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FATE OF ^{14}C-ALLYLALCOHOL HERBICIDE IN SOILS AND CROP RESIDUES

Key Words: ^{14}C-allylalcohol, soil, residues, carrots, lettuce

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ABSTRACT

Residue disappearance and leaching of ^{14}C-allylalcohol from different soils were studied in laboratory experiments. Additionally, the uptake of residues by lettuce and carrots was investigated in the greenhouse. In laboratory experiments, residue disappearance and leaching from soils was correlated negatively to the organic matter content. In greenhouse experi-

ments with a sandy loam soil at an application rate normally used in practice, an average of 12.5 % of the applied radioactivity was recovered after an eight day interval between application and sowing. Furthermore, an average of 8 % (sum in soil and plants) of the applied radioactivity was recovered after lettuce or carrot growing. Uptake of residues was higher by carrots than by lettuce, and higher by lettuce roots than by lettuce tops. No bioaccumulation was observed. The residues in soils and plants were, to a high percentage, unextractable and, to a smaller extent, fully water-soluble products. Unchanged allylalcohol could not be detected by the analytical methods used.

INTRODUCTION

Allylalcohol (Trade name in Germany: "Shell Unkrauttod A ®") is used as a preplanting herbicide against germinating weed seeds in sowing and planting beds prepared in greenhouses for vegetables and ornamentals. The herbicide is reported to disappear from the soil within seven to nine days after application; after this period, all kinds of crops can be sown without plant damages [1].

The disappearance of allylalcohol residues from soil was concluded mainly from the disappearance of herbicidal activity. This, however, does not necessarily imply total degradation. Biological degradation studies in water were performed by chemical and biological oxygen demand and total organic carbon determinations [2-3]. A 50 - 80 % degradation after 1 - 5 days of retardation was found in river water at 20°C by biological oxygen demand determination [2]. For soil, balance studies with radiolabelled chemical are appropriate for assessing total residue losses which occur either by total degradation or by volatilization of the parent compound or conversion products. Such studies give information also on migration and leaching of radioactive residues in soil and their uptake by plants. According to our knowledge, such studies have not been reported.

Likewise, very little information is available on the chemical nature of metabolites of allylalcohol in organisms. A scheme of identified and of suspected metabolic pathways in the biosphere is presented in Fig. 1.

In rats, allylalcohol is converted to mercapturic acid [4-5]. The fungus Botrytis cinerea oxidizes allylalcohol to acrolein [6]. As to the conversion of allylalcohol in

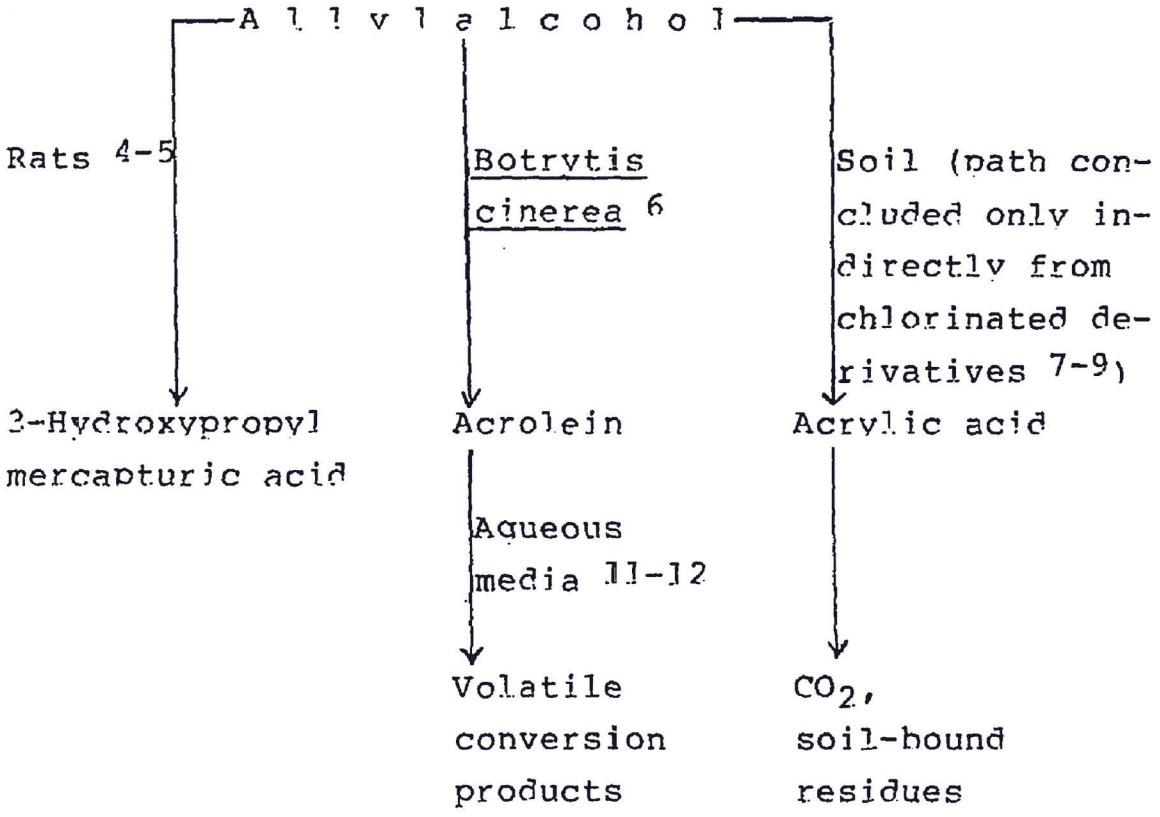

FIGURE 1. Identified and Suspected Metabolic Pathways of Allylalcohol in the Biosphere

soil, some further conclusions can be drawn from experiments with pesticides having a similar chemical structure. Cis- and trans-3-chloroallylalcohol, intermediates in the degradation of the corresponding 1,3-dichloropropenes (preplant fumigants used for the control of parasitic nematodes and fungi), are converted to carbon dioxide and chloride ion by a Pseudomonas species isolated from soil, isomeric 3-chloroacrylic acids being intermediates [7-8]. In soil, both chloroallylalcohols were in part strongly bound, in part

converted to the corresponding chloroacrylic acids which, in turn, were partly complexed or bound also [9].

By studies with herbicides containing chlorinated thioallylalcohol moieties [10], it was shown that soil binding increases with decreasing chlorine content. Thus, it may be predicted that unsubstituted allylalcohol is strongly bound via acrylic acid to soil so rapidly that, after one growing period, free acrylic acid will not be identifiable. Acrolein, also, is probably only an intermediate since it decays to conversion products which also dissipate rapidly [11-12]. Therefore, the present study concentrates on the determination of soil bound products and of volatilization/mineralization by means of balance studies, rather than identifying intermediates. Laboratory screening of degradation (including volatilization) and leaching is followed by corresponding studies in large greenhouse boxes; the uptake of radioactivity by lettuce and carrots is included in the investigations.

MATERIALS AND METHODS

Materials

Allylalcohol-2,3-^{14}C (specific activity 0.46 mCi/mmole, 707 mg with 2 mg p-methoxyphenol) was sup-

TABLE 1

Properties of Soils Used

Soil	Particle size distribution (%)				Organic C	pH
	0.002	0.002-0.02	0.02-0.2	0.2	(%)	
(1) Sand	4.0	3.5	35.4	57.1	0.51	6.8
(2) Sand	6.8	9.6	30.1	53.5	2.89	6.9
(3) Sandy loam	9.2	12.4	37.6	40.8	1.00	6.1
(4) Sandy loam	11.4	34.2	44.3	10.1	1.16	6.5

Soil 1-3 used in laboratory experiments, soil 4 in greenhouse

plied by New England Nuclear in a sealed vial. For the laboratory studies, the substance was mixed with non-radioactive technical formulation "Shell Unkrauttod A" (active ingredient: 850 g/litre), resulting in a specific radioactivity of 0.0035 µCi/mg. The application rate was 970 ppm to soil. For the greenhouse experiments, 727 µl of the original allylalcohol-^{14}C, 56.86 ml of the technical preparation and 11.52 l of water

were mixed for application to eight boxes 60 x 60 cm surfaces, resulting in the recommended application rate of 17 g active ingredient/m^2 and a specific radioactivity of 0.093 μCi/mg.

The properties of the soils used are shown in Table 1.

All solvents and reagents used were analytical grade.

Laboratory Experiments with Soils

For degradation (including volatilization) studies, soils 2 and 3 (Table 1) were air-dried; stones, gravel and other coarse byproducts were removed by sifting through a 1-mm-sieve. After determination of maximal water-holding capacity [13], distilled water was added to the soils for 40 % of the maximal capacity. Nine 100 g (dryweight) samples of soil 2 and ten 100 g samples of soil 3 were treated with 97 mg of allylalcohol dissolved in 300 μl of water and mixed by vigorous shaking. The samples were kept in bottles closed with cotton plugs at 22°C in the dark; at 3 day intervals, water loss was determined by weighing, the evaporated amount of water was restored, and the sample mixed by shaking.

After different time intervals, one sample of each soil was extracted with acetone in a soxhlet for

16 hours. For the longest testing period (85 days), triplicates or duplicates were run in order to check the repeatability of the method. The radioactivity was determined in solutions as well as in the extracted soils.

For leaching studies, 28.46 mg samples of ^{14}C-allylalcohol were dissolved in 1.5 ml of water and applied to soils 1-3 (Table 1) filled in glass columns, length 300 mm, 50 mm in diameter, the lower end fitted with a glass frit D2, 50 mm in diameter. During 2 days, the radioactivity was eluted with about 400 ml of water. The radioactivity in the water was determined.

Greenhouse Experiments

Greenhouse experiments were carried out with eight boxes 60 x 60 x 70 cm constructed from water-resistant plywood. The base of the boxes contained holes to permit the drainage of any eventual excess of irrigation water which could be collected in a metal splash tray. The boxes were wrapped in aluminum foil on the outside to prevent temperature increases in the soil. The bottom 25 mm of the boxes was packed with stone chips of about 25 mm in diameter and these with a 25 mm layer of sand. The boxes were filled with soil 4 (Table 1) to 1 cm from the top. The soil was allowed

to settle for 1 month before planting. The boxes were placed in a greenhouse (2.6 x 6.5 m, height 2.4 m).

^{14}C-Allylalcohol, corresponding to 17 g active ingredient/m^2 in 4 l water, was poured on the soils with a sprinkling can. After 8 days, soil samples were taken from each box to a depth of 10 cm. Then the soil was treated with 10 g "Nitrophoska blau" fertilizer/box. Crops were sown in two rows/box, intervals 20 cm, as listed in Table 2. Immediately, each box was irrigated with 1.5 litres of water. Carrots were refertilized with 10 g "Nitrophoska blau"/box after seven weeks. Growth conditions are shown in Table 3; crop yields are included in Table 2.

At harvest, the crops were separated into tops and roots. The roots were washed with water and dried shortly at room temperature. Roots and tops were separately prepared for analysis. The total quantity of each sample was chopped, homogenized in acetone with an Ultra-Turrax, and filtered. This filtrate was assumed to be free of artifacts from working up procedure and was used for residue characterization.

The filter residue was washed ten times with cold acetone, then reextracted in a soxhlet with acetone for 48 hours. The radioactivity was determined in the extracts as well as in the extracted material. The sum of radioactivity in the extracts was defined as "ex-

TABLE 2

Crop Yields in Greenhouse Experiments with ^{14}C-Allylalcohol, Carrots and Lettuce (area 60 x 60 cm)

Box number	Crop	Variety	Yield (roots)	Yield (tops)
1	Carrots	"Nantaise, Typ Marktgärtner"	0.75 kg	0.87 kg
2	"	"	0.74 kg	0.9 kg
3	"	"Pariser Markt"	0.6 kg	0.65 kg
4	"	"	0.55 kg	1.2 kg
5	Lettuce	"Attraktion"	0.09 kg	0.85 kg
6	"	"	0.09 kg	0.9 kg
7	"	"Brauner Trotzkopf"	0.07 kg	1.0 kg
8	"	"	0.06 kg	0.8 kg

tractable", the radioactivity left in the plant material as "unextractable".

Soil samples (about 500 g each) were taken at harvest from each box at depths of 0 - 10 cm, 10 - 20 cm, 20 - 30 cm, and 30 - 50 cm from the surface. Aliquots (50 g) were used for determination of water content by drying at room temperature to constant weight in a vacuum desiccator. The remaining sample was first extracted with cold acetone as described for the plant

TABLE 3

Conditions for Greenhouse Experiments with ^{14}C-Allylalcohol, Lettuce and Carrots

		Interval between application and sowing	Lettuce growth	Carrot growth
Time		8 days	2 months	3 months
Watering (cumulatively)		none	10 litres/box	30 litres/box
Air temperature (^{o}C)	mean daily max.	26	29	28
	mean daily min.	17	15	15
Air humidity (rel.%)	mean daily max.	75	90	90
	mean daily min.	55	70	70
Atmospheric pressure (mm Hg)	max.	769	764 (mean weekly)	764 (mean weekly)
	min.	757	758 (mean weekly)	755 (mean weekly)
Light (lux) at noon			13 000 - 16 000	10 000 - 12 000

material to characterize the residues, then reextracted in a soxhlet with acetone for 48 hrs, and the "extractable" and "unextractable" radioactivity was determined.

For characterization of residues, the extracts obtained by cold extraction were evaporated at room temperature with a rotary evaporator (condenser -20^{o}C;

loss < 5 %). After evaporation of the solvent, a water fraction was left which was extracted twice with ether. Etheric and aqueous phase were analyzed for radioactivity.

Determination of Radioactivity

For determination of radioactivity in extracts and water, liquid scintillation counters "Tri-Carb" 3375, 3380 and 3385, Packard, were used (scintillation liquid based on dioxane). For determination of unextractable residues, the extracted soil and plant samples were air-dried. After homogenization, aliquots of 100 - 200 mg were combusted in an automatic oxidizer "Oxymat", Intertechnique, to $^{14}CO_2$ which was absorbed in a scintillation liquid based on toluene and containing phenethylamine, and counted in a liquid scintillation counter ("Tri-Carb" 2425, Packard).

RESULTS AND DISCUSSION

Laboratory Experiments with Soil

The results of the studies on residue disappearance are presented in Tables 4 and 5. Additional tests run for 85 days showed a recovery of 21.5 and 20.8 % for sand (2) and 10 % for sandy loam (3), indicating the repeatability of recovery data under the experimental conditions used.

TABLE 4

Radioactive Residues in Sand Soil (2) following Incubation with ^{14}C-Allylalcohol at Room Temperature (970 mg/kg)

Time (days)	Total radioactivity recovered (% of applied amount)	Extractable radioactivity (% of applied amount)	Extractable radioactivity (% of recovered amount)
4	67.5	57.4	85.0
6	62.2	42.5	68.3
8	53.2	24.0	45.2
12	53.5	16.2	30.2
19	33.5	7.6	22.8
30	23.7	1.2	5.7
85	23.4	0.6	2.5

TABLE 5

Radioactive Residues in Sandy Loam (3) following Incubation with ^{14}C-Allylalcohol at Room Temperature (970 mg/kg)

Time (days)	Total radioactivity (% of applied amount)	Extractable radioactivity (% of applied amount)	Extractable radioactivity (% of recovered amount)
4	59.2	16.4	27.7
6	50.6	6.7	13.2
8	16.6	1.3	7.8
10	21.4	1.5	7.0
12	12.5	0.7	5.8
18	9.8	0.9	9.4
25	11.1	1.0	9.0
36	15.8	0.9	5.8
85	10.9	0.9	8.3

When the residue data in the two soil types are compared, it is evident that the half-life of residues is longer in the sand than in the sandy loam. This may be explained by the higher organic carbon content of this soil (see Table 1).

Binding of radioactivity resulting in unextractable residues is nearly constant from day 8 until day 85 of the experiment with sandy loam; for about 30 days, it is higher than in the sand soil. From this observation it is evident that the formation of unextractable residues follows other mechanisms than the total residue decline which is mostly due to loss of extractable, non-bound compounds. Information on the chemical nature of unextractable residues and on the site of binding is very limited up to now. For some chemical compounds, it has been demonstrated that the organic matter of soil is the site of chemical binding. However, for allylalcohol the data presented here suggest that the binding site of unextractable residues is not only the organic matter but also inorganic soil constituents, at least during the first 30 days of experiment. The inorganic binding sites could be clay minerals, which are an important constituent in loam but less in sand (Table 1). The interaction of adsorbed allylalcohol molecules, filling the

inter-layer space of clay minerals, with OH-groups and cations on the surface has been reported [14].

The results of leaching experiments are shown in Table 6. It can be seen from this table that leaching is fastest in the sand (1) and slowest in the sand (2) with highest humus content. This indicates that humus is the soil constituent most important for retardation of leaching .

Greenhouse Experiments

The results obtained from greenhouse experiments with soil, carrots and lettuce in boxes 1 - 8 are presented in Tables 7 - 10.

An examination of the mass balance of radioactivity (last columns in Tables 7 - 10) reveals that only between 11 and 15 % (average: 12.5 %) of the radioactivity applied was left after the 8 days between

TABLE 6

Radioactivity leached from Soil Columns (% of applied amount; 2 days, 400 ml water), after Application of ^{14}C-Allylalcohol

Soil Type	% leached after 2 days (% of applied amount)
Sand Soil (1)	100
Sand Soil (2)	83.3
Sandy Loam (3)	98.6

TABLE 7

Radioactive Residues in Soil and Carrots ("Nantaise, Typ Marktgärtner") after Application of ^{14}C-Allylalcohol to Soil under Greenhouse Conditions

Sample	mg/kg/Box 1			mg/kg/Box 2			% of appl. radioact. Box 1	% of appl. radioact. Box 2
	extract.	unextr.	total	extract.	unextr.	total		
Soil, 0-10 cm depth after application (calculated)	153.2	-	153.2	153.2	-	153.2	100	100
Soil, 0-10 cm depth before sowing	2.0	16.2	18.2	1.8	15.1	16.9	11.9	11.0
Soil, 0-10 cm depth after harvest	0.9	9.3	10.2	0.7	8.8	9.5	6.7	6.2
Soil, 10-20 cm depth after harvest	0.5	0.6	1.1	0.1	0.3	0.4	0.7	0.2
Soil, 20-30 cm depth after harvest	0.1	0.2	0.3	<0.1	<0.1	0.1	0.2	<0.1
Soil, 30-50 cm depth after harvest	<0.1	0.2	0.2	<0.1	<0.1	<0.1	0.1	<0.1
Carrot roots	2.3	2.2	4.5	2.4	1.9	4.3	0.1	0.1
Carrot tops	1.0	4.4	5.4	0.9	3.8	4.7	0.1	0.1
Recovery (total) after harvest							7.9	6.6

TABLE 8

Radioactive Residues in Soil and Carrots ("Pariser Markt") after Application of ^{14}C-Allylalcohol to Soil under Greenhouse Conditions

Sample	mg/kg/Box 3			mg/kg/Box 4			% of appl. radioact. Box 3	% of appl. radioact. Box 4
	extract	unextr.	total	extract	unextr.	total		
Soil, 0-10 cm depth after application (calculated)	153.2	-	153.2	153.2	-	153.2	100	100
Soil, 0-10 cm depth before sowing	1.8	18.3	20.1	2.5	18.0	20.5	13.1	13.4
Soil, 0-10 cm depth after harvest	1.7	15.4	17.1	0.9	7.9	8.8	11.2	5.7
Soil, 10-20 cm depth after harvest	0.1	0.3	0.4	< 0.1	< 0.1	0.1	0.2	< 0.1
Soil, 20-30 cm depth after harvest	0.1	0.1	0.2	< 0.1	< 0.1	< 0.1	0.1	< 0.1
Soil, 30-50 cm depth after harvest	0.1	0.1	0.2	< 0.1	n.d.	< 0.1	0.1	< 0.1
Carrot roots	2.8	2.4	5.2	2.5	1.5	4.0	< 0.1	< 0.1
Carrot tops	0.7	3.6	4.3	1.0	3.1	4.1	< 0.1	0.1
Recovery (total) after harvest							11.6	5.8

n.d. = not detected

TABLE 9

Radioactive Residues in Soil and Lettuce ("Attraktion") after Application of ^{14}C-Allylalcohol to Soil under Greenhouse Conditions

Sample	mg/kg/Box 5			mg/kg/Box 6			% of appl. radioact. Box 5	% of appl. radioact. Box 6
	extract	unextr.	total	extract	unextr.	total		
Soil, 0-10 cm depth after application (calculated)	153.2	-	153.2	153.2	-	153.2	100	100
Soil, 0-10 cm depth before sowing	1.9	17.7	19.6	1.8	15.6	17.4	12.8	11.4
Soil, 0-10 cm depth after harvest	1.1	6.4	7.5	1.0	11.5	12.5	4.9	8.2
Soil, 10-20 cm depth after harvest	< 0.1	0.1	0.1	0.1	0.7	0.8	0.1	0.5
Soil, 20-30 cm depth after harvest	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Soil, 30-50 cm depth after harvest	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Lettuce roots	0.7	3.1	3.8	0.8	2.2	3.0	< 0.1	< 0.1
Lettuce tops	0.3	1.8	2.1	0.3	1.3	1.6	< 0.1	< 0.1
Recovery (total) after harvest							5.0	8.7

n.d. = not detected

TABLE 10

Radioactive Residues in Soil and Lettuce ("Brauner Trotzkopf") after Application of ^{14}C-Allylalcohol to Soil under Greenhouse Conditions

Sample	mg/kg/Box 7			mg/kg/Box 8			% of appl. radioact. Box 7	% of appl. radioact. Box 8
	extract	unextr.	total	extract	unextr.	total		
Soil, 0-10 cm depth after application (calculated)	153.2	-	153.2	153.2	-	153.2	100	100
Soil, 0-10 cm depth before sowing	1.8	15.8	17.6	2.0	20.9	22.9	11.5	14.9
Soil, 0-10 cm depth after harvest	1.1	12.3	13.4	0.7	11.2	11.9	8.7	7.8
Soil, 10-20 cm depth after harvest	0.1	1.2	1.3	0.1	1.3	1.4	0.9	0.9
Soil, 20-30 cm depth after harvest	< 0.1	0.1	0.1	n.d.	n.d.	n.d.	0.1	n.d.
Soil, 30-50 cm depth after harvest	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Lettuce roots	0.8	2.6	3.4	0.9	2.1	3.0	< 0.1	< 0.1
Lettuce tops	0.6	1.8	2.4	0.5	1.4	1.9	< 0.1	< 0.1
Recovery (total) after harvest							9.7	8.7

n.d. = not detected

application and crop sowing. This residue disappearance was completely due to volatilization of radioactivity, in the form of either unchanged allylalcohol, or of conversion products, or of CO_2, since the total residue content of the upper soil layer was determined and leaching of radioactivity to depths >10 cm was excluded due to the absence of irrigation. After the harvest, mass balances were established by analyzing all soil layers, crops, and the leaching water drained from the base of the boxes (last columns in Tables 7-10).

It turned out that leaching of radioactive substances to deeper soil layers was small during the crop growing period, in spite of frequent irrigations (Table 3). During the 2 month lettuce growing period, traces of radioactivity (0.1 - 0.9 % of applied radioactivity) were found in a depth of 10 - 20 cm (with exception of one box where additionally 0.1 % was found at a depth of 20 - 30 cm). During the 3 months' carrot growing period, leaching had occurred to a depth of 50 cm; the amount leached to depths of 10 - 50 cm varied between < 0.1 and 1 % of the applied amount. No radioactivity was detected in the water drained from the base of the boxes. The uptake of radioactivity by both plant species was 0.1 % or less

and, thus, was not relevant for the total balance. The residue disappearance at the application site (soil, 0 - 10 cm depth) during the growing period was almost entirely due to volatilization. The total amount recovered in soil and plants was, on an average, 8 % of the applied radioactivity; there was no significant difference between lettuce and carrot experiments.

The uptake of radioactivity by crops in terms of mg/kg plant weight (Tables 7 - 10, first columns) was lower for lettuce than for carrots, whereas no clear differences were discernible between the crop varieties. For carrots, residues in roots and greens were comparable, whereas for lettuce the uptake into roots was higher than that into tops. Bioaccumulation (concentration in plants higher than in soil) was not observed in any experiment.

Upon investigation of characteristics of residues, it turned out that the major part was unextractable by acetone, also by vigorous methods. This applied to the soil before sowing as well as to all other soil and plant samples. The extractable portion was, on an average, 10 % of total residue in the soils before sowing. Upon harvest it was 9 % in the 0 - 10 cm layer and 30 % in the deeper layers. This suggests a slight migration of soluble radioactivity which is

not immediately bound. The extractable radioactivity was 56 % of total residues in carrot roots and only 19 - 24 % in the other plant parts (carrot greens, lettuce and lettuce roots).

The major portion of extracted radioactivity was water-soluble and extractable with ether from aqueous solution only to a very limited extent. The radioactive substances partitioned into the etheric phase were so low that further clean-up and gas chromatographic identification was not possible. However, from the partition behaviour it may be concluded that unchanged allylalcohol, if at all, is present only in very low amounts. Likewise, the presence of acrolein and acrylic acid in plants is very unlikely since these products are only intermediates which are readily complexed in soil [9] or volatilized [11-12]. It cannot be excluded that part of the radioactive residues in plants, the soluble as well as the unextractable portion, are natural plant constituents formed from allylalcohol degradation products via the natural carbon cycle.

CONCLUSION

Allylalcohol-derived residues disappear rapidly from soil: less rapidly from soil with higher humus

content than from soil with lower humus content. Leaching from the soil surface to deeper layers is slow, the ranking being sand > sandy loam > humus sand. The residues in soil, to their major part, are unextractably bound and, to a smaller extent, fully water-soluble products. Limited uptake of residues by agricultural plants occurs but no bioaccumulation takes place. Unchanged allylalcohol is not detectable by the available analytical methods. The chemical nature of unextractable and water-soluble conversion products and their importance in the crops is not known.

REFERENCES

1. "Shell Unkrauttod A, Unkrautbekämpfungsmittel zur Vorsaatanwendung, insbesondere in Baumschulen sowie im Gemüse- und Gartenbau", Instructions of the Manufacturer.
2. M. Sago, J. Japan Sewage Works Association, 2, 20 (1965).
3. M. Dore, N. Brunet, and B. Legube, Trib. CEBEDEAU, 28, 3 (1975).
4. C.M. Kaye, Biochem. J., 134, 1093 (1973).
5. R.A. Alarcon, Cancer Treat. Rep., 60, 327 (1976).
6. D.S. Fukuda and D.R. Brannon, Appl. Microbiol., 21, 550 (1971).
7. C.E. Castro and N.O. Belser, J. Agric. Food Chem., 14, 69 (1966).
8. N.O. Belser and C.E. Castro, J. Agric. Food Chem., 19, 23 (1971).
9. T.R. Roberts and G. Stoydin, Pestic. Sci., 7, 325 (1976).
10. W. Ebing and I. Schuphan, in: Deutsche Forschungsgemeinschaft, Forschungsbericht Herbizide (DFG, ed.), p. 112; Harald Boldt Verlag, Boppard (1979).
11. K.H. Bowmer and M.L. Higgins, Arch. Environ. Contam. Toxicol., 5, 87 (1976).

12. C.L. Kissel, J.L. Brady, A.M. Guerra, J.K. Pan, B.A. Rockie and F.F. Caserio, Jr., J. Agric. Food Chem., 26, 1338 (1978).
13. E. Schlichting and H.P. Blume, Bodenkundliches Praktikum; Verlag Paul Parey, Hamburg - Berlin (1966).
14. Y.I. Tarasevich and N.M. Radul, Gliny Ikh Mineral., Svoistva Prakt. Znachemie, Itogi Vses, Soveshch. Issled. Ispol'z. Glin, 2nd 1967 (Pub. 1970), 139; CA 74, 116289 h (1971).

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