HERBICIDES IN TROPICAL SOILS AND WATER

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INTRODUCTION

In the U. K., the amount of herbicides used on about 4.15 million hectares of agricultural land in 1973 was considered enough to provide 30 ppm if mixed evenly into the top 0.5 cm of the treated area (Greaves et al., 1976). How soon quantities of this kind will be used in the topics is not known. It is the responsibility of agriculturalists to maintain the productivity of the soil, and one aspect of this task is to ensure that levels of herbicides in soils and water are kept low.

The accumulation of herbicide residues can be minimized by: (a) employing integrated control methods; (b) using minimum dosages recommended; (c) adhering to proper application methods with regard to formulation, rate, and distribution; (d) avoiding movement or drift from target area; (e) using selected short-residual herbicides; and (f) rotating herbicides (Burnside, 1974).

FATE OF HERBICIDES IN SOILS AND WATER

Herbicides applied to soils or vegetation are subjected to the processes shown in Figure 1. These processes may be classed as either transfer or degradative processes (Weber, 1977). In transfer reactions herbicide molecules remain intact and:

(1) Are absorbed, retained, accumulated, and exuded by organisms.

(2) Are absorbed by soil colloids and other surfaces.

(3) Move in the vapor, liquid, and solid states through the atmosphere, soil, and water.

Degradation of herbicides may be biological, chemical, or by photo-decomposition. According to Burnside (1974), the major problems resulting from herbicide use are due to spray drift, volatility, and the accumulation of potential phytotoxic residues in soil. The major danger is to crops and other desirable plant life. Fortunately, herbicide drift, vapor movement, and persistence are easily detected.

TRANSFER REACTIONS

Absorption, retention, accumulation and exudation. Organisms in water containing herbicide may absorb and accumulate the chemical. For example, Najas spp. and Potamogeton spp. in water treated with 0.5 ppm diquat and 0.5 ppm paraquat were found to contain 20-40 ppm of these herbicides (Frank, 1970). Mobile herbicides, such as picloram (Foy, 1976), are easily absorbed and Lee et al. (1976) observed that nitrogen was bioconcentrated and stored in tissues of algae, snails, mosquitoes, and fish. Exudation of herbicides has also been documented (Kearney, 1970; Weber, 1977).

Adsorption. Most herbicides are adsorbed onto clay and organic colloids although some anionic compounds are repelled by these negatively charged surfaces (Sheets and Kaufman, 1970). The properties of herbicides and soils which promote adsorption have been documented by Sheets and Kaufman (1970) and by Crosby (1973).

Adsorption of picloram increases with decreasing soil pH, increasing organic matter content and increasing levels of hydrated iron and aluminium oxides (Foy, 1976). Diquat and paraquat are strongly adsorbed by clay minerals (Calderbank and Slade, 1976) and chloramben by organic matter (Frear, 1976). The effect of organic matter on adsorption is so great that Warren (1973) considers it crucial to know the level of organic matter in a soil before the correct herbicide application rate can be calculated. It would appear that tropical soils require low herbicide rates because of their low organic matter content.

Volatilization, leaching and drift. Although the majority of organic pesticides have low vapor pressures (circa 10^{-3}mm Hg at 20^{o}C) (Plimmer, 1976), their limited ability to volatilize is significant in relation to the quantities applied and also to their biological activity. Volatilization losses are rapid for some herbicides, such as the phenoxyalkanoic compounds and other aromatics, at soil surface temperatures which occur frequently in temperate and tropical regions. (Frank, 1970; Plimmer, 1976). Kearney et al. (1964) found that the volatility of seven s-triazines was correlated with their vapor pressures so that the order of volatility from metal planchets at 25^{o}C in descending order was:

Prometone = trietazine >atrazine ≃ametryne ≃prometryne >propazine ≃simazine.

Volatilization of picloram is insignificant although it may be leached to a depth of 61 cm in light soils (Foy, 1976). TBA is volatilized from soil when water content is low and temperatures are high (Frear, 1976). Therefore, the process is likely to be important in light tropical soils. Sheets and Kaufman (1970), however, do not consider herbicide losses by volatilization to be of any practical significance in agriculture.

The water soluble herbicides, such as 2, 4-D, are very mobile and are most easily leached. The ionic dipyridilium herbicides are virtually immobile in water, although leaching efficiency varies with soil type (Crosby, 1973).

Drift depends largely on spray droplet size (Plimmer, 1976) and wind velocity. Evidence for drift is the fact that pesticides have been detected at levels of the order of parts per billion in rainwater and remote Islands (Crosby, 1973).

DEGRADATION

Chemical decomposition. The mechanism of chemical decomposition is not well understood. It is complex and includes oxidations, reductions, hydrolyses, and hydroxylations (Crosby, 1973). As with biological decomposition, it tends to increase polarity and decrease volatility (Crosby, 1973). Most organic herbicides used in aquatic weed control are resistant to chemical attack. Although some, like the phenoxyalkanoic acids, are converted to salts, the basic molecule remains intact (Frank, 1970). The chemical decomposition of paraquat and diquat is also insignificant (Calderbank and Slade, 1976). Chemically decomposed herbicides include picloram (Foy, 1976), atrazine (Armstrong *et al*., 1967), trifluralin, and benefin (Crosby, 1973).

Photodecomposition. Most herbicides are decomposed by ultra violet light. This is particularly the case with those with aromatic nuclei, because of the strong energy of absorption. Several authors (Frank, 1970; Calderbank and Slade, 1976; Crosby, 1976; Frear, 1976) have summarized the data on this. Photodecomposition has been observed among certain aliphatic and phenoxy acids, aromatic acids and derivatives, amines and anilides, carbamates and ureas, phenols, and the heterocyclic compounds. Herbicides not photodecomposed include the polyhalogenated aromatic, TIBA, and the carbamate IPC. Some data exist showing that photolysis can occur in the field in sunlight (Crosby, 1976).

Microbiological degradation. Several herbicides are microbiologically detoxified in soil and water. It has been demonstrated that 2, 4-D, silvex, and dichlobenil are biodegraded in static water (Frank, 1970), but it is difficult to measure biodegradation in moving water.

Data are more abundant on biodegradation in soil than in water. Hance (1973, 1974) reported that inorganic salts, straw, or organic residue increased atrazine degradation in two soils, but linuron was not readily degraded. Picloram is also resistant to degradation, 80-97.5% of the herbicide was retained after one year (Foy, 1976). Ametryne degradation in two tropical soils was found to be mainly microbial, with rapid accumulation of polar products and slow decomposition to CO_2 (Goswami and Green, 1975).

EFFECTS OF HERBICIDES ON SOIL MICRO-ORGANISMS

The activities of soil micro-organisms may be stimulated by herbicides (Table 1). This happens only to a limited extent at normal field rates of herbicide application, and no lasting effects are known (Sheets and Kaufman, 1970; Grossbard and Davies, 1976; Johnen and Drew, 1977). The most sensitive micro-organisms are the algae, because of the vulnerability of the photosynthetic process, and the least sensitive are the actinomycetes (Grossbard and Davies, 1976). However, Greaves et al. (1976) found that the growth of 30 species of actinomycetes and 50 species of bacteria was inhibited by 13,000 ppm dalapon in pure culture. In the same study, of 14 yeast species, three were inhibited and one was stimulated; of 33 species of fungi five were inhibited and eight were stimulated.

The data on the general effects of herbicides on microbial processes are at times conflicting; the differences are probably due to soil types, environmental situations, and methods of investigation.

HERBICIDE RESIDUES IN SOILS AND WATER

The rate of loss of all herbicides used in 1977 for selective weed control was found to exceed 50% per year; in most cases it was over 80% per year (Sheets and Kaufman, 1970). The levels of residues found in soil and water at any moment reflect the total outcome of transfer and degradation reactions. Residue levels change with time. The longer a herbicide remains in soil or water, the greater the chance of its loss.

Of 11 common herbicides examined by Kearney *et al.* (quoted in Crosby, 1973), the order of decreasing persistence under the prevailing experimental conditions was picloram, simazine, TBA, diphenamid, diuron, trifluralin, 2, 4, 5-T, MCPA, dalapon, 2, 4-D, and IPC. Picloram persisted for 70 weeks, IPC for under five. According to Burnside (1974), the chlorobenzoic acids, picloram, substituted ureas, triazines, and uracils persist over one season.

Data on residue levels in tropical soils and water often do not include information on the mode of loss. Usoroh (1976) reported that under the prevailing conditions at Ibadan, Nigeria, the maximum half-lives of atrazine, linuron, and simazine were 8, 9, and 11.5 weeks, respectively. Young *et al.* (1973) were unable to detect residues of bromacil 12 months after field application. Sodium arsenite was found to be absorbed more strongly by clay than sandy soils in Malaysia, and this resulted in toxic effects on rubber, soybean, and groundnut in sandy soils sprayed at rates suitable for clay soils (Woo, 1973).

When diquat and paraquat are applied to water bodies, they persist for several months before microbial degradation commences (Table 2). Fenac and dichlobenil also persist, but endothal and 2, 4-D do not (Table 3). A pond treated with 4 ppm fenac was found to have residues of 2.4 ppm 202 days after application. Although dichlobenil is less persistent, it has been recovered from water after 100 days and from soil after 312 days (Frank, 1970). The levels of herbicides in water will depend on the means by which they enter it (Table 4). Significantly lower residue levels are to be expected from surface run-off water than from the spraying of aquatic weeds.

RESIDUE REMOVAL

Objectionable levels of residues in soils and water can be removed or have their effects minimized in several ways. According to Burnside (1974), one or more of the following practical procedures can be followed to avoid damage from residues in soil: (a) planting of tolerant crops; (b) use of plant protectants such as activated charcoal; (c) fallowing and tilling the land; (d) plowing the soil to incorporate the herbicide; (e) irrigating to dissipate the herbicide; (f) adding adsorbents such as activated charcoal and organic matter to the soil; (g) adding microbes that can biodegrade the herbicide; (h) adding chemicals to alter soil properties, e.g., alter pH to enhance decomposition or volatilization.

CONCLUSION

The removal of herbicides from soils and water is the result of transfer and degradative reactions which depend largely on the chemical properties of the herbicide and on the prevailing climatic and edaphic conditions. Because herbicides are normally exhaustively tested only in temperate environments during their development, it is recommended that governments of tropical countries review and evaluate each herbicide before it is introduced into their countries. Particular attention should be paid during such investigations to the effects of the chemicals on aquatic life and to public health aspects of their usage. Manufacturers could be requested to assist in such evaluation schemes.

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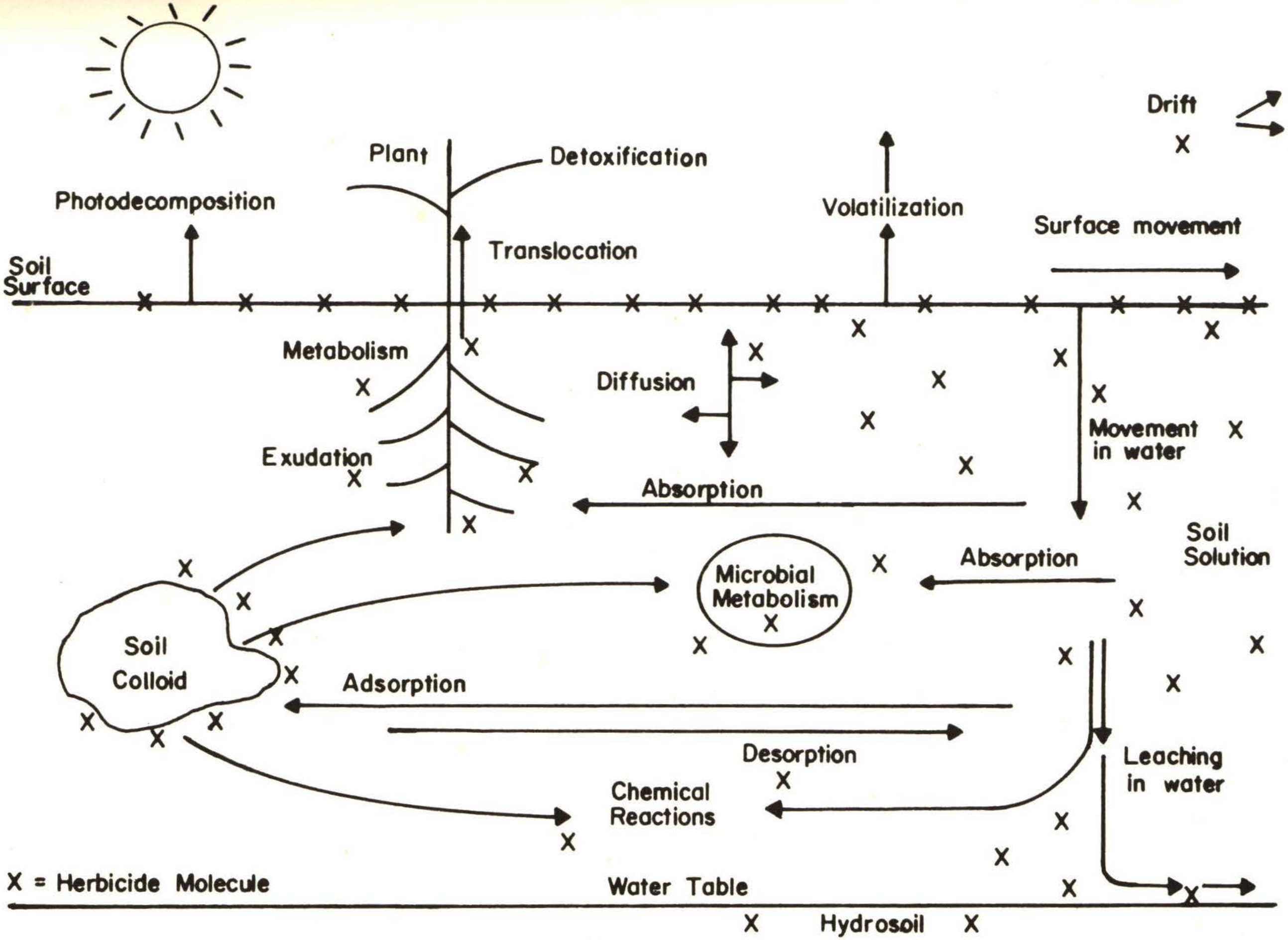

Figure 1. Diagrammatical sketch of the interrelations of the processes that lead to detoxication, degradation, and disappearance of herbicides. (Adapted from Frank, 1970 and Greaves *et al*, 1976).

Table 1. Effects of herbicides on soil microbes and their activities.

Microbial activity/microbe	Herbicide	Rate kg a.i./ha	Effect	Source[1]
Urease	Dinoseb	5	Stimulation	(1)
	Paraquat	3.75	Stimulation	(1)
	2,4-D	2	Stimulation	(1)
	Chlorpropham	1[2]	Inhibition	(1)
	Linuron	100[2]	Inhibition	(1)
	Simazine	2	Stimulation	(1)
	Simazine	10	Inhibition	(1)
Dehydrogenase	Paraquat	250[2]	Inhib/None	(2)
Cellulolysis	Linuron	-	Inhib/None	(3)
Nitrification	2,3,6-TBA	2.2	Inhibition	(1)
	Asulam	5[2]	Inhibition	(1)
	Propanil	50[2]	Inhibition	(1)
	Fenuron	1.5	Inhibition	(1)
	Simazine	6[2]	Inhibition	(1)
	Picloram	20[2]	Inhibition	(4)
	Diuron	20[2]	Inhibition	(4)
	Ametryne	100[2]	Inhibition	(4)
	Paraquat	250[2]	None	(2)
	Chloroxuron	100[2]	None	(5)
C + N mineral	Chloroxuron	100[2]	None	(5)
Rhizobia/ Azotobacter	Dinoseb	-	Inhibition	(6)

[1] Sources: (1) Grossbard and Davies, 1976; (2) Agbahungba and Ayanaba, unpubl.; (3) Torstensson, 1974; (4) Dubey, 1969; (5) Odu and Horsefall, 1971; (6) Torstensson, 1975.

[2] Rate in ppm.

Table 2. Residues in ppm in soil and water samples from ponds treated with 2, 4-D, paraquat, diquat, and amine salt of endothall (Frank, 1970)[1].

Days after treatment	2,4-D		Paraquat		Diquat		Endothall
	Water	Soil	Water	Soil	Water	Soil	Water
1	0.024	4.96	0.55	3.56	0.48	0.47	0.15
2	0.029	2.40	0.48	11.70	0.12	0.85	0.18
4	0.034	1.02	0.21	36.90	0.01	2.14	0.11
8	0.048	2.67	0.02	42.16	< 0.001	1.23	0.017
12	0.053	0.60	< 0.001	42.14		5.38	0.023
18	0.067	0.45		35.46		7.40	0.002
24	0.019	0.66		47.23		20.12	<0.001
36	<0.001	0.06		37.82		12.57	<0.001
56		0.10		20.51		36.80	
85		<0.005		10.73		35.55	
160						24.23	

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[1] Each value is the average of three samples taken from the same pond.

Table 3. Residues in ppm in soil and water samples from ponds treated with dichlobenil and fenac (Frank, 1970).[1]

Days after treatment	Dichlobenil				Fenac			
	Pond 1		Pond 2		Pond 1		Pond 2	
	Water	Soil	Water	Soil	Water	Soil	Water	Soil
1	0.19	10.65	0.16	6.41	1.03	12.42	0.68	1.31
2	0.18	9.51	0.18	8.82	1.25	3.12	0.68	1.12
4	0.23	9.62	0.18	4.88	1.37	0.11	0.52	1.17
8	0.25	8.96	0.23	5.63	1.33	0.46	0.71	0.72
12	0.28	5.47	0.17	5.76	1.39	1.03	0.67	1.20
18	0.29	5.14	0.12	1.90	1.61	0.91	0.61	1.43
24	0.23	4.26	0.10	0.67	1.49	1.45	0.50	1.18
36	0.32	4.70	0.04	1.06	1.34	2.67	0.29	1.45
56	0.22	3.94	0.02	0.50	1.25	1.74	0.13	0.39
85	0.05	2.95	0.006	0.18	0.77	0.66	0.07	0.18
120	0.003	1.34	0.002	0.23	0.57	0.59	0.09	0.15
160	0.004	ND	0.001	0.12	0.38	0.26	0.07	0.08

[1] Each value is the average of three samples taken from the same pond.

ND no significant level detected.

Table 4. Levels of residues in water (Frank, 1970).

Means of entry into water	Herbicide	Maximum level detected ppm
Surface runoff	Fenuron	0.43
	2,4-D esters	0.18×10^{11}
	(Many others)	$<0.10 \times 10^{11}$
Post submerged weed treatment	Dichlobenil	0.23-0.32
	2,4-D ester	0.067
Post floating weed treatment	PGBE	0.16×10^{1}
	2,4-D esters	0.65-1.0
After treatment of marginal and ditchbank weeds	(Many)	0.50×10^{11}