

## *Formation and Alteration of Mixtures by Biotic and Abiotic Processes in Soil*

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### ABSTRACT

Chemical mixtures are formed in soil either from single compounds or by alteration of mixtures. Physical environmental processes, such as volatilization and adsorption-desorption or uptake by biota, result in an alteration of the quantitative composition pattern of the mixture, or the complete removal of components. Chemical and biochemical processes also include total degradation (mineralization) and the formation of new compounds, either by biotic or abiotic conversion of single components, or by direct chemical reactions between two or more components. Examples are given for each kind of mixture alteration. The dependence of the behaviour of single components in these environmental processes upon their physical and chemical properties is discussed, as well as the influence of other mixture components on the behaviour of each component. Possible reasons for this altered behaviour are also presented. The applicability of methods, described in the literature for single compounds, to mixtures is discussed.

### 1 INTRODUCTION

Chemical mixtures are formed in soil either from single compounds by abiotic or biotic processes resulting in the additional formation of new compounds, or by alterations of mixtures, present as such in the soil, by various environmental processes. The biotic formation of mixtures from single compounds in the soil is the result of well-known microbial conversions, for which abundant literature including review articles is available (Alexander, 1981; Klein and Scheunert, 1978); the part abiotic reactions play in the transformation of chemicals in soil has been investigated much less since it is difficult to assess abiotic reactions separately from those mediated by enzymes and/or organisms. From the multitude of conversion processes reported for natural unsterilized soil, this chapter will present only one example, which will not be discussed in detail.

In fact, the emission of a single chemical into the soil is far less frequent than the emission of chemical mixtures. Pesticides applied intentionally to the soil are

chemical mixtures, either by their active ingredients which may be a complex mixture of isomers and chemicals with closely related molecular structures (toxaphene, technical BHC (lindane), chlordane, heptachlor, and endosulfan), by impurities (pentachlorophenol: Plimmer *et al.*, 1973; Rappe and Nilsson, 1972; pentachloronitrobenzene: Kotzias *et al.*, 1978; malathion: Fukuto, 1983; Turner and Corden, 1963), or by formulating agents.

## 2 FORMATION OF MIXTURES FROM SINGLE COMPOUNDS

The action of biotic or abiotic environmental factors upon a chemical normally results in the formation of a chemical mixture since the quantitative conversion of a single compound into a single second product under environmental conditions is extremely rare. Thus, a mixture of at least two compounds—the parent compound and one conversion product—is formed; the formation of multicomponent mixtures is much more frequent. Although by definition the toxicity of a metabolite mixture formed by an organism, to this organism, is the same as that of the parent chemical, the mixture released into the environment may differ significantly from those of the parent compound and have toxic effects on other organisms.

In soil, a multitude of biotic and abiotic factors act upon a chemical and convert it into a complex mixture; it is difficult to separate the components into those resulting from abiotic reactions and those resulting from biotic reactions. In Figure 1, the herbicide buturon is presented as an example (Haque *et al.*, 1977).

The methodology to determine the conversion of single chemicals into mixtures in soil has been described in numerous publications on the metabolism of foreign compounds in soil (e.g. Haque *et al.*, 1977). It is also included in review articles on biotransformation processes (Klein and Scheunert, 1978, 1985). It should be noted that by conventional analytical methods such as gas-liquid chromatography, only known and expected conversion products can be determined. The complete detection of all mixture components formed is possible only if the parent compound is  $^{14}\text{C}$ -labelled.  $^{14}\text{C}$  methodology is generally applicable only under controlled laboratory conditions (Kloskowski *et al.*, 1981); however, some examples have also been reported for studies in lysimeters under outdoor conditions (Haque *et al.*, 1977; Klein *et al.*, 1973). Although conversion rates in laboratory tests are not the same as those under field conditions, it has been shown that, in principle, an extrapolation of laboratory data to field situations is possible (Kloskowski *et al.*, 1981; Scheunert *et al.*, 1983).

## 3 ALTERATIONS OF MIXTURES BY PHYSICAL PROCESSES

Alterations in the composition pattern of chemical mixtures by physical processes occur primarily during transport between or within different phases of the environment. In soil, processes like volatilization, adsorption, desorption, mig-

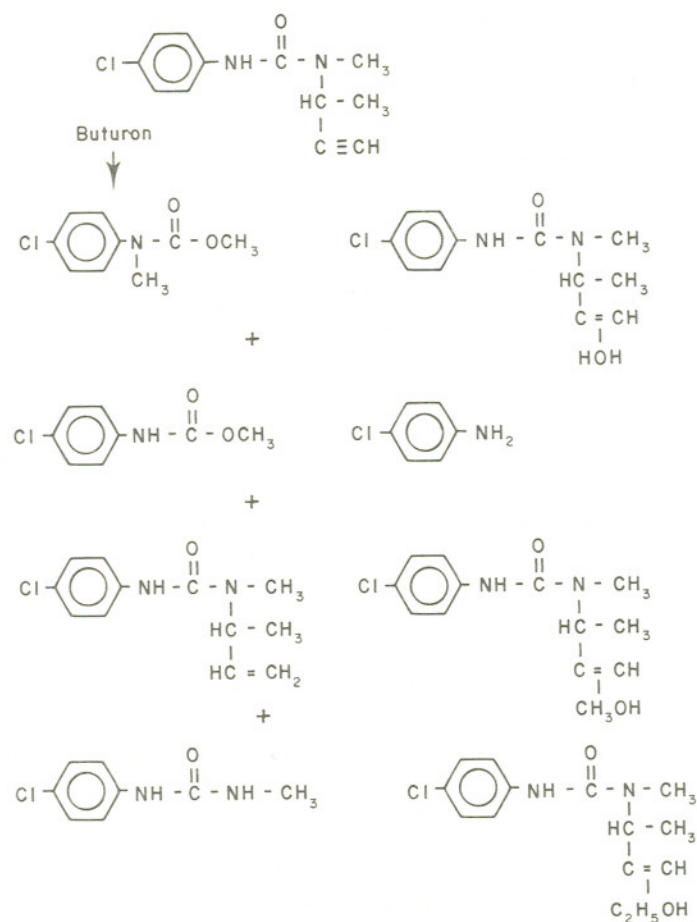


Figure 1 Formation of a chemical mixture from one single compound (buturon) in soil. (The exact positions of substituents after addition of HOH, CH<sub>3</sub>OH, or C<sub>2</sub>H<sub>5</sub>OH to the triple bond were not established.) From Haque *et al.* (1977). Reproduced by permission of Academic Press

ration in soil, and leaching from soil into water, or selective uptake of mixture components by biota, result in fractionation and separation of mixtures. After such a procedure, the qualitative composition of the mixture may be changed due to the disappearance of certain components, and the quantitative composition pattern of the mixture may also be quite different. Additionally, it must be recognized that the behaviour of a chemical in such an environmental process may differ for the chemical within a mixture from that of the isolated chemical. Mutual influences of one mixture component upon the other have to be included



during considerations of the alteration of mixtures by environmental physical processes; such influences will be discussed in detail for each environmental process considered in the following paragraphs.

### 3.1 Alterations by Volatilization

Volatilization processes from soil result in an accumulation of less volatile mixture components in soil and the appearance of volatile components in the atmosphere.

According to our present knowledge, volatilization of chemicals from the unsaturated zone of the soil proceeds via volatilization from the water phase rather than from the adsorbed state (Hamaker, 1972). Therefore, the mechanisms for the volatilization of chemicals from unsaturated soils should be similar to those for the volatilization from water, provided that adsorption-desorption coefficients in soil are taken into consideration. However, due to the much greater complexity of the moist soil system, information on interactions between components of mixtures is very limited.

Physicochemical properties relevant to volatilization of substances from water are vapour pressure, water solubility, and the diffusion coefficients in the liquid and gaseous components of soil as well as in the air, which in turn are related to molecular weight and molecular volume (Mackay and Leinonen, 1975; Reid *et al.*, 1977).

It should be noted that normally the volatilization of water and that of its different solutes at environmental temperatures are independent of each other; mutual influences on the evaporation rates occur only at temperatures near the boiling point, e.g. in the case of steam distillation (Spencer *et al.*, 1973). However, dependence of the volatility of one component of the mixture upon the other components at environmental temperatures has been demonstrated in some special cases. Although the mechanisms of such inhibitions are not known, one explanation could be that inhibiting substances affect in some way either diffusion of the volatilizing compounds, water solubility, vapour pressure, or several of these factors.

For the influence of a chemical on the water solubility of a second chemical that is hydrophobic, two mechanisms are discussed.

The first of these is solubilization of a pollutant by incorporation into micelles. A micelle consists of an aggregate of surface-active molecules (surfactants), each molecule possessing a hydrophobic chain and an ionizable hydrophilic group. The solubilization of a pollutant hydrocarbon is thought to occur by association of the hydrocarbon with the hydrophobic core of the micelle, or with the polar surface of the micelle, or both. A critical micellar concentration must be attained before solubilization of a pollutant is effected, and the concentrations of surface-active substances in natural soil water are generally far from sufficient to cause micelle formation (Bedding *et al.*, 1983; Harrison *et al.*, 1975). However, for atrazine it has been shown that volatilization from soil is enhanced by the

presence of 10 ppm of an anionic detergent (Hofmann, 1984; Scheunert and Korte, 1985). This phenomenon may be explained by an increase of the atrazine portion in the soil water as a result of the presence of the detergent.

The second mechanism is hydrotropy, the enhancement of the solubility of an organic compound as a result of the introduction of another organic compound or compounds not associated with colloid or micelle formation. In the case of polynuclear aromatic hydrocarbons, a wide variety of organic compounds can increase their apparent solubility in water. However, the concentrations in the soil liquid are likely to be too low to bring about the solubilization of contaminants (Bedding *et al.*, 1983).

For acidic or basic volatiles, the simultaneous presence of acids or bases affecting water pH results in a change of volatility half-life, since the ratio between non-ionic and ionic forms is changed and, consequently, also the water solubility and vapour pressure of the non-ionic-ionic compound mixture (Klöpffer *et al.*, 1982).

A number of calculation methods, models, laboratory test methods, and field tests have been reported to determine the volatility of chemicals, both surface-applied and incorporated, from dry and moist soils. An overview of test methods has been given recently (Scheunert and Klein, 1985). It should be mentioned that only those tests where the volatilized substances are trapped completely and, thus, are determined directly can give correct volatilization figures. The indirect determination based on concentration decline in the soil (e.g. Haque *et al.*, 1974) yields correct data on volatility only if other sources of concentration decline, such as photochemical or biological degradation or removal by leaching into deeper layers, can be excluded.

If these methods, which have all been developed for individual substances, are applied to mixtures, the suitability of experimental equipment, such as trapping devices and agents, for all mixture components must be ascertained. Potential interactions between the components thus are included in the determination, whereas theoretical methods rarely can predict them thus far.

### 3.2 Alterations by Adsorption-Desorption Processes

The fractionation of chemical mixtures by adsorption-desorption processes proceeds according to the adsorption coefficients of the components, which have been reported to depend on their water solubility and *n*-octanol-water partition coefficients (Briggs, 1981). However, the physical basis proposed for these assumptions is that adsorption of non-ionic organic compounds on soil organic matter is a 'partition' process between the aqueous phase and a hydrophobic surface; the evidence presented in the literature for the dominance of a partition mechanism is insufficient to prove its general applicability. For example, systems in which a distinct hydrophobic phase at the solid surface does not exist are shown to exhibit the uptake behaviour presumed to characterize partition.



Theoretically, as well as practically, surface uptake cannot be simply defined as 'adsorption' or 'partition', but rather there is a continuum of possible interactions starting with fixed site adsorption and ending with true partition between three-dimensional phases (Mingelgrin and Gerstl, 1983). Thus, potential influences of one mixture component on the adsorption coefficient of another component are hardly predictable at present. There may be influences on water solubility by mechanisms similar to those discussed in section 3.1; competition for adsorption sites is a phenomenon which may be closely related to changes in water solubility.

In terrestrial systems, adsorption-desorption processes play an important part in the migration of chemicals in soils and their run-off and leaching into groundwater and aquatic systems. Physical adsorption retards the mass flux which is a function of dispersion (diffusion and convection) and removal by biological and chemical reactions (Weber, 1972).

Mixtures of chemicals are separated in a chromatographic-like manner by the differences in mobility of the components, which is related to adsorption coefficients on the one hand and flow velocity and dispersion coefficients on the other hand (Bear, 1979). Figure 2 shows, as an example, the leaching behaviour of a chemical mixture formed in soil from the insecticide aldrin (Klein *et al.*, 1973; Moza *et al.*, 1972). This mixture is formed by chemical reactions and is fractionated by physical processes so that only one component of the mixture, dihydrochlordene dicarboxylic acid (which is very hydrophilic due to the two carboxyl groups), reaches the water at a depth of about 60 cm.

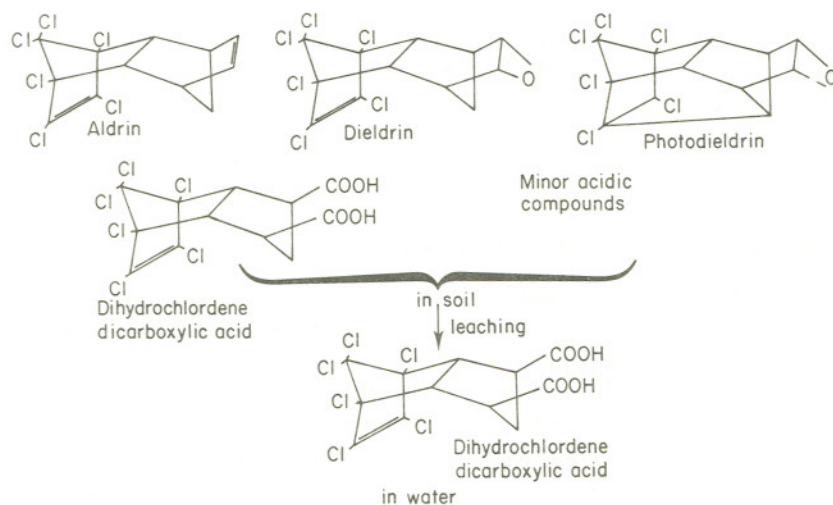


Figure 2 Selective leaching of one component of a chemical mixture formed from the insecticide aldrin in soil

It should be considered, however, that the presence of chemicals in leaching water is not predictable from physical properties and processes alone. A chemical compound reaches the water after passing through a soil column only if it is so stable that it is not degraded during the time span required to pass through the soil (e.g. it is not a carbon source that is readily usable by the soil microorganisms present at different zones in the soil). Thus, the composition of chemical mixtures in leaching water, groundwater, or well-water near solid waste landfills or rapid infiltration sites reflects both the mobility and chemical persistence of the components of the mixture (De Walle and Chian, 1981; Kotzias *et al.*, 1975; Tomson *et al.*, 1981). The same applies to water purified by river-bank filtration (Sontheimer, 1980).

Most of the information regarding mutual influences of one mixture component on the mobility of another is available on the effects of surfactants on pesticides. Koren (1972) reported that the addition of three surfactants (one non-ionic-anionic-cationic and two non-ionic) at a concentration of 2% of the spray volume increased both the depth of water penetration and the movement of the herbicides trifluralin and oryzalin into the soil. It was concluded that increased leaching was due to an effect of surfactants on the sorption-desorption balance rather than on improved penetration of water. Scheunert and Korte (1985) demonstrated an increase in the soil mobility and leaching of atrazine by an anionic detergent under outdoor conditions; the results were confirmed by laboratory tests (Hofmann, 1984). Studies by Bayer (1967) showed that the depth of leaching of the urea herbicide diuron in soil was altered by anionic, cationic, or non-ionic surfactants in different ways; the effects of two cationic surfactants on the leaching of linuron, monuron, neburon, and diuron may reflect a sorption complex of the substituted urea herbicide, surfactant, and the soil. This sorption appeared to be closely associated with the dilauryl portion of the surfactant molecule. From laboratory soil mobility studies, Singhal and Bansal (1978) concluded that a positive mobility effect is observed when the surfactant is adsorbed; however, if this is not the case because of the chemical nature of the surfactant or of a high concentration, the surfactant molecules presumably aggregate into micelles in which the pesticide becomes entrapped, resulting in a decrease in its mobility.

Test methods to determine adsorption coefficients in the laboratory have been reported for single chemicals. In the OECD Chemicals Testing Programme (1981), a screening adsorption-desorption test as well as an advanced test including the time-course of adsorption up to an equilibrium state, the plotting of adsorption isotherms, and the determination of mass balance, are recommended. This method, in principle, can also be applied to chemical mixtures if one keeps in mind the limitation of the method; volatile substances or substances which are biodegraded, hydrolysed, or irreversibly bound within the adsorption time of about 16 hours cannot be tested satisfactorily since the adsorption is determined indirectly by measuring the substances left in the aqueous phase.



If laboratory methods developed for the determination of mobility of individual chemicals in soil, such as column methods (e.g. Lambert *et al.*, 1965), liquid chromatography (McCall *et al.*, 1980), or soil thin-layer chromatography (Helling, 1971a-c), are used for chemical mixtures (Bayer, 1967; Koren, 1972; Singhal and Bansal, 1978), then the methods used must be regarded as appropriate for all mixture components. The same applies to field studies (La Fleur *et al.*, 1973). The use of  $^{14}\text{C}$ -labelled compounds is not possible in the field; however, such studies can be performed under field-like conditions in lysimeters. This method also ensures the detection of metabolites (Klein *et al.*, 1973; Moza *et al.*, 1972; Scheunert and Korte., 1985). As in the case of volatility measurements, interactions between the chemicals can be determined by experimental methods, but thus far they cannot be predicted by calculations.

### 3.3 Alterations by Selective Uptake by Organisms

Although toxic actions of mixtures and their components are not the subject of this paper, uptake by organisms is discussed because it is another way of physically altering chemical mixtures. Selective uptake of individual components of a mixture by terrestrial plants results in a mixture in the organisms with the respective components in an accumulated form.

Interactions between chemicals during uptake by plants have been reported. The absorption of the herbicide prometryne at  $1\ \mu\text{M}$  concentration in nutrient solution by bean plants was increased in the presence of 10, 1, or  $0.1\ \mu\text{M}$  of the insecticide phorate (Parks *et al.*, 1972). Such effects are not limited to experiments in hydroponic culture. Similar 'synergistic' ('synergistic' is used here in the sense of promoted uptake which does not necessarily imply toxic effects) effects were observed also when plants were grown in soil. Schulz *et al.* (1976) observed an enhanced uptake of  $^{14}\text{C}$  from the radiolabelled organophosphorus insecticide phorate from soil (2 ppm) by corn greens when 5 ppm of the herbicide Eptam (ethyl dipropylcarbamoate) were added to soil. The addition of Eptam antidote (Stauffer, R-25788) counteracted the effects of Eptam; thus, corn greens grown in  $^{14}\text{C}$ -phorate-treated soil also containing Eptam and its antidote took up similar amounts of  $^{14}\text{C}$  to those that had been treated with  $^{14}\text{C}$ -phorate alone. Since the radioactivity in plants consisted not of parent phorate but only of metabolites, it is supposed that the effect of Eptam on the uptake of phorate-derived residues was an effect on the formation of metabolites in soil or young seedlings.

'Antagonistic' effects have also been reported. The uptake of the radiolabelled herbicide bromacil by oats from nutrient solution was nearly double that of  $^{14}\text{C}$ -bromacil when combined with picloram (Sterrett *et al.*, 1972).

It seems plausible that surfactants that influence the adsorption processes of organic chemicals in soil also affect the uptake of chemicals by plants. Lichtenstein *et al.* (1967) reported that linear alkylbenzene sulphonate (50 ppm in



soil) did not affect the penetration of lindane or aldrin into roots and significantly reduced the amounts of parathion that penetrated the root system. On the other hand, Scheunert and Korte (1985) demonstrated an increase in the uptake of atrazine and its metabolites into maize plants when 10 ppm of dodecylbenzene sulphonate were present in soil. It is evident that—analogue to the effects in soils discussed above—plant uptake may be affected in both directions, depending on the chemical nature of surfactant and pesticide and on the concentrations.

Interactions between inorganic chemicals with respect to plant uptake have been reported also. Cataldo *et al.* (1978) reported an inhibition of the absorption of  $\text{Ni}^{2+}$  by soybean plants and its transfer from root to shoot by the presence of  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Co}^{2+}$ . Competition kinetic studies showed  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  to inhibit  $\text{Ni}^{2+}$  absorption competitively, suggesting that  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Zn}^{2+}$  are absorbed using the same carrier site. The mechanism of inhibition of  $\text{Ni}^{2+}$  in the presence of  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  was not resolved by classical kinetic relations.

The influence of salinity (sodium chloride) on the uptake of heavy metals by plants, including phytotoxic metals (Maas *et al.*, 1972), is either positive or negative depending on the plant species and concentration, and could play a role in the widely discussed problem of tree damage as a consequence of salt application on roads in winter; the positive influence of acids present in soil on toxic metal uptake (Lutz *et al.*, 1972) could contribute to the controversial discussions on acid precipitations and their potential adverse effects on forests.

Fertilizer-pesticide mixtures are not discussed in this paper because fertilizers in general are not regarded as unwanted foreign compounds in the environment. However, if fertilizers (e.g. nitrates) migrate through the soil into underlying aquifers, or are accumulated in food or feed plants, they may be regarded as undesired residues of agricultural chemicals. Thus, the increased occurrence of nitrate in plants under the influence of herbicides in soil should be mentioned here, although, because of the simultaneous increase in protein content, the effects of the herbicides have been interpreted in a positive way (Eastin and Davis, 1967; Gramlich and Davis, 1967; Hiranpradit *et al.*, 1972a, b; Kay, 1971; Ries and Wert, 1972).

In the methodology to assess the uptake of chemicals by plants some problems are involved, both if single compounds and if mixtures are studied. Plant uptake of non-ionic organic chemicals is a complex process which includes not only the normal root uptake into conduction channels but also uptake and transport through oil channel systems (for oil-containing plants; Hulpke and Schuphan, 1970), from vapour in the surrounding air (Harvey, 1974; Hulpke, 1970; Kloskowski, 1981; Nash, 1974; Nash and Beall, 1970), and through external contamination by soil or dust followed by dissolution in the waxes of the cuticle (Grimmer, 1979).

Results of experiments in nutrient solution (e.g. Maas *et al.*, 1972; Parks *et al.*, 1972; Ries and Wert, 1972) cannot be extrapolated quantitatively to the

environment since the influences of soil adsorption are not taken into consideration and the volatility of chemicals from aqueous solution and, thus, the uptake of chemical vapour by the plants are much higher than in the case of soil. Results of uptake experiments from sand or soil in small-scale laboratory tests (Lichtenstein *et al.*, 1967; Lutz *et al.*, 1972; Schulz *et al.*, 1976; Sterrett *et al.*, 1972) also have to be considered with caution for all chemicals, since root uptake rates from small laboratory pots are higher than those from large boxes or fields. For non-ionic chemicals, most of which are more or less volatile, the uptake of vapour via the air can falsify the results, especially in closed systems with a low airflow rate where the ratio between root uptake and uptake via air is quite different than under field conditions (Scheunert and Klein, 1985). This latter point is especially important for mixtures whose components may affect the volatility behaviour of each other (see section 3.1). For such mixtures, only field studies or studies under field-like conditions, e.g. in open-air lysimeters, give exact data on the uptake and accumulation of components by higher plants (Scheunert and Korte, 1985).

#### 4 ALTERATIONS OF MIXTURES BY CHEMICAL AND BIOCHEMICAL PROCESSES

In contrast to alterations of mixtures by physical processes, alterations in the composition pattern of mixtures by chemical and biochemical processes include the disappearance of compounds by total degradation (mineralization) and the appearance of new compounds. The principle mechanisms are abiotic or biotic conversion of individual components, or direct chemical reactions between two components or their metabolites. The first group of reactions is discussed in section 4.1, whereas the formation of new compounds by chemical reactions between two mixture components will be discussed in section 4.2.

##### 4.1 Alterations by Conversion and Degradation of Components

Alterations of chemical mixtures by selective conversion and degradation of components occur by abiotic and biotic processes in the soil according to their chemical and biochemical stability. Numerous publications are available about pesticide combinations and their degradation behaviour in soil.

Decrease of the persistence of a pesticide under the influence of another may be due either to chemical reactions between the mixture components, as discussed in section 4.2, or to promotion of enzymatic degradation by another pesticide present. According to well-known principles, adaptation to a given substrate generally involves simultaneous adaptation to all intermediates in the degradation pathway. It follows, therefore, that microorganisms may be induced to at least partially metabolize a seemingly resistant molecule if pre-induced on a similar homologous substrate (Kaufman, 1972). Table 1 gives some results of laboratory experiments related to this case. Experiments were conducted with soil



Table 1 Decreased persistence of chemicals in soil as a result of microbial induction by other chemicals

Degraded substance	Chemical group	Inducing substance	Chemical group	Reference
Dicamba	Substituted benzoic acid	2,4-D	Phenoxyacetic acid	Kaufman (1975)
MCPA*	Phenoxyacetic acid	2,4-D	Phenoxyacetic acid	Audus (1964)
2,4-D	Phenoxyacetic acid	MCPA	Phenoxyacetic acid	Audus (1964)
2,4,5-T	Phenoxyacetic acid	MCPA	Phenoxyacetic acid	Audus (1964)
2,4-D	Phenoxyacetic acid	2,4-Dichloro-phenol	Chlorinated phenol	Stenson and Walker (1958)
MCPA	Phenoxyacetic acid	2,4-Dichloro-phenol	Chlorinated phenol	Stenson and Walker (1958)
2,4-D	Phenoxyacetic acid	4-Chloro-2-methylphenol	Chlorinated phenol	Stenson and Walker (1958)
MCPA	Phenoxyacetic acid	4-Chloro-2-methylphenol	Chlorinated phenol	Stenson and Walker (1958)
<i>m</i> -Nitro-phenol	Nitrophenol	<i>p</i> -Nitrophenol	Nitrophenol	Raymond and Alexander (1971)

\* 2-(4-Chloro-2-methylphenoxy)acetic acid.

as well as with selected soil microorganisms. It can be seen that most examples reported belong to the groups of substituted benzoic acids, phenoxyacetic acids, or phenols.

The increase of persistence of pesticides in soil due to other pesticides present is much more frequent than a decrease. In Table 2, some examples are listed for experiments with soil or isolated soil microorganisms. The increase of pesticide persistence under the influence of other pesticides may result from a general inhibition of the proliferation of metabolizing microorganisms; this has been

Table 2 Increased persistence of chemicals in soil as a result of microbial inhibition by other chemicals

Degraded substance	Chemical group	Inhibiting substance	Chemical group	Reference
Chlorpropham	<i>N</i> -Phenyl-carbamate	Carbaryl	<i>N</i> -Methyl-carbamate	Kaufman (1972, 1977), Kaufman <i>et al.</i> (1970)

Table 2 (Cont'd)

Degraded substance	Chemical group	Inhibiting substance	Chemical group	Reference
Chlorpropham	<i>N</i> -Phenyl-carbamate	<i>p</i> -Chlorophenyl-methylcarbamate	<i>N</i> -Methyl-carbamate	Kaufman (1977), Priest and Stephens (1975)
Propham	<i>N</i> -Phenyl-carbamate	<i>p</i> -Chlorophenyl-methylcarbamate	<i>N</i> -Methyl-carbamate	Kaufman (1977)
CDAA (allidochlor)	Acetamide	<i>p</i> -Chlorophenyl-methylcarbamate	<i>N</i> -Methyl-carbamate	Kaufman (1977)
Propanil	Acylanilide	<i>p</i> -Chlorophenyl-methylcarbamate	<i>N</i> -Methyl-carbamate	Kaufman <i>et al.</i> (1971)
Fluometuron	Phenylurea herbicide	<i>p</i> -Chlorophenyl-methylcarbamate	<i>N</i> -Methyl-carbamate	Kaufman (1977)
Diuron	Phenylurea herbicide	<i>p</i> -Chlorophenyl-methylcarbamate	<i>N</i> -Methyl-carbamate	Kaufman (1977)
Fluometuron	Phenylurea herbicide	Aldicarb	<i>N</i> -Methyl-carbamate	Gomaa <i>et al.</i> (1975)
Solan	Acylanilide	Metmercapturon (methiocarb)	<i>N</i> -Methyl-carbamate	Wallnöfer <i>et al.</i> (1977)
Chlorpropham	<i>N</i> -Phenyl-carbamate	Diazinon (dimpylate)	Organo-phosphate	Kaufman (1977)
Chlorpropham	<i>N</i> -Phenyl-carbamate	Phorate	Organo-phosphate	Kaufman (1977)
	Several acylanilides and acetamides	Diazinon (dimpylate)	Organo-phosphate	Kaufman (1972)
	Several acylanilides and acetamides	Parathion	Organo-phosphate	Kaufman (1972)
Chlorpropham	<i>N</i> -Phenyl-carbamate	Potassium azide	Azide	Kaufman (1977)
Chlorpropham	<i>N</i> -Phenyl-carbamate	Pentachloro-nitrobenzene	Substituted benzene	Kaufman (1972)
Chlorpropham	<i>N</i> -Phenyl-carbamate	Heptachlor	Organo-chlorine	Kaufman (1972)
Chlorpropham	<i>N</i> -Phenyl-carbamate	DDT + captan	Organo-chlorine + phthalimide	Kaufman (1972)
Dalapon	Aliphatic carboxylic acid	Amitrole	Triazole	Kaufman (1966)



shown for the triazole herbicide amitrole which inhibits the degradation of the chemically quite different dalapon molecule (Kaufman, 1972). A second mechanism of degradation retardation is inhibition of microbial enzymes active in pesticide degradation, either directly by the inactivation of the enzyme, or indirectly by competition. Competitive inhibition has been demonstrated, for example, by the increased persistence of phenylcarbamates and acylanilides in soil in the presence of *N*-methylcarbamates.

The phenomenon of increased persistence of combined pesticides in soil is of enormous importance for environmental quality; thus, further research should be done in this respect.

The methods to detect and quantify different chemicals in soil after soil treatment with mixtures are the same as those of soil metabolism studies where only one chemical is applied (see section 2). Because in the former case more compounds have to be separated and determined, more efficient chromatographic separation methods have to be used.  $^{14}\text{C}$ -labelling of mixture components or of the mixture as a whole results in the possibility of complete detection and determination of all conversion products. Moreover, total degradation of the labelled compounds to carbon dioxide can be measured directly by trapping and counting  $^{14}\text{C}$ -labelled carbon dioxide; a compilation of such methods is given by Klein and Scheunert (1985). However, if more than one mixture component is labelled, the origin of the labelled carbon dioxide cannot be attributed to a definite compound.

#### 4.2 Chemical Reactions Between Mixture Components

Chemical reactions between mixture components resulting in the formation of new foreign compounds are not frequent in soil, since normally the concentrations occurring are too low and the reactivity of environmental chemicals is in general not sufficient. However, a few examples have been reported for chemicals in soils.

Although various reactions between chemicals, including catalytic actions of metals, are assumed to occur in landfills, this topic has not been investigated systematically thus far. In normal agricultural soil only a few examples of the formation of new xenobiotics by reaction between components of pesticide mixtures have been reported.

The fumigant sodium *N*-methyldithiocarbamate (Vapam) is decomposed in soil, resulting in a mixture of chemicals whose components may react with each other to form a new chemical (Turner and Corden, 1963). The concentration of active sodium *N*-methyldithiocarbamate applied to soil was about 500 ppm. Figure 3 shows this chemical reaction.

The same pesticide was shown to react in soil with halogenated hydrocarbons contained in certain nematocides. Sodium *N*-methyldithiocarbamate is alkylated at its sulphide group by ethylene dibromide, 1,2-dibromo-3-chloropropane,

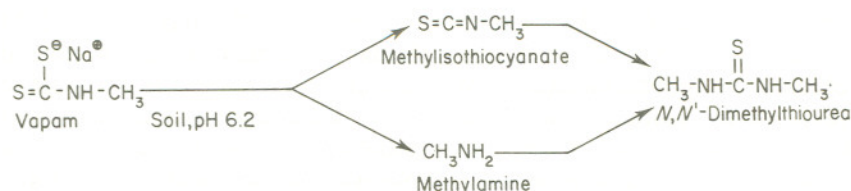


Figure 3 Formation of a new chemical by reaction between degradation products of sodium *N*-methylthiocarbamate (Vapam) in soil

1,3-dichloropropene, and related chlorinated hydrocarbons, as shown in Figure 4 (Miller and Lukens, 1966). The concentration range in soil was about 40–90 ppm.

In contrast to these two examples which have been reported for higher concentrations of the respective pesticides in soil, coupling products between pesticide metabolite molecules have also been reported for low concentrations in agricultural soils (about 1 ppm of the respective metabolites). Aromatic amines in soil undergo one-electron oxidation mediated by peroxidases, resulting in intermediates as shown in Figure 5. Three couplings are possible ( $\text{N}^\bullet + \text{N}^\bullet$ ,  $\text{N}^\bullet + \text{C}^\bullet$ , and  $\text{C}^\bullet + \text{C}^\bullet$ ) but the latter reaction is not likely to occur unless the  $\text{N}^\bullet + \text{N}^\bullet$  and  $\text{N}^\bullet + \text{C}^\bullet$  mechanisms are inhibited by steric factors (Parris, 1980).

At low concentrations and under field conditions, only the  $\text{N}^\bullet + \text{N}^\bullet$  coupling has thus far been observed. Azobenzenes and their oxidation products, azoxybenzenes, have been detected in experiments under open air conditions after application of 4-chloroaniline (Freitag *et al.*, 1984) and 3,4-dichloroaniline (Viswanathan *et al.*, 1978) to soil in 1 ppm concentrations. Mixed azobenzenes from two different pesticides were obtained in the laboratory at much higher concentrations than in soil. Kearney *et al.* (1969) demonstrated the condensation of 3-chloroaniline with 3,4-dichloroaniline to form 3,3',4'-trichloroazobenzene (Figure 6). Similarly, Bartha (1969) reported the formation of asymmetric 3,3',4'-trichloro-4'-methylazobenzene from the herbicides propanil and Solan (pentanochlor) via the respective anilines. Since it was shown that these condensation reactions occur, in principle, in the field in the 1 ppm range, the occurrence of such hybrid residues in the field must be taken into account if



Figure 4 Formation of new chemicals by reaction of sodium *N*-methylthiocarbamate (Vapam) with halogenated hydrocarbons in soil. From Miller and Lukens (1966). Reproduced by permission of the American Phytopathological Society



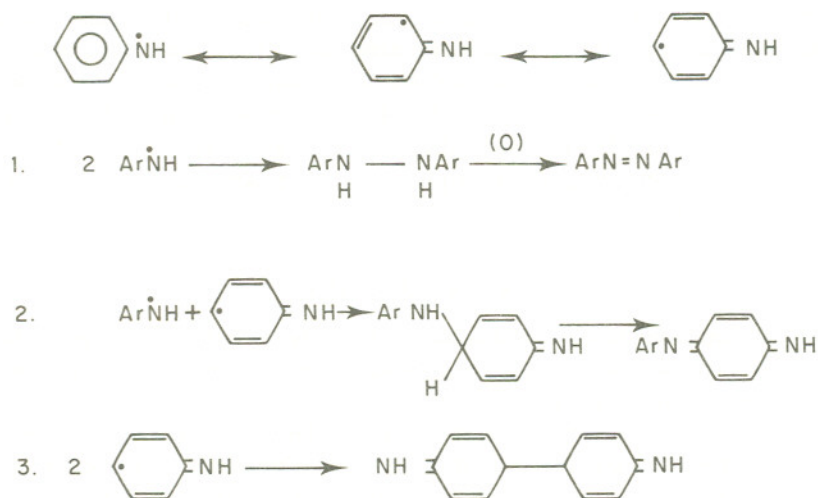


Figure 5 One-electron oxidation of anilines in soil and possible coupling pathways. From Parris (1980). Reproduced by permission of Springer-Verlag

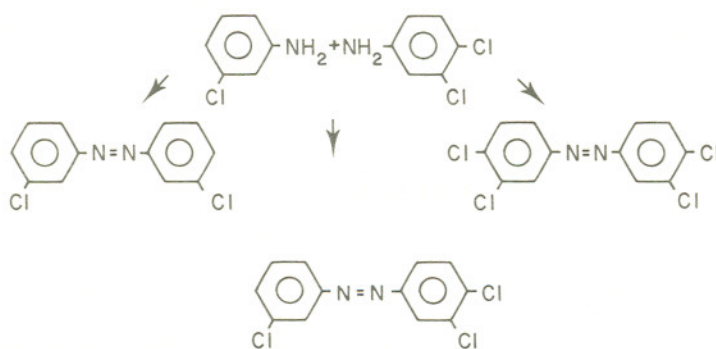


Figure 6 Formation of a new chemical by reaction between metabolites of different pesticides. Reprinted with permission from Kearney et al. (J. Agric. Food Chem., 17, 1418–1419). Copyright (1969) American Chemical Society

pesticides are expected to produce aniline metabolites at 1 ppm concentrations or more. The formation of other condensation products of anilines, like triazines and phenoxazines, has only been observed so far in the laboratory at high concentrations (80–100 ppm in culture medium: Engelhardt *et al.*, 1977; Minard *et al.*, 1977); mixed condensation products of this kind have not so far been reported.

The results of tests to determine chemical reactions between mixture components are relevant to the environment only if environmental conditions are maintained, especially if the concentrations that are expected to occur in natural soil or a landfill are regarded. Outdoor experiments should be preferred (e.g. Freitag *et al.*, 1984; Viswanathan *et al.*, 1978). The methodology of separating and identifying reaction products is the same as that discussed in sections 2 and 4.1.

## 5 CONCLUSIONS

It may be concluded that it is not sufficient to study the behaviour of individual chemicals in physical or chemical and biochemical environmental processes in soil. Since the behaviour of a chemical within a mixture may be different from that of the isolated compound due to mutual influences, the environmental behaviour should be studied at least for those combinations which occur most frequently. Only limited information is available on the formation of new compounds by chemical reactions between components of the mixture. Studies should be undertaken at least on potential reactions in landfills. Although reactions between pesticides and their metabolites in agricultural soil are probably not frequent, this possibility should be considered. If methods developed for the study of single compounds are used for mixtures, their applicability to each component as well as to the mixture as a whole should be critically examined.

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