

## PESTICIDE-MICROBIAL INTERACTIONS IN SOIL

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### INTRODUCTION

Pesticides reach the soil environment by direct input for control of soil-dwelling pest species, and by several routes of indirect input. Examples of the indirect routes are: incidental application when spray drift or drip contacts the soil surface, incorporation into soil with plants or animals (or their wastes) that contain residues of pesticides, or through precipitation that is contaminated.

The fate of these chemicals in the soil is influenced by many factors, including biological, chemical, and physical determinants. The degradation and movement of pesticides are functions of their chemical structure and physical properties, environmental factors, as well as, abiotic and biotic components of the soil. Important physical properties include water solubility, volatility, and partition coefficient. Chemical properties that affect pesticide fate in soil include the reactivity and stability. Environmental factors of principal importance are moisture, temperature, and various management practices. Abiotic characteristics of the soil that figure prominently in determining the ultimate fate of pesticidal chemicals in the soil are the pH, percent organic matter, composition (sand, silt, and clay), and tilth. Some biotic factors in the soil that influence a compound's degradation and movement are microorganisms, invertebrates, vertebrates, plants, and soil enzymes. This paper will focus primarily on the interactions between pesticides and microorganisms, which play a highly significant role in the fate of the chemicals.

### ENHANCED MICROBIAL DEGRADATION

One special pesticide/microbe interaction that has come to light in the past decade is that called enhanced microbial degradation (EMD). It is defined as the phenomenon by which a pesticide is degraded more rapidly by populations of microorganisms which have been previously exposed to the pesticide. This adaptation may develop very slowly (years) or quite quickly, e.g. a single treatment of some soils with certain pesticides can condition the soil to rapid degradation of that compound. Not all soils are susceptible to developing an EMD capability, and not all pesticides are susceptible to the development of EMD. However, in cases where control of pests in the soil (insects, weeds, fungi) is required for a

period of weeks or months, considerable economic loss can be sustained if a product is only effective for a period of days. A book has recently been published reviewing this subject (1).

The problem occurs in many crop protection situations and can develop with certain insecticides, herbicides, and fungicides. Many questions remain unanswered regarding why the condition develops, how it can be prevented or predicted, and what corrective actions can be employed to remedy the situation. However, some basic questions regarding the specificity and mechanisms have been addressed, helping to delineate the properties of EMD and evaluate the potential for its prevention. It is basically a natural selection process, and it develops in a manner that parallels the development of pesticide resistance in pest species (insects, weeds, pathogens). Consequently, some of the questions asked and management strategies considered are also parallel to those associated with the development of resistance.

Specificity. Of utmost importance and great concern to crop producers is the question of the level of specific EMD that develops. If a microbial population has adapted a rapid degradation capability for one pesticide, can it also break down other pesticide molecules quickly? The concern over the cross-adaptation has been proven quite valid in some instances, while other cases show no tendency for cross-adaptation at all.

In cases where specificity was examined, carbamate insecticides often showed cross-adaptations, with carbofuran inducing rapid degradation of other carbamates (2-4). The extent of cross-over enhanced degradation depends on the structural similarity of the carbamate that conditions the soil to the one that is subsequently degraded more rapidly (5). Organophosphates showed no tendency for cross-adaptation when the specificity of enhanced degradation of isofenphos-conditioned soils and fonofos-conditioned soils were examined (6). Metabolites of soil-applied pesticides have also been shown to induce more rapid degradation of the parent molecule (7).

Mechanism. Repeated treatment with the same soil pesticide can condition the soil, depending on many factors. Bacteria that can utilize the pesticide or its degradation product have a selective advantage over other soil microorganisms, and they may flourish. Strains of soil bacteria have been isolated that can live on a pesticide (e.g., isofenphos) as a sole carbon source (8), or as a sole nitrogen source, e.g., carbofuran (9). Some pesticides do not undergo enhanced microbial degradation due to their toxicity, or toxicity of their degradation products, to bacteria (10). In addition to the nutrient role and toxicity factor, the bioavailability of the pesticide or its metabolites in the soil may also influence the development of EMD.

In most cases, EMD is a 2-step process, requiring an initial hydrolysis of the pesticide, followed by the utilization of at least one metabolite as a nutrient (Fig. 1). For some chemicals, e.g., chlorpyrifos, the hydrolysis step was rate-limiting, and the persistence of the parent molecule was not altered by a history of treatments, even though the dissipation of the hydrolysis product, a trichloropyridinol, was more rapid in the soils chemical treated in the past (11). In cases where Step 2 is rate-limiting, i.e., no fragment is of any nutritional value, there is no selective pressure toward the development of EMD. Only when both steps can be easily facilitated does the microbial population adapt to degrade a pesticide more rapidly.



Figure 1. Enhanced microbial degradation of some pesticides is a 2-step process.

Pesticide degradation products can be toxic to target species, enhancing or extending the efficacy. Likewise, they may enhance or extend the toxicity of a pesticide to non-target species, thus generating concerns over worker and consumer safety, as well as environmental quality. Toxicity of metabolites to soil or water microbes can also be important (e.g. EMD) to the environmental fate of a pesticide.

**Management.** Strategies that have been tried for remediation or prevention of EMD problems are numerous. Carbamate EMD and isofenphos EMD conditions were shown to persist for years after treatment stopped, but some other conditioned soils did not retain their enhanced degradation capabilities (1). Rotation of pesticides, especially of classes of pesticides, seems to be one tactic that slows the development of EMD. Extenders, chemicals that inhibit microbial growth, have been utilized in certain situations, but limitations do exist. The conditioned microbe population can sometimes overcome the extender by developing the capability to degrade it quickly as well. New chemistry entering the soil insecticide market includes some more persistent molecules, with 6-8 halogens present to impart greater resistance to degradation. More frequent or more specifically timed insecticide applications also are alternatives that may help overcome EMD problems.

## PESTICIDE DEGRADATION PRODUCTS

Although a pesticide may degrade in the soil, the total impact of the chemical may not be understood until more details are known: the degradation products formed, their toxicological significance if any, and their ultimate environmental fate. The transformations that occur in the soil may be the result of biological agents or chemical reactions.

The biotic components that are most prevalent are microorganisms, including bacteria, fungi, and actinomycetes. Under normal conditions, the microbes degrade pesticide molecules that they encounter via the co-metabolism process, i.e., biotransformations coincidental to their growth and reproduction. Some compounds are taken up by the microbes, then transformed, while others are degraded by extracellular enzymes secreted by the microorganisms. In certain circumstances, enhanced microbial degradation occurs, as already discussed, as a catabolic use of the pesticide molecule, if a bacterial strain can adapt to utilize it as an energy or nutrient source.

Chemical degradation reactions that occur most commonly in the soil are oxidations and hydrolyses. Reduction reactions also take place, usually under anaerobic conditions such as saturated or submerged soils. In general, most insecticides, herbicides, and fungicides are primarily degraded in soil via microbial processes. However, numerous exceptions can be noted for specific pesticides in certain soils and under a particular set of soil conditions

(e.g., moisture, temperature). Between the biotic and chemical degradative agents at work in the soil, many types of reactions occur. A review of the reactions has been published recently (12).

**Toxicological considerations.** The resultant degradation products have, in many cases, no obvious adverse effects on humans or the environment. In some cases, however, the pesticide transformation products retain toxicological significance, due to their impact, or potential impact, on organisms.

Organophosphorus insecticides applied to the soil were shown to degrade via several pathways, including oxidations, hydrolyses, and even reductions. The phosphoramidate isofenphos was oxidized to the oxon form (13) which retains toxicity against corn rootworm larvae (14). Two other oxidation products, as shown in Table 1, also have in vivo and in vitro toxicological significance to insects (14, 15). One hydrolysis product, isopropyl salicylate is toxic to bacteria, while the second one, salicylic acid, has no toxicity (17). The insecticide phorate also was converted to bioactive metabolites in the soil, specifically the sulfoxide and sulfone (19). The biological activity of those products, as well as other oxidized metabolites, is evident in Table 2. All six compounds are extremely toxic to rootworm larvae and to chickens. The oxon forms of phorate are not produced readily in the soil, but rather via an oxidative activation inside an organism.

Table 1. Toxicity of isofenphos and its metabolites (by 24-h topical bioassay) to adults and 3rd-instar larvae of the southern corn rootworm, *Diabrotica undecimpunctata howardi* Barber, and to the larvae in a 48-h soil bioassay (18).

Chemical	LD <sub>50</sub> (μg/g)		Soil LC <sub>50</sub> (ppm)
	Adults	Larvae	Larvae
isofenphos	2.4	5.9	0.3
isofenphos oxon	2.7	8.2	1.9
des-N-isopropyl isofenphos	1.7	6.1	1.2
des-N-isopropyl isofenphos oxon	1.8	6.3	> 10

**Persistence.** Many transformation products have relatively short half-lives in the environment, but some notable exceptions have caused problems historically. Among chlorinated hydrocarbons, the degradation of DDT to DDE results in a very long-lived residue, and oxidation of heptachlor generates the very stable molecule heptachlor epoxide. Some organophosphates also have breakdown products that persist long enough to be of concern toxicologically. Examples include des-bromoleptophos and the sulfones of phorate and terbufos. The sulfoxide and sulfone of the carbamate insecticide aldicarb are sometimes much more persistent than the parent compound.

**Mobility.** The degradation products of a pesticide, or any organic molecule, are in general, more mobile in the environment than is the parent material. Oxidation or

hydrolysis of a pesticide molecule commonly results in products that are more water soluble than the initial chemical. Movement of the oxidized or hydrolyzed molecules is therefore facilitated more readily, both through leaching and preferential flow downward through the soil profile and laterally in run-off during precipitation events. Soil characteristics also play a major role in determining the rates of leaching: soil pH, organic matter, clay content, cation exchange capacity, and water-holding capacity (22). While water solubility correlated with mobility of the pesticide and their degradation products on soil thin-layer chromatography plates, the partition coefficient ( $K_{ow}$ ) was a better predictor of rate of movement.

Table 2. Toxicity of phorate and its metabolites to southern corn rootworm larvae (by 24-h topical bioassay) (20) and to chickens (in acute oral toxicity tests) (21).

	Rootworm LD <sub>50</sub> ( $\mu$ g/g)	Chicken LD <sub>50</sub> (mg/kg)
phorate	3.5	1.02
-sulfoxide	3.1	0.3-0.6
-sulfone	4.2	1.73
-oxon	2.1	0.3-0.6
-oxon sulfoxide	3.3	0.3-0.6
-oxon sulfone	3.1	0.3-0.6

The binding of chemicals to soil retards or limits their movement, and it also restricts their bioavailability. This, in turn, governs their rates of biodegradation by microorganisms in the soil and their potential toxicity to organisms. In summary, the interactions between mobility/availability, persistence, and toxicity are multi-faceted and highly dependent on environmental factors.

**Significance.** Recent research on degradation products and new awareness of potential problems that could be caused by them have resulted in the following changes in the pesticide industry and in regulatory policy:

1. the development process for new pesticides will include more extensive toxicology and environmental fate testing,
2. management practices, such as no-till and ridge-till agriculture will be examined for their influence on pesticide fate, and
3. groundwater and surface water quality will be scrutinized more carefully.

## CONCLUSIONS

Environmental questions. The risks and benefits of pesticides in the future will need to be analyzed more fully with regard to the following factors:

1. degradation vs. persistence,
2. mobility/availability,
3. water quality, and
4. non-target species.

Currently, environmental questions are focused heavily on the potential mobility of pesticides toward groundwater sources. As a result, numerous new candidate pesticides with a high tendency to adsorb to soil are being developed and tested. These have low water solubility, often accompanied by considerable persistence. Polyhalogenated hydrocarbons (e. g., teflubenzuron, fenfluthrin, sulfluramid) are once again becoming factors in the pesticide market.

Regulatory concerns. As the questions arise more rapidly, the answers will probably still come slowly. Some of the complex pesticide issues that will demand increased attention are:

1. significance of residues,
2. health effects,
3. economic considerations, and
4. consumer uncertainty.

Driven by public opinion and the current knowledge of pesticide effects, regulatory agencies will continue to be situated in the difficult position of trying to make decisions based on limited data, using models, relatedness, and extrapolations.

Commercial implications. The pesticide industry will also face the following new challenges as it develops new products or re-examines fate and effects of old ones:

1. enhanced microbial degradation,
2. mobility,
3. degradation products,
4. costs of registration processes, and
5. alternative pesticides.

Driven by the profit motive, companies will find increased competition for markets that will not be expanding. It will also be necessary for them to keep abreast of the environmental and regulatory concerns mentioned above.

The landscape is changing rapidly, and it will continue to become only more complex in the future.

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