisture, bacteria, pH, etc. all affect the pesticides in different ways and cause them to break down at varying rates. The point is, pesticide breakdown, thus half life, is dependent on many and varying factors when applied under normal use conditions. Some pesticides are more stable than others under the same conditions.

For this reason, half life is not a single number (5 days or 20 days, etc.). Half life should only be used as a guide to pesticide residual time.

The behavior of pesticides is dependent on many factors, all affecting the pesticide at the same time. The net result is that any given

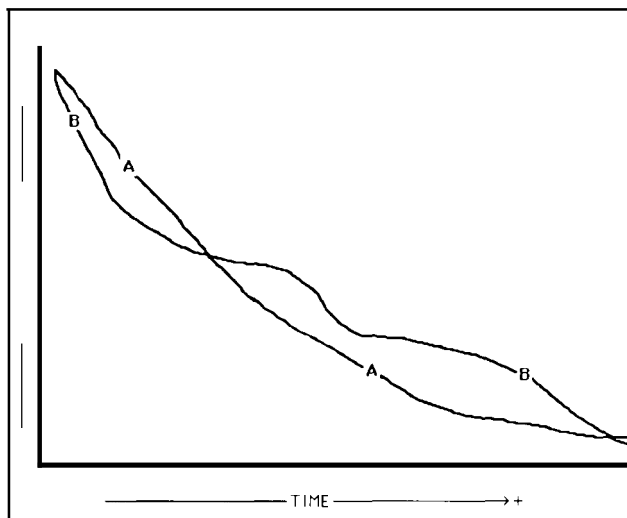


Figure 10

pesticide, under the various field situations, can last for short, intermediate or even a long period of time.

When applying any pesticide, it is important to recognize that all the factors (light, temperature, moisture, pH, bacteria, etc. ) will impact to a greater or lesser extent on the active ingredient. The breakdown rate affects the time the pesticide is available for pest control, off target movement, groundwater, surface water and other possible environmental contamination.

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