

Degradation of the herbicide diclofop-methyl in soil and influence of pesticide mixtures on its persistence

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MS received 7 May 1984; revised 31 August 1984

Abstract. The degradation of the herbicide [^{14}C]-diclofopmethyl was investigated in moist parabrown podzol soil at 22°C. Radiochemical procedures were used to monitor the herbicide breakdown. The mineralization of the uniformly labelled aromatic ring was pursued by trapping the $^{14}\text{CO}_2$ generated for 96 days. Diclofop-methyl was rapidly degraded in the soil with a half-life of about 8 days. The major breakdown product was the corresponding acid-diclofop, formed by a very rapid hydrolysis of the esterbond. With time the acid appeared to undergo strong binding or complexing to the soil. An intermediate 4-(2,4-dichlorophenoxy) phenol was recovered from the treated soil. Concentration of the phenoxyphenol increased upto 6 days followed by quick decline. Insecticide combination of parathion + Demeton-S-methylsulphoxide partially inhibited diclofop degradation in the soil.

Keywords. Diclofop-methyl; herbicide; degradation; pesticide mixtures; soil.

Introduction

The herbicide diclofop-methyl, (\pm)-methyl 2-[4-(2,4-dichlorophenoxy) phenoxy] propionate, is the active ingredient (36%) in the commercial formulation Illoxan[®]. This formulation is recommended in the Federal Republic of Germany as a post emergence herbicide for the control of annual grasses in sugar-beet crop. Studies of Anderson and Domsch (1978) with agriculturally feasible combinations of chemicals, applied at recommended concentrations have revealed that the degradation of a thiol carbamate herbicide diallate is partially inhibited by an insecticide chlorpyrifos in soil (personal communication). Such findings prompted us to look into pesticide combinations that can retard the degradation of diclofop-methyl in soil. Nevertheless in order to assess the persistence and eventual detoxification of diclofop-methyl, information is needed about such partial inhibition of degradation by simultaneously or successively added pesticides.

This paper describes the results of laboratory investigations designed to study the rate of degradation and influence of selected pesticides on both the rate and pattern of degradation of the herbicide diclofop-methyl in an agricultural soil.

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Materials and methods

Chemicals

Diclofop-methyl, diclofop and diclofop-methyl [^{14}C]-uniformly labelled in the dichlorophenyl ring moiety were obtained from Farbwerke Hoechst AG, Frankfurt, Germany (specific activity 10 $\mu\text{Ci}/\text{mg}$; purity 97%). Acetone solution of the [^{14}C]-diclofop-methyl was prepared (500 $\mu\text{g}/\text{ml}$) with a specific activity of 3.13 $\mu\text{Ci}/\text{ml}$ and used in the experiment. Other pesticides listed in table 1 and all reagents were purchased locally.

Table 1. Common and chemical names, chronology, formulations and uses of pesticides recommended for sugar-beet crop.

Common name	Commercial name	Chemical name	Formulations* and active ingredient	Uses**
Pyrazon	Pyramine	1-phenyl-4-amino-5-chloro-pyridazon	W.P. 65%	H
Lindane	Nexit	1,2,3,4,5,6,hexachloro-cyclohexane	E.C. 25.5%	I
Phenmedipham	Betanal	3-(methoxycarbonylamino-phenyl)-N-(3'-methyl-phenyl) carbamate	E.C. 16.2%	H
Diclofop-methyl	Illoxan	(\pm)-methyl 2-[4-(2,4-dichlorophenoxy) phenoxy] propionate	E.C. 36%	H
Parathion + Demethon-S-methyl-sulphoxide mixture	E605-combi	0,0-diethyl-0-(4-nitrophenyl)monothiophosphate + 0,0-dimethyl-S-(2-ethyl-sulphonylethyl) thiophosphoric acid ester	E.C. 20% + 17.5%	I
Demethon-S-methyl-sulphoxide	Meta-systox	0,0-dimethyl-S(2-ethyl sulphonylethyl) thiophosphoric acid ester	E.C. 25%	I

* W.P. = Wettable powder; E.C. = Emulsifiable concentrate.

** H = Herbicide; I = Insecticide.

Soil

The soil used in the study was a parabrown podzol collected from an experimental field of the Institute. The soil had the following characteristics. Total carbon: 1.26%, total nitrogen: 0.11%, pH (KCl): 5.4, water holding capacity: 36.2 g water/100 g dry soil. The soil was passed through 2 mm sieve before use.

Treatment with the herbicide

Two ml of acetone solution containing 1000 μg [^{14}C]-diclofop-methyl was mixed with 1000 g of soil to give an uniform concentration of 1 ppm. This approximately

corresponded to the recommended application rate of 3 litres formulation per hectare. Aliquots of treated soil (40 g) were weighed into ground-glass jointed flasks (100 ml capacity) and fitted with similarly jointed glass columns. Each column contained granular soda lime (8 g) held between 2 glass wool plugs, to trap evolved $^{14}\text{CO}_2$ and another top layer of soda lime (4 g) to protect the $^{14}\text{CO}_2$ trap from saturation with atmospheric CO_2 . Air diffused through the column provided for an O_2 concentration within the flasks equal to that of the ambient air. Flasks were incubated for 96 days in the dark at 22°C , with 12.5% moisture content.

Treatment with pesticide mixtures

Pesticides used in this study alongwith ^{14}C -diclofop-methyl, the quantities added as well as the sequence of application were patterned as per spray programme for sugar-beet crop, where this herbicide is used as a post emergence herbicide. Common and chemical names, chronology in which they are recommended for sugar-beet cultivation, formulations and uses of the pesticides included in the experiments are listed in table 1. Treatment and extraction schedules are detailed in table 2. All samples were incubated in the dark at 22°C and at stated intervals diclofop-methyl and its breakdown products were extracted and analysed.

Table 2. Treatment and extraction schedule.

days	Soil treatments				
	I	II	III	IV	V
0	—	1 + 2	1 + 2	1 + 2	1 + 2
33	3	3	3 + 4	3 + 4	3 + 4
47	—	—	—	5	5
75	—	—	—	—	6
105	—	—	—	—	—

Numbers 1 to 6 names of pesticides as in table 1 added to soil.

— No further treatment. Samples were taken for extraction.

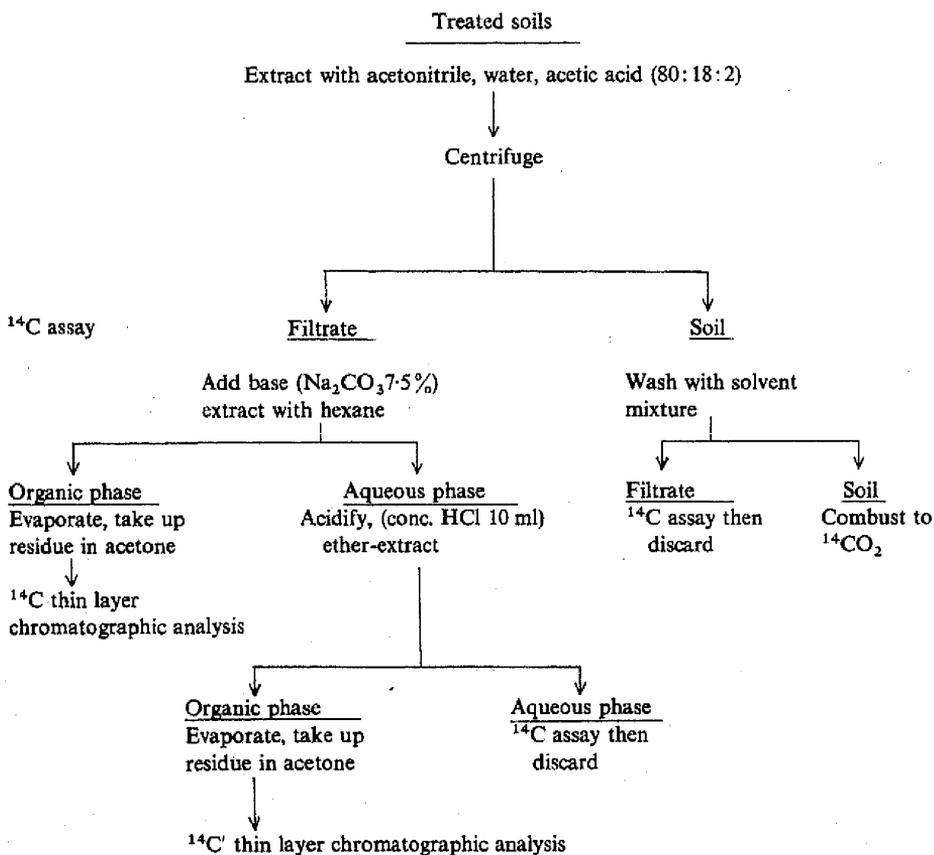
Extraction and analysis

The method employed to extract diclofop-methyl from the soil was similar to that reported by Smith (1977) with some modifications as outlined in flow-chart 1.

Thin-layer chromatography

Acetone extracts were applied to pre-coated thin layer chromatography plates (silica Gel 60F 254-E. Merck) and developed in the solvent system benzene: methanol : acetic acid (85:10:5 v/v). The radioactive areas on the developed plates were located by means of a scanner (Berthold and Friscke, type II) and when more than one radioactive spots were present, they were scrapped off and measured directly in a toluene based scintillation solvent.

Flow-chart 1. Outline of procedures used for the extraction and analysis of [^{14}C]-diclofop-methyl and its degradation products from soils. Thin layer chromatography solvent system:benzene:methanol:acetic acid (85:10:5).



Soil combustion

Soil-bound residue was estimated by burning 1 g portion of the extracted soil with 300 mg cellulose powder in a packard sample oxidizer and trapping the evolved $^{14}\text{CO}_2$ in Carbosorb[®]

Extraction of $^{14}\text{CO}_2$

The $^{14}\text{CO}_2$ trapped by soda lime granules was released by acid treatment and quantitatively transferred to a mixture of ethanolamine: methanol (3:7 v/v) for analysis as described by Anderson and Domsch (1978).

Radioactivity measurements

The radioactivity in the various solutions was measured using a liquid scintillation spectrometer (Nuclear-chicago Mark II). A commercial scintillation solution Unisolve I

(Zinsser, Frankfurt, Germany) was added to all samples containing water and for others toluene-based scintillation solution was used. The radioactivity measured was corrected for both background and for counting efficiency using the external standard.

Results and discussion

Degradation in soil

The mode of degradation of diclofop-methyl in soil for a period of 96 days is shown in figure 1. Diclofop-methyl disappeared rapidly from the soil. In between application and extraction (*Ca* 3 h) 35% was degraded and in 2 days approximately 90% of the applied 1 ppm herbicide was metabolized. Further degradation was slow and after 96 days, about 1.5% was still extractable. This is due to a certain amount of the applied herbicide getting bound to the humic fraction of the soil (Smith, 1977), which may not be available for degradation. Diclofop, (\pm)-2-[4-(2,4-dichlorophenoxy) phenoxy] propionic acid is known to be the first degradation product of this herbicide. Concentration of this acid increased in soil to *Ca* 70% within a day and thereafter gradually decreased to 5.5% at the end of the experiment.

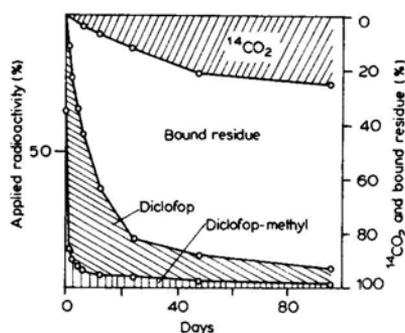


Figure 1. Degradation pattern of the herbicide [^{14}C]-diclofop-methyl in parabrown podzol soil.

Using [^{14}C]-diclofop-methyl, the degradation of the herbicide was studied further. As shown in figure 1, about 25% of the added herbicide was converted to $^{14}\text{CO}_2$ in 96 days. Similar observations were made by Martens (1978). Since the radioactivity was present in the dichlorophenyl ring of the herbicide, it is clear that the herbicide was completely degraded in order to yield $^{14}\text{CO}_2$.

Most of the diclofop-methyl added (1 ppm) was converted into bound residues and was therefore resisting solvent extraction. At the end of the experiment as much as 65% of the added radioactivity was still unextractable and a maximum of 70% was detected as bound residues on day 24. While studying the aerobic degradation of diclofop-methyl in 3 prairie soils, Smith (1977) has also observed 40–60% resting in the soil. It was suggested that diclofop and the further metabolites can undergo binding or complexing to soil components making them resistant to extraction. However the

incorporation in to the microbial biomass is another way of rendering the chemical unextractable.

Diclofop-methyl has a half-life of about 8 days in the soil under the experimental conditions. It is reported that both diclofop-methyl and diclofop have herbicidal activity. Therefore concentrations of these two components were considered in determining the half-life (the length of incubation after which 50% of the applied herbicidal chemicals could no longer be extractable from the soil). At the half-life, about 5% of the herbicide was completely metabolized as evidenced from the evolved $^{14}\text{CO}_2$ and 44% got converted into bound residues.

Degradation products could be resolved well from the diclofop-methyl in the chromatographic system used and a typical thin layer chromatography separation of the extracts after 2 days of incubation with the herbicide is shown in figure 2. At all sampling times the ether extract contained exclusively diclofop. However, the *n*-hexane phase which had only diclofop-methyl on day 0 showed two more radioactive peaks as the incubation continued. Judging from the mobility of the compounds in thin layer chromatographic plates and also comparing the observations of earlier reports (Martens, 1978; Smith, 1979), one metabolite with an R_f value of 0.43 could be identified as 4-(2,4-dichlorophenoxy) phenol. The identity of this chemical was later confirmed by comparing its R_f values with authentic dichlorophenoxyphenol in different solvent systems and also by co-chromatography. Table 3 reveals the R_f values

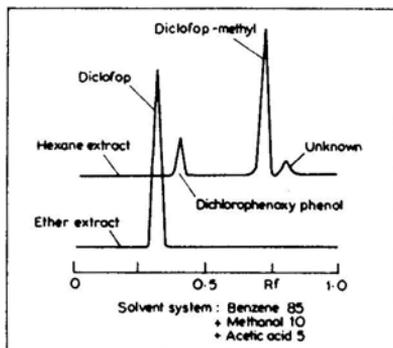


Figure 2. Radiochromatogram scanning of thin layer chromatographic plates showing diclofop-methyl and its degradation products.

Table 3. R_f values of compounds studied.

Compound	R_f			
	a	b	c	d
Diclofop-methyl	0.25	0.53	0.67	0.95
Diclofop	0.00	0.00	0.34	0.17
4-(2,4-dichloro- phenoxy) phenol	0.10	0.22	0.43	0.65

(a) Benzene-*n*-hexane (1:1); (b) benzene; (c) benzene-methanol-acetic acid (85:10:5); (d) benzene-methanol (10:1).

of compounds studied. No attempts were made to identify the metabolite(s) with an R_f value of 0.8. Since the concentration of these metabolites at any given time did not exceed 3% of the total activity, they are shown together with the diclofop-methyl fraction in figure 1.

Formation and disappearance of 4-(2,4-dichlorophenoxy) phenol in the soil is shown in figure 3. This substance was detected on the first day after treatment with diclofop-methyl. The concentration increased upto 2.5% of the added activity (day 6) and then came down to 0.4% in 96 days. Considering a slight but definite accumulation of the phenolic intermediate until day 6 and faster degradation thereafter, also, the lapse of 5 days between the appearance of extractable maxima for diclofop and its immediate intermediate, one can assume that the capability for the degradation of the phenolic compound in the soil appeared only after its formation.

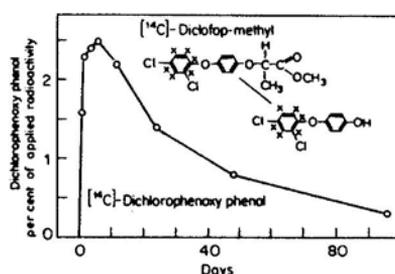


Figure 3. Formation and degradation of dichlorophenoxy-phenol in the soil.

Effect of pesticide mixtures on diclofop-methyl degradation

In the combinations and at the concentrations applied, none other than E605-combi had significant influence on either the rate or the pattern of degradation of diclofop-methyl in the soil (table 4). The insecticide mixture of parathion + demeton-S-methyl sulphoxide (E605-combi) slightly reduced the herbicide degradation. The partial inhibition was evident after the first sampling interval (day 75) and at the end of the experiment (day 105) there occurred about 20% inhibition in the degradation of diclofop-methyl with the consequent drop in $^{14}\text{CO}_2$ formation. However thin layer chromatographic analyses of the soil extract displayed no difference in the pattern of degradation.

In order to confirm the effect of E605-combi on diclofop-methyl degradation, a separate experiment was set up wherein increasing concentrations of E605-combi was added to the herbicide treated soil (table 5). Between the concentration range of 2 to $50 \mu\text{g} \times \text{g}^{-1}$ of the insecticides, the rate of degradation of diclofop-methyl was almost comparable to that of the control. However, soil-bound activity and $^{14}\text{CO}_2$ production decreased with increasing concentrations of E605-combi, mainly due to the reduced rate of diclofop transformation. The mechanisms of interaction will be interesting study.

Table 4. Influence of pesticide mixtures on the degradation of [¹⁴C]-diclofop-methyl in soil.

Day	Distribution of radioactive compounds ^a	Treatments*				
		I	II	III	IV	V
33	Diclofop-methyl	48.0	48.5	49.5	—	—
	Diclofop	52.0	51.5	50.9	—	—
	Soil bound	0.0	0.0	0.0	—	—
47	CO ₂	8.8	7.6	7.8	7.7	—
	Diclofop-methyl	5.8	5.9	6.1	6.2	—
	Diclofop	31.9	30.0	30.9	32.2	—
	Soil bound	53.5	56.4	55.2	53.9	—
75	CO ₂	19.9	19.9	19.6	16.5	17.6
	Diclofop-methyl	3.1	3.3	3.4	3.7	3.8
	Diclofop	9.0	9.7	11.0	10.5	10.7
	Soil bound	68.0	67.0	66.1	69.3	67.5
105	CO ₂	23.6	24.5	24.0	19.7	23.2
	Diclofop-methyl	2.3	2.5	2.5	2.7	2.4
	Diclofop	6.8	7.3	7.0	8.2	8.5
	Soil bound	67.4	65.8	66.4	69.3	65.8

^a Results are average from triplicates and presented as % of recovered radioactivity. Recovery 99.2 ± 2.2% of added activity

* Refer to treatment schedule in table 2.

Table 5. Diclofop-methyl degradation in soil as affected by increasing concentration of E605-combi.

Day	Distribution of radioactive compounds ^a	Treatment with E605-combi (μg × g ⁻¹)				
		0	2	5	10	50
43	CO ₂	12.8	11.9	13.1	10.3	9.6
	Diclofop-methyl	2.7	2.7	2.8	2.7	2.7
	Diclofop	15.5	19.3	19.7	23.5	32.6
	Soil bound	69.0	66.1	64.4	63.5	55.1
85	CO ₂	21.1	19.5	22.2	17.4	18.0
	Diclofop-methyl	1.5	1.6	1.7	1.7	2.1
	Diclofop	5.3	7.1	8.3	9.6	20.0
	Soil bound	72.1	71.8	67.8	71.3	59.9

^a Results are average from duplicates and presented as % of recovered radioactivity. Recovery 98.4 ± 7% of added activity.

Acknowledgement

Financial assistance of Deutsche Forschungsgemeinschaft, Federal Republic of Germany is gratefully acknowledged.

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