

Chapter 12

Interactions Between Pesticides and Their Major Degradation Products

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The interactions between parent pesticide compounds and their degradation product(s) can influence the fate of both pesticides and degradation products. The role of pesticide degradation products in influencing the persistence and degradation of parent compounds, and the enhanced degradation of degradation products are discussed. The significance of these interactions in crop protection is also addressed.

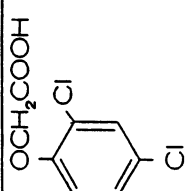
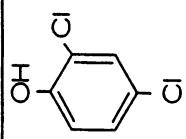
Pesticides applied to agricultural lands are degraded through biological, chemical, and physical mechanisms (1). Some pesticides have very low persistence levels, resulting in rapid transformation to degradation products. For example, 50% of applied terbufos was oxidized to its sulfoxide within three days of application (2). More than 90% of applied metham-sodium was transformed to methyl isothiocyanate within 3 hrs (3). In the environmental matrices, parent compounds and their degradation products have been detected simultaneously. The interactions between pesticides and their degradation products could be synergistic, antagonistic, or additive. This paper focuses on the interactions between some of the commonly used pesticides and their major degradation products (Table I).

Degradation Products as Inducers of Pesticide Degradation

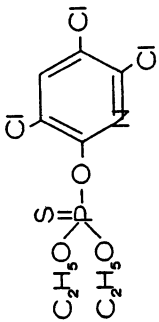
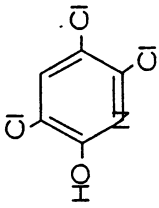
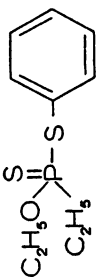
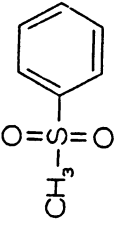
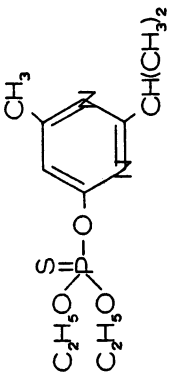
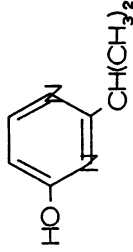
The failure of some soil-applied pesticides to control their target pests (4) has resulted in significant research on microbial adaptation to pesticides (5). The enhanced biodegradation of some pesticides has been attributed to the substrate value of their degradation products (6-8). Degradation products of pesticides belonging to different classes such as phenoxyacetic acids, carbamothioates, N-methyl carbamates, and organophosphates have been reported to condition soils for rapid degradation of their respective parent compounds (Table II).

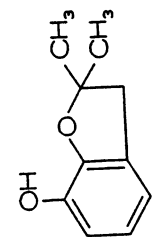
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Table I. Structures of Some Commonly Used Pesticides and their Degradation Products

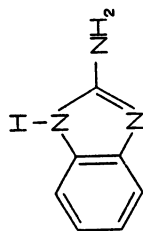
Pesticide	Structure	Degradation product	Structure
2,4-D		2,4-Dichlorophenol	
EPTC	$\text{C}_2\text{H}_5\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-N}\begin{matrix} \text{C}_3\text{H}_7 \\ \text{C}_3\text{H}_7 \end{matrix}$	EPTC sulfoxide	$\text{C}_2\text{H}_5\text{-}\overset{\text{O}}{\parallel}\text{S}\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-N}\begin{matrix} \text{C}_3\text{H}_7 \\ \text{C}_3\text{H}_7 \end{matrix}$
Butylate	$\text{C}_2\text{H}_5\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-N}\begin{matrix} \text{CH}_2\text{-CH}(\text{CH}_3)_2 \\ \text{CH}_2\text{-CH}(\text{CH}_3)_2 \end{matrix}$	Butylate sulfoxide	$\text{C}_2\text{H}_5\text{-}\overset{\text{O}}{\parallel}\text{S}\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-N}\begin{matrix} \text{CH}_2\text{-CH}(\text{CH}_3)_2 \\ \text{CH}_2\text{-CH}(\text{CH}_3)_2 \end{matrix}$
		Butylate sulfone	$\text{C}_2\text{H}_5\text{-}\overset{\text{O}}{\parallel}\text{S}\text{-}\overset{\text{O}}{\parallel}\text{S}\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-N}\begin{matrix} \text{CH}_2\text{-CH}(\text{CH}_3)_2 \\ \text{CH}_2\text{-CH}(\text{CH}_3)_2 \end{matrix}$

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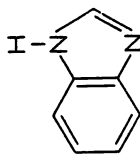
Pesticide	Structure	Degradation product	Structure
Chlorpyrifos		3, 5, 6 Trichloro-2-pyridinol	
Fonofos		Methyl phenyl sulfone	
Diazinon		2-Isopropyl-6-methyl-4-hydroxypyrimidine	



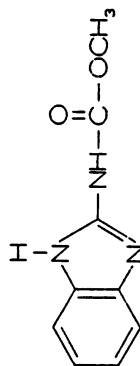
Carbofuran phenol



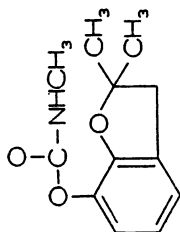
2-Aminobenzimidazole



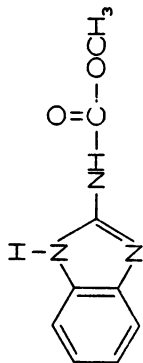
Benzimidazole



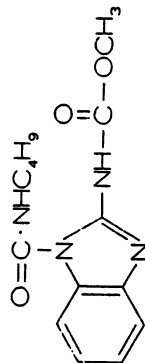
Carbendazim



Carbofuran



Carbendazim



Benomyl

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Pesticide	Structure	Degradation product	Structure
Diphenamid		Diphen M-1	
		Diphen M-2	
Metham-sodium	$\text{CH}_3\text{NH}\cdot\overset{\text{S}}{\parallel}\text{CS}-\text{Na}^+$	Methyl isothiocyanate	$\text{CH}_3-\text{N}=\text{C}=\text{S}$

Table II. Degradation products as inducers of pesticide degradation

Inducer/ substrate	Susceptible pesticide	Reference
Inducers of their respective parent compounds		
2,4-dichlorophenol	2,4-D	(8,9)
EPTC sulfoxide	EPTC	(10)
butylate sulfoxide	butylate	(10)
carbofuran phenol	carbofuran	(7)
1-naphthol	carbaryl	(7)
p-nitrophenol	parathion	(6,8,11)
salicylic acid	isofenphos	(8)
2-aminobenzimidazole	carbendazim	(12)
Inducers of degradation of other parent compounds		
butylate sulfoxide	EPTC	(10)
EPTC sulfoxide	butylate	(10)

Hydrolysis Products. Hydrolytic reactions seem to play an important role in the initiation of pesticide metabolism by adapted soil microorganisms (13,14). In several instances, the presence of pesticide hydrolysis products has resulted in induction of a pesticide degrading population of soil microorganisms (6,7). In one of the first studies on the biodegradation of pesticides, Newman and Thomas (9) observed decreased persistence of 2,4-D in soils pretreated with its hydrolysis metabolite, 2,4-dichlorophenol. In that study, pretreatment of soils with closely related compounds such as phenoxyacetic acid and 2-chlorophenol, however, had no effect on the persistence of 2,4-D. Steenson and Walker (15) reported the ability of an *Achromobacter* strain to use 2,4-dichlorophenol as a substrate. In a recent study in our laboratory, the mineralization rate of 2,4-D increased with the number of pretreatments with 2,4-dichlorophenol (8).

Fungicide carbendazim rapidly degraded in soils previously treated with its metabolite 2-aminobenzimidazole. (12,16) 2-Aminobenzimidazole and carbendazim were equally effective in conditioning the soil to carbendazim. Pretreatment of soils with another potential metabolite, benzimidazole, however, resulted in only a slight reduction in the parent compound's persistence. Benzimidazole rings are generally less susceptible to microbial degradation (17), and the benzimidazole-induced nonenhanced degradation of carbendazim (12) is not clearly understood.

Carbofuran phenol, a hydrolysis product of carbofuran, conditioned soils for enhanced degradation of carbofuran under anaerobic environment (7) but did not have any effect in aerobic conditions (8,18). Although the presence of carbofuran phenol in anaerobic soils accelerated carbofuran hydrolysis, the phenol was not used as an energy source and accumulated in the soil. This finding suggests that besides substrate value, other properties of

degradation products may be involved in the induction process. The different results obtained from aerobic and anaerobic soils reveal the importance of environmental factors in the interaction between pesticides and their degradation products.

Oxidation Products. The sulfoxides of EPTC and butylate induced enhanced degradation of their parent compounds, and the potential of the sulfoxides to promote rapid degradation of their parent compounds was similar to that of the parent compounds themselves (10). Although butylate sulfoxide conditioned the soils, pretreating soils with butylate sulfone did not have any effect on the rate of degradation of the parent compound.

Cross-enhancement. Degradation products can also enhance the degradation of pesticides other than their precursors. Prior exposure of soils to butylate sulfoxide accelerated the degradation of EPTC (10). Similarly, a higher butylate degradation rate was observed in soils exposed to EPTC sulfoxide. This type of cross-enhancement is generally limited to structurally similar pesticides. Location differences were also observed in cross-enhancement tests for EPTC and butylate degradation in soils pretreated with sulfoxides of EPTC or butylate, suggesting the role of soil properties in intensifying the enhancement (10).

Degradation Products as Promoters of Pesticide Persistence

Most of the available information on degradation products indicates their potential to accelerate the degradation of subsequently applied pesticides. Contrary to this, some degradation products could prolong the persistence of pesticides in soil.

Hydrolysis Products. Particularly when applied to the soil repeatedly, 3,5,6-trichloro-2-pyridinol (TCP), a hydrolysis metabolite of chlorpyrifos and trichlopyr, slowed the degradation of chlorpyrifos (8). At 100 ppm, TCP inhibited the degradation of carbofuran and DOWCO 429X in problem soils but did not have any effect at 1 and 10 ppm (19). Recent studies have demonstrated the antimicrobial activity of this metabolite (20,21); the inhibitory effect of TCP could be a result of its microbial toxicity. The levels required to affect the microbes, however, are so high that the effect of a single application of chlorpyrifos or trichlopyr may not be sufficient to produce a significant effect. In contrast, under field conditions, pesticides are not homogeneously distributed through soil but are concentrated in and around the particles of a granular formulation. This could result in a high concentration of the pesticide or metabolite in a particular microenvironment.

Cross-retardation. Fonofos, an organophosphorus insecticide, increased the persistence of EPTC in problem soils (22). Dietholate, an extender used in the new formulations of EPTC, is structurally very similar to fonofos. In laboratory toxicity studies, methyl phenyl sulfone (a metabolite of fonofos) was more toxic to *Photobacterium phosphoreum*, a bioluminescent bacterium phylogenetically related to several important soil bacteria, than

fonofos (20). The antimicrobial activity of fonofos (22) could result from the toxicity of its degradation product, methyl phenyl sulfone. The mechanism of the inhibitory effect of fonofos under field conditions has yet to be clearly elucidated, however.

Enhanced Degradation of Degradation Products

Repeated applications of some pesticides can also accelerate the degradation of the products formed (Table III). 2-Aminobenzimidazole rapidly dissipated in soils exposed to its parent, carbendazim, with only 6% remaining 4 days after application (16). In these soils, degradation of 2-aminobenzimidazole was faster than that of the parent. The rate of degradation of benzimidazole, a structurally similar metabolite, however, was not affected by carbendazim history. Carbendazim, also a fungitoxic hydrolysis product of benomyl, degraded more rapidly in soil with a benomyl history than in a soil without one (23). The half-life of carbendazim was reduced from 11 to 4 days in benomyl-treated soils. This reduction has been attributed to the short lag-period observed in these soils.

The degradation of desmethyl-diphenamid (diphen M-1), a monodemethylated metabolite of diphenamid, was much faster in soils pretreated with its parent compound than in an untreated soil (24). There was no difference in the degradation rate of Diphen M-2, a bidemethylated product of diphenamid, in soils with and without a diphenamid history. The rate of degradation of diphen M-2 was also much slower than for diphenamid or diphen M-1.

Repeated applications of metham-sodium enhanced its transformation rate to methyl isothiocyanate and subsequent mineralization of the pesticidal metabolite. The half-life of methyl isothiocyanate ranges from 0.5 to 50 days with the shorter half-life in soils previously treated with metham-sodium (3).

Laboratory studies have investigated the fate of degradation products as influenced by their prior treatment (8,12). The purpose of these studies was to confirm the substrate value of the degradation products. Self-enhancement of methyl isothiocyanate (3), 2-aminobenzimidazole (12), and 2,4-dichlorophenol (8) has been previously reported. The microbial adaptation to degradation products is significant, particularly when the pesticidal effect is caused by the degradation product.

Table III. Pesticide degradation products susceptible to enhanced degradation

Susceptible degradation product	Reference
2-aminobenzimidazole	(16)
carbendazim	(22)
methyl isothiocyanate	(3)
desmethyl-diphenamid	(24)

Conclusions

A better understanding of the mechanisms of pesticide-degradation product(s) interactions is important for studying the fate and the effects of pesticides in the environment. Synergistic interactions could result in inadequate host protection leading to restricted use or withdrawal of parent compound and thus influence the pesticide class to be used in subsequent applications. The information generated from such studies will help make effective use of existing biodegradable pesticides by promoting an understanding of the specificity and development of enhanced biodegradation.

Acknowledgements

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12. SOMASUNDARAM & COATS *Pesticide-Degradation Product Interaction* **171**

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