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Fate of [^{14}C]Monolinuron in Potatoes and Soil under Outdoor Conditions

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[*phenyl*-^{14}C]Monolinuron was applied (2.5 and 1.9 kg/ha) to the soil surface of an outdoor lysimeter in two successive years; then, potatoes were grown. Total recovery of ^{14}C in soil, plants, and leached water was about 55% (of ^{14}C applied) after the first growing period and about 43% after the second growing period. Radioactivity in soil contained 77.1% (based on total ^{14}C recovered in soil) bound residues, 15% monolinuron, and the following conversion products: *N*-(4-hydroxyphenyl)-*N*′-methoxy-*N*′-methylurea, *N*-(4-chlorophenyl)-*N*′-methylurea, *N*-(4-chlorophenyl)methylcarbamate, *N*-(4-chlorophenyl)-*N*-methyl-methylcarbamate, and 4-chloroformanilide. The leachate contained 0.8% (based on total ^{14}C recovered in leachate) *N*-(4-hydroxyphenyl)-*N*′-methoxy-*N*′-methylurea. Potato plants contained 0.106 mg/kg radioactive residues in peeled tubers after one growing period and 15.94 mg/kg in the tops; after two growing periods, peeled tubers contained 0.091 mg/kg and tops contained 18.87 mg/kg radioactive residues. These residues consisted of bound ^{14}C (57.9% of total ^{14}C recovered in plants), *N*-(4-hydroxyphenyl)-*N*′-methoxy-*N*′-methylurea, *N*-(4-chlorophenyl)-*N*′-methylurea, *N*-(4-chlorophenyl)methylcarbamate, *N*-(4-chlorophenyl)-*N*-methyl-methylcarbamate, and 4,4′-dichloroazobenzene.

INTRODUCTION

Monolinuron (*N*-[4-chlorophenyl]-*N*′-methoxy-*N*′-methylurea) is used against weeds, primarily as a preemergence herbicide in potatoes and other vegetables. It is classified as a medium persistent pesticide. Its microbial degradation (*Aspergillus niger*) has been reported to follow the pathway shown in Fig. 1, as shown by experiments with urea-^{14}C-labeled herbicide. After the removal of the *N*′-methoxy- or the *N*′-methyl groups, resulting in the formation of the metabolites *N*-(4-chlorophenyl)-*N*′-methylurea (conversion product **A**) or *N*-(4-chlorophenyl)-*N*′-methoxyurea (conversion product **B**), respectively, the remaining molecular moieties are degraded via *N*-(4-chlorophenyl)-urea (conversion product **C**) to 4-chloroaniline (conversion product **D**), carbon dioxide, and ammonia (Börner, 1967). Metabolite **B** was also formed by *Rhizopus japonicus* (Wallnöfer *et al.*, 1973). In the soil fungus *Cunninghamella echinulata* Thaxter, conversion products **A**–**C** were formed, too, along with *N*-(4-chlorophenyl)-*N*′-methoxy-*N*′-hydroxymethylurea, which was assumed to be an intermediate in the formation of the demethylated product **B** (Tillmanns *et al.*, 1978). The fungus *Fusarium oxysporum* Schlecht formed six metabolites from phenyl-^{14}C-labeled monolinuron, three of which could be identified. One was product **A** (Fig. 1). Additionally, 4-chloroacetanilide and a hydroxylated 4-chloroacetanilide were identified (Engelhardt *et al.*, 1979). These

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latter substances are secondary products formed from the degradation product 4-chloroaniline (Fig. 1, product **D**).

In soil, various chemical and physical processes interact with microbial degradation and influence the fate of the compound. The compound was not eliminated from soil by leaching even after 18 months of watering outdoor lysimeters. After 3–15 months the leachate from lysimeters (1.35 m high) filled with sand contained between 100

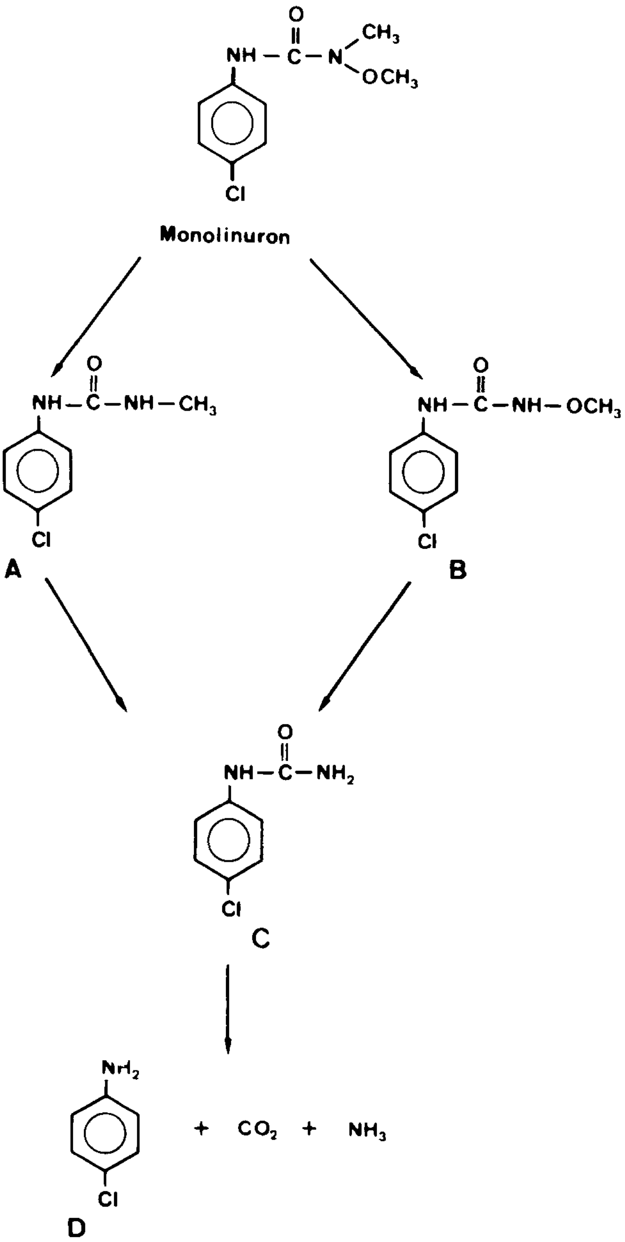


FIG. 1. Pathway of microbial degradation of monolinuron.

and 200 μg/liter monolinuron; after 16–18 months, the concentration decreased to 30 μg/liter (Herzel and Schmidt, 1979). The adsorption varied for different soil types; it was less for inorganic soil constituents (Bentonit M) and greater for organic soil constituents such as humic acids and humin (Süss and Wagner, 1969). In addition to involvement of hydrogen bonding, electron donor–acceptor processes involving organic free radicals play a prominent role in the interaction of monolinuron and other substituted urea herbicides with soil humic acids, which leads to the possible formation of charge–transfer complexes (Senesi and Testini, 1983). Biotic as well as abiotic hydrolysis yielding *N,O*-dimethylhydroxylamine is important for the degradation in soil. This was shown by experiments with *O*-[*methyl*-^{14}C]monolinuron in sterile versus nonsterile soils (Schuphan, 1974). The rate of degradation in soil is dependent upon temperature (Galiulin *et al.*, 1979) as well as soil type (Galiulin *et al.*, 1979; Süss and Eben, 1978). Carbon dioxide is formed not only from the ureido group but also from the methyl group and the phenyl ring, the latter being degraded more slowly than both of the other groups (Süss and Eben, 1978). After nitrogen fertilization with two different doses of urea (50 and 100 kg N/ha), ^{14}C-labeled residues in soil resulting from [^{14}C]monolinuron application were higher than those in controls (Sotiriou *et al.*, 1980).

In a closed laboratory system, phenyl-^{14}C-labeled monolinuron was applied to soil with spinach, cress, and potato plants (Schuphan and Ebing, 1978; Ebing and Schuphan, 1979). After 125 days, conversion products identified in soil corresponded to those found in studies with microorganisms (Tillmanns *et al.*, 1978); i.e., metabolites **A–C** in Fig. 1 plus the potential intermediate for metabolite **B**, *N*-(4-chlorophenyl)-*N'*-methoxy-*N'*-hydroxymethylurea were detected. $^{14}CO_2$ was also found. The fate of the intermediate *N*-(4-chlorophenyl)-*N'*-methoxy-*N'*-hydroxymethylurea was investigated further (Ebing and Haque, 1981). It was synthesized as a ^{14}C-ring-labeled β-glucoside and applied to soil. The main conversion product in soil was *N*-(4-chlorophenyl)-urea (Fig. 1, **C**), in addition to *N*-(4-chlorophenyl)-*N'*-methoxy-*N'*-hydroxymethylurea, *N*-(4-chlorophenyl)-*N'*-hydroxymethylurea, and *N*-(4-chlorophenyl)-*N'*-methoxyurea (Fig. 1, **B**). Traces of 4-chloroaniline (Fig. 1, **D**) and significant amounts of 4-chloroacetanilide and *N*-(4-chlorophenyl)methylcarbamate were also found. Soil-bound residues were detected, too; 29% of these were bound to the fulvic acid fraction, 20% to the humic acid fraction, and 9% to humin. These soil-bound residues were shown to be similar to the free metabolites of the glucoside applied (Haque *et al.*, 1981). Among soil-bound metabolites liberated by various methods, there were also ring-hydroxylated products. Bound and conjugated residues were available both to earthworms and to ryegrass (Haque *et al.*, 1982).

In plants, experiments were carried out with carbonyl-^{14}C-labeled (Börner *et al.*, 1969) and with phenyl-^{14}C-labeled compounds (Schuphan and Ebing, 1978; Ebing and Schuphan, 1979; Sotiriou *et al.*, 1980). With carbonyl-^{14}C-labeled monolinuron, a rapid uptake by both weeds and crops was demonstrated (Börner *et al.*, 1969). *N*-(4-Chlorophenyl)-*N'*-methoxyurea (Fig. 1, **B**) and *N*-(4-chlorophenyl)-urea (Fig. 1, **C**) were identified as metabolites. The presence of *N*-(4-chlorophenyl)-*N'*-methylurea (Fig. 1, **A**) or of *N*-(4-chlorophenyl)-*N'*-methyl-*N'*-hydroxyurea was uncertain. The concentrations of ring-labeled monolinuron-derived residues in potatoes and barley were lower after fertilization with various doses of urea than without fertilization (Sotiriou *et al.*, 1980). In spinach, cress, and potatoes grown in soil treated with phenyl-^{14}C-labeled monolinuron, *N*-(4-chlorophenyl)-*N'*-methoxy-urea (Fig. 1, **B**), *N*-(4-chlorophenyl)-*N*′-methylurea (Fig. 1, **A**), *N*-(4-chlorophenyl)-urea (Fig. 1, **C**), *N*-(4-chlorophenyl)-*N*′-hydroxymethylurea, and *N*-(4-chlorophenyl)-*N*′-methoxy-*N*′-hydroxymethylurea were identified (Schuphan and Ebing, 1978; Ebing and Schuphan, 1979). The fate of the intermediate, *N*-(4-chlorophenyl)-*N*′-methoxy-*N*′-hydroxymethylurea-β-glucoside was investigated further. In spinach, it was hydrolyzed and converted to *N*-(4-chlorophenyl)-*N*′-hydroxymethylurea, *N*-(4-chlorophenyl)-*N*′-methoxyurea (Fig. 1, **B**), *N*-(4-chlorophenyl)-urea (Fig. 1, **C**), and *N*-(4-chlorophenyl)-methylcarbamate (Ebing and Haque, 1981).

Complete mass balances of monolinuron, both carbonyl-^{14}C- and phenyl-^{14}C-labeled, were established in closed laboratory soil–plant systems (Schuphan and Ebing, 1978; Ebing and Schuphan, 1979; Schärer, 1983). Outdoor mass balance studies with methyl-^{14}C-labeled monolinuron were reported by Süss (1978). In plants (corn, wheat, and carrots) grown in monolinuron-treated soil, radioactivity was detectable only during the first year; the residual radioactivity found in the soil 4–5 years after application was 5–8% of the original level.

In spite of the large amounts of information on fate and metabolism of monolinuron in soil and plants, complete mass balances of monolinuron and all of its conversion products under outdoor conditions have not been reported. In the outdoor experiment reported by Süss (1978), ^{14}C in soil was neither separated nor characterized. Also, methyl-^{14}C-labeling does not account for the fate of the more stable part of the molecule, the phenylurea ring. Since mass balance is quite different between closed and open systems, in the present study experiments on the mass balance of ^{14}C-ring-labeled monolinuron during two growing seasons are reported under open-air conditions. The second aim of this paper is to isolate and identify further conversion products of monolinuron, which were not reported thus far from laboratory experiments. The isolation and identification of plant metabolites imply realistic plant uptake rates. These are not given if small pots with limited root space for the plants are used (Caro, 1969). Therefore, in the present investigation larger experimental units were used. Conversion products in soil and plants were isolated, identified, and quantified.

MATERIALS AND METHODS

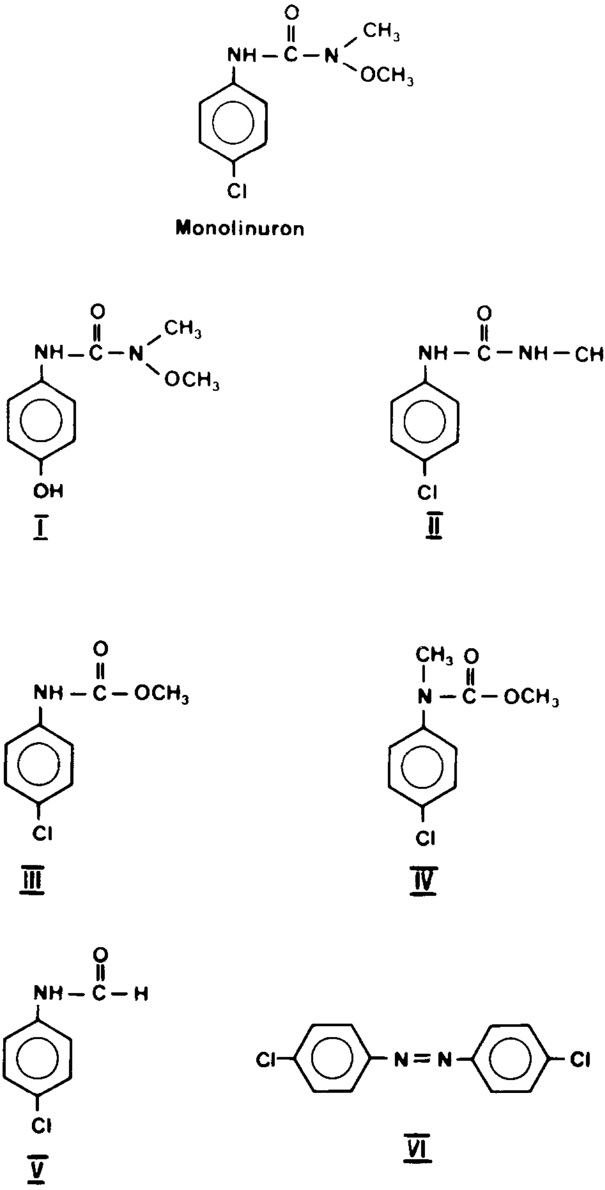
Apparatus

Radioactivity of liquid samples (leached water, methanolic extracts, chromatographic fractions, dissolved isolated conversion products) was determined by measuring 100-, 200-, and 500-μl aliquots in a liquid scintillation counter (Packard Tri-Carb 3375 or 3380). The remaining radioactivity in extracted solid samples was determined by combustion in a sample oxidizer Packard Tri-Carb 306. For the localization of radioactive zones on thin-layer plates, a radio TLC scanner LB 2722 from Berthold (FRG) was used. Column chromatography fractions were assayed for radioactivity with a flow-through scintillation counter with a glass scintillation cell from Berthold/Frieseke (FRG). Mass spectra were taken with a combined gas chromatograph/mass spectrometer (GC/MS) LKB 9000 from LKB Produkter AB S-1165, Bromma, Sweden.

Reagents

[*phenyl*-^{14}C]Monolinuron was synthesized in this Institute (Attar *et al.*, 1973); specific activity was 5 mCi/mmol, and radiochemical purity 99%. Formulating agents were supplied by Farbwerke Hoechst (Frankfurt/Main, FRG).

Authentic reference compounds for the conversion products identified were synthesized according to well-known methods described in the literature. Conversion product **I** (Fig. 2, *N*-[4-hydroxyphenyl]-*N'*-methoxy-*N'*-methylurea) was synthesized from 4-aminophenol, phosgene, and *N*-methyl-*O*-methyl-hydroxylamine, analogous to the synthesis of the buturon metabolite, *N*-[4-hydroxyphenyl]-*N'*-methyl-*N'*-isobutinylurea (Haque *et al.*, 1977). Conversion products **II** (Fig. 2, *N*-[4-chlorophenyl]-*N'*-methylurea) and **III** (Fig. 2, *N*-[4-chlorophenyl]-methylcarbamate) were prepared as described by Haque *et al.* (1976). Conversion product **IV** (Fig. 2, *N*-[4-chlorophenyl]-



IG. 2. Conversion products of monolinuron isolated from soil and plants after long-term outdoor exposure.

N-methyl-methylcarbamate) was made according to Haque *et al.* (1976) and Tanaka and Wien (1973), product **V** (Fig. 2, 4-chloroformanilide) according to Slosson (1895), and product **VI** (Fig. 2, 4,4′-dichloroazobenzene) according to Burns *et al.* (1928).

The particle size distribution of the soil used was: coarse sand (0.2–2.0 mm) 49.2%, fine sand (0.06–0.2 mm) 27.0%, silt (0.002–0.06 mm) 10.3%, clay (<0.002 mm) 13.5%. Organic matter was 1.2%, pH 7.0.

For scintillation counting of liquid samples, a scintillation liquid based on dioxane was used. $^{14}CO_2$ obtained after the combustion of extracted soil samples was trapped and counted in a toluene-based scintillation liquid containing phenethylamine.

For precleaning extracts by TLC, 20 × 20-cm plates were self-coated with silica gel G from Macherey, Nagel & Co. (FRG). For further purification steps, ready-coated 20 × 20-cm silica gel plates (PSC, without fluorescence indicator, 2-mm thickness, Merck, FRG) were used.

Gel permeation was carried out using Merckogel PVA 500, excluding weight 500, and acetone as the mobile phase.

For gas chromatography/mass spectrometry, glass columns 2 m × 4 mm with 1% OV-1 on Chromosorb or 1 m × 4 mm with 1% XE-60 on Chromosorb were used.

Procedure

Plant growing and sample preparation. Experiments were carried out in an outdoor lysimeter as described by Scheunert *et al.* (1977, 1986). Plants were grown in a water-resistant plywood box (60 × 60 × 60 cm) with a perforated base. The box was placed in a metal tray to collect the leached water. The box was filled with 160 kg of soil to 1 cm from the top and was kept in a large pit with the upper surface of the soil at the same level as the surrounding ground. In each of two summers, potatoes were grown; each growing period covered the time between planting (spring) and harvest (autumn). Four potatoes were planted 8–10 cm deep and about 20 cm apart. Fertilization was the same as that in agricultural practice. Before emergence, [^{14}C]monolinuron was sprayed on the soil surface as a 47% formulation; doses, growing times, and climatic conditions are listed in Table 1. The dose given in the second year was calculated as a supplement to the residue left in soil from the dose of the first year in order to obtain similar soil concentrations in both years.

TABLE 1

EXPERIMENTAL CROP GROWING CONDITIONS AFTER APPLICATION OF [^{14}C]MONOLINURON TO SOIL

Growth parameter	First growing period	Second growing period
Dose of [^{14}C]monolinuron	90 mg = 2.5 kg/ha	69 mg = 1.9 kg/ha
Crop	Potatoes	Potatoes
Duration of growth	15 weeks	13 weeks
Daily maximum air temperature, range of average per week	21–33°C	18–26°C
Daily minimum air temperature, range of average per week	10–18°C	7–15°C
Rainfall	138 mm	213 mm

During the experiment, supplemental water was supplied to the plants only during very dry periods. The leached waters were collected in the metal trays after every heavy rainfall and analyzed immediately for radioactivity.

After the harvest, the different parts of the plants were separated, weighed, and stored at −20°C until analysis. Immediately after harvest, four representative soil samples of about 400–600 g each were taken from different depths with the help of an auger. These samples were also stored at −20°C until analyzed. The moisture content of soil samples was determined by drying to constant weight in a vacuum desiccator at room temperature.

Soil samples were extracted twice by stirring with cold methanol for 48 hr; a third extract contained less than 1% of the radioactivity extracted by the first stirring procedure. The leachate was extracted by shaking twice with diethylether. The plant samples were homogenized with cold methanol in an Ultraturrax and extracted, similarly to the soil samples, by stirring twice with cold methanol.

Radioactivity measurements. The radioactivity in the extracts and in the leached water was determined by counting in a liquid scintillation counter. From each liquid, aliquots of 50, 100, 200, and 500 μl were counted four times each; the coefficients of variation between aliquots were, depending on radioactivity level, between ±0.9 and ±6.2%. Unextracted radioactivity in plants and soil was determined by combustion. Aliquots of 150–350 mg extracted soil or plant material were combusted, and $^{14}CO_2$ was trapped. Each $^{14}CO_2$ sample was counted four times in a liquid scintillation counter. The coefficients of variation between aliquots were, depending on radioactivity, ±1.5–±10%. The coefficients of variation between the four measurements were ±0.3–±7.4%, depending on radioactivity. Total radioactivity in each soil or plant sample was calculated as the sum of radioactivity in the extracts and unextractable radioactivity. The coefficient of variation of total radioactivity among the four soil samples from the same depth was about ±18%. The four plant samples could not be analyzed separately because of low radioactivity. They were combined and analyzed.

Isolation of conversion products. For isolation of conversion products *in soil*, the methanol extracts were concentrated in a rotary evaporator and precleaned on self-coated silica gel thick-layer plates using dichloromethane as a solvent. Three radioactive zones having R_f values of 0–0.12, 0.18–0.71, and 0.82–0.97 were obtained. Each of these radioactive fractions was extracted from silica gel with methanol and the corresponding fractions of each year were combined. The extracts were concentrated and rechromatographed with ethylacetate as a solvent. Most of the natural by-products coextracted from the soil moved to the solvent front and were discarded. The three fractions were purified and separated further by TLC using solvent mixtures of increasing polarity (*n*-hexane; benzene; dichloromethane; benzene/ethylacetate, 3/1; ethylacetate).

The radioactive material *extracted from the leachate* was purified by repeated TLC with benzene and dichloromethane as solvents. The radioactivity consisted of only one compound.

For isolation of conversion products *in plants*, the methanol extracts of both years were combined and concentrated in a rotary evaporator. The radioactive products were separated from most of the coextracted biological by-products by gel permeation. They were eluted twice with acetone from a gel bed with an excluding weight of 500. The fractions obtained were further purified by repeated TLC with solvent mixtures as described for soil fractions.

Identification. In order to identify monolinuron and its conversion products **I** and **III** (Fig. 2), mass spectra were taken by direct inlet into the mass spectrometer at 20–200°C. The mass spectra of the other conversion products were taken after gas chromatography; column temperature was 100–230°C. Ionization energy of mass spectrometry was 70 eV. Detection was by determination of the total ion current. The mass spectra were compared with those of authentic reference compounds.

RESULTS AND DISCUSSION

Mass Balance and Residues

The mass balance of radioactivity in the soil–plant system after application of [^{14}C]monolinuron to soil is shown in Table 2. It can be seen that even after one growing period only about half of the radioactivity applied was recovered. The loss is considerably higher than that from biomineralization to CO_2 observed in closed laboratory systems. Süss and Eben (1978) found 9–23% of $^{14}CO_2$ formed from phenyl-^{14}C-labeled monolinuron in various soils after 16 weeks; Ebing and Schuphan (1979) found only about 5% in closed laboratory soil–plant systems after 125 days. However, the recovery of ^{14}C derived from the ^{14}C-labeled phenylurea herbicide buturon under outdoor conditions (49%; Haque *et al.*, 1977) was similar to that found in this monolinuron experiment. The more rapid residue loss in our study probably is partly due to higher volatilization as a consequence of the application procedure in which the soil surface was sprayed whereas in literature studies monolinuron was incorporated into the soil. Furthermore, differences in soil properties are potential causes for different residue losses between various experiments.

The amounts of radioactivity taken up by plants and those leached into water were not significant with regard to total mass balance.

After the second growing period, the residues in soil, plants, and leachate decreased, demonstrating continuous degradation.

The radioactive residues in different soil layers and plant parts, expressed as milligrams (calculated as monolinuron) per kilograms soil or plant mass, are listed in Table

TABLE 2

MASS BALANCE OF ^{14}C IN A SOIL/POTATO SYSTEM AFTER APPLICATION OF [^{14}C]MONOLINURON TO SOIL

Sample	% after first growing period	% after second growing period[a]
Soil	53.94	41.36
Plants	0.90	0.57
Leachate	0.11	0.09
Plants, 1st period		0.51
Leachate, 1st period		0.06
Sum	54.95	42.59
Loss into the atmosphere	45.05	57.41

Note. Values are percentages of total ^{14}C initially applied.

[a] A second application was performed at the beginning of the 2nd growing period; values are percentages of the sum of both applications.

3. The table shows that in soil the highest concentration is in the upper layer where the herbicide had been applied; with increasing depth, the residues decrease. After the second growing period, the residues in the upper soil layer were lower than after the first growing period; however, in the deeper layers they were higher, indicating leaching of ^{14}C-labeled residues into the soil. The unextractable portions of radioactivity exceeded extractable ones by a factor of 3–5. These ratios are in the range of those found by Süss and Eben (1978) in various soils in laboratory experiments, whereas Ebing and Schuphan (1979) found nearly equal amounts of extractable and unextractable radioactivity.

Residues were low in tubers and high in plant shoots. The accumulation of monolinuron especially in leaves was reported by Börner *et al.* (1969). After two vegetation periods, concentrations in tubers and roots were lower than after one vegetation period, whereas residues were higher in shoots. In plants, the unextractable portions of radioactivity were also considerable.

Identification and Quantification of Conversion Products

The conversion products isolated, identified, and quantified in soil, leachate, or plants are listed in Table 4. The data listed in this table are related to total residues after 2 years.

The parent compound, monolinuron, was detected only in soil, not in plants. The radioactivity detected in soil at the end of the experiments, as well as that in leachate and plants, corresponded to six identified conversion products, to unidentified extracted metabolites, and to unextractable residues. The latter represented by far the largest portion of radioactive substances in all parts of the soil–plant system.

The formula of monolinuron and its identified conversion products are presented in Fig. 2. When Fig. 2 is compared with Fig. 1, it is obvious that the conversion

TABLE 3

RADIOACTIVE RESIDUES IN SOIL AND POTATO PLANTS AFTER APPLICATION OF [^{14}C]MONOLINURON TO SOIL

	After first period			After second growing period		
Sample	Extractable	Unextractable	Total	Extractable	Unextractable	Total
Soil, 0–20 cm depth	0.150	0.426	0.576	0.178	0.392	0.570
Soil, 20–30 cm depth	0.011	0.056	0.067	0.043	0.110	0.153
Soil, 30–40 cm depth	0.006	0.028	0.034	0.028	0.082	0.110
Soil, 40–50 cm depth	0.002	0.008	0.010	NA	NA	NA
Peeled tubers	0.075	0.031	0.106	0.075	0.016	0.091
Peels	0.171	0.230	0.401	0.092	0.151	0.243
Shoots	3.91	12.03	15.94	11.68	7.19	18.87
Roots	1.81	10.87	12.68	0.71	4.87	5.58

Note. NA, not analyzed. Milligrams, calculated as monolinuron, per kilograms air-dried soil or fresh plant mass.

TABLE 4

RADIOACTIVE PRODUCTS ISOLATED FROM SOIL, LEACHATE, AND POTATO PLANTS AFTER APPLICATION OF [^{14}C]MONOLINURON TO SOIL

Metabolite number	Compound	% in soil	% in leachate	% in plants
Parent compound	Monolinuron (*N*-[4-chlorophenyl]-*N*′-methoxy-*N*′-methylurea)	15.0	ND	ND
I	*N*-(4-Hydroxyphenyl)-*N*′-methoxy-*N*′-methylurea	0.2	0.8	1.0
II	*N*-(4-Chlorophenyl)-*N*′-methylurea	2.0	ND	10.5
III	*N*-(4-Chlorophenyl)-methylcarbamate	2.5	ND	8.0
IV	*N*-(4-Chlorophenyl)-*N*-methylmethylcarbamate	0.5	ND	0.02
V	4-Chloroformanilide	0.2	ND	ND
VI	4,4′-Dichloroazobenzene	ND	ND	0.1
	Unidentified extracted metabolites	2.5	ND	22.5
	Unextractable residues	77.1	99.2	57.9

Note. ND, none detected. Values are percentages of total ^{14}C present in soil, leachate, or plants.

products detected after long-term exposure under outdoor conditions were only partially identical with those formed by microbial degradation in the laboratory.

Conversion product **I** (Table 4 and Fig. 2), *N*-(4-hydroxyphenyl)-*N*′-methoxy-*N*′-methylurea, is the largest molecule among the conversion products. The only change which occurred is the replacement of chlorine by hydroxyl at the phenyl ring. This product was detected in small amounts in soil and plants and was the only extractable and identifiable conversion product in the leachate. It was not reported thus far in former works on monolinuron in the soil–plant system; however, an analogous product was isolated from leachate after application of the phenylurea herbicide buturon (Haque *et al.*, 1977).

Conversion product **II** (Table 4 and Fig. 2), *N*-(4-chlorophenyl)-*N*′-methylurea, was the only product among the microbial transformation products shown in Fig. 1 which could be detected in these outdoor studies. The other products shown in Fig. 1 (**B**–**D**), as well as the intermediates, *N*-(4-chlorophenyl)-*N*′-methoxy-*N*′-hydroxymethylurea and *N*-(4-chlorophenyl)-*N*′-hydroxymethylurea, found by Schuphan and Ebing (1978) in the laboratory were not detected. It is assumed that these products were transformed further to unknown secondary products under long-term outdoor conditions or mineralized completely. It seems that metabolic processes occurred slower in the laboratory than under outdoor conditions, due to different soil types and to less favorable environmental conditions.

Conversion product **III** (Table 4 and Fig. 2), *N*-(4-chlorophenyl)-methylcarbamate, possibly is formed by abiotic reactions in soil and then taken up by plants; it has been reported to be formed by heating phenylurea herbicides with methanol or by irradiation of monolinuron in aqueous solutions (Kotzias *et al.*, 1974). Since, in our study, extraction was performed with cold methanol, this conversion product cannot be regarded as an artifact. It might be a product formed by sunlight irradiation or by enzymes. It was also found by Ebing and Haque (1981) after application of the intermediate metabolite *N*-(4-chlorophenyl)-*N'*-methoxy-*N'*-hydroxymethylurea-β-glucoside to plants and soil and by Haque *et al.* (1976, 1977) as a conversion product of the phenylurea herbicide buturon in soil and wheat plants.

Conversion product **IV** (Table 4 and Fig. 2), *N*-(4-chlorophenyl)-*N*-methyl-methylcarbamate, represents a methylation product of conversion product **III.** It was also found by Haque *et al.* (1976, 1977) as a conversion product of the phenylurea herbicide buturon in soil, leachate, and wheat plants.

Conversion products **V** (Table 4 and Fig. 2), 4-chloroformanilide, and **VI** (Table 4 and Fig. 2), 4,4'-dichloroazobenzene, result from further biological reactions of the microbial metabolite 4-chloroaniline (Fig. 1, **D**). Neither has been identified thus far as a metabolite of monolinuron in the soil–plant system; however, both were isolated from soil and plants after soil application of 4-chloroaniline (Freitag *et al.*, 1984). *N*-Formylation, resulting in conversion product **V,** is known as an enzymatic process; e.g., the fungus *Fusarium oxysporum* is able to convert free amino and/or hydroxyl groups to acetyl or formyl derivatives (Kaufman, 1974). For 4-chloroaniline, this formylation product was found in algae (Anagnostopoulos *et al.*, 1978); however, the enzymatic origin could not be proven unequivocally. In our outdoor system, the formylated 4-chloroaniline was detected only in soil, not in plants.

Dimerization products of anilines, such as the azobenzene **VI** (Table 4 and Fig. 2), are postulated to be formed only from higher concentrations of anilines (Parris, 1980). However, the azobenzene **VI** was detected in soil after application of only 1.25 ppm 4-chloroaniline (Freitag *et al.*, 1984). It is assumed that 4-chloroaniline is accumulated in soil microorganisms to a concentration which makes the dimerization possible. In our outdoor study, **VI** was detected only in plants which contained considerable concentrations of monolinuron-derived ^{14}C.

Some more conversion products extracted from soil and plants were isolated; however, they could not be identified. No attempts were made to solubilize and identify soil-bound residues.

CONCLUSION

It may be concluded that monolinuron is rapidly degraded in the soil–plant system and is transformed to various conversion products of abiotic and/or biotic origin. The structures of these conversion products were elucidated by GC/MS; they comprised alterations of the side chain as well as a dimerization product of 4-chloroaniline. It may be also concluded from this study that environmental conditions play an important role in conversion reactions of monolinuron. Under outdoor conditions, intermediates are subjected to ongoing conversion processes to form further soluble or soil-bound products or carbon dioxide.

Special attention should be paid to the presence of residues of conversion products in edible parts of crops.

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