CHEMICAL: Metolachlor (108801)

FORMULATION: ^{14}C-Metolachlor

CITATION: Sumner, D.D.; Cassidy, J. E. (1974) Uptake of Noextractable Soil Metabolites of ø-^{14}C-CGA-24705 by Winter Wheat: CAAC-74-58. Received March 26, 1975 under 5F1506. (Unpublished report prepared by CIBA-GEIGY Corp., Greensboro, N. C.; CDL: 94385-G).

TRADE SECRET CLAIM: Yes

REASON FOR REVIEW: Generic Standard for Metolachlor

DATE OF REVIEW: January 23, 1978

TEST TYPE: Rotational Crop Uptake Study - Corn

OBJECTIVE:

1. To determine the uptake of radicactivity by winter wheat grown in soil containing only aged and bound residues of (GA-24705).

EXPERIMENTAL:

Aromatic ring labeled ^{14}C-CGA-24705, specific activity 5.08 mg/mM was applied to a silt loam soil in a field plot at 2 lbs/acre as described by D.D. Sumner and J.E. Cassidy, CAAC-74022, "The Uptake and Distribution of ø-^{14}C-CGA-24705 in Field Grown Corn". Eight months after application a 1 x 3 foot portion of the plot was removed to laboratory. Four 1500 gram portions were extracted with MeOH(9:1 v/v), 1 liter for 60 minutes followed by filtration and washing with additional MeOH: H_2O. The filtrate and washings were continued and assayed for radioactivity. The extraction was then repeated with 1500 ml of ethanol and the soil was then air dried. 1200 gram portions of extracted and control soil in duplicate were placed specially equipped glass beakers having a drain hole in the bottom and a thin-layer glass wool between the bottom of the beaker and the soil.

After seeding with Centruk Wheat at 0.5 inch depths plants were grown indoors at 78°F on a 16/8 lite-dark cycle. Samples were collected 7, 21 and 28 days after germination by clipping close to the soil surface.

Plant and soil samples were ground with dry ice (Simaneaux, Bard Roger, J., AG-233, "Binding of Soils and Homecenization of Biological Materials for Radioassay and Extraction"). A Harvey Biological Oxidizor was used for

direct assay of radioactivity (Hermes, P. AG-252" Radioassay of ^{14}C in Biological Materials by Combusiton Using the Harvey Biological Analyzer" Ground plants were extracted by the procedure of (Hermes, P. AG-214. "Biphasic Extraction of Radioactive Metabolites from Treated Biological Material") which utilizes chloroform, methanol and water to provide for aqueous organic polar (non polar) and non-extractable fractions. The ionic character of the H_2O/MeCH soluble polar metabolites was further elucidated by the ion-exchange technique of Keezer, W., AG-156, "Ion Exchange Characterization of Metabolites of Radioactive Pesticides.)

Thin-layer (TLC) systems used to analyze the soil extract were a) 80:20 hexane: Ethyl Acetate and 60:20:20 Hexane: Chloroform: Ethyl Acetate using Analtech Silica gel plates.

RESULTS:

Major findings of the study are outlined in Table I and II. Eight months after the initial application of 2 lbs/acre ^{14}C-CGA-24705 the 3 inch layer of soil contained 0.34 ppm of residue, expressed as ^{14}C-CGA-24705. A MeOH: H_2O (9:1 v/v) extraction followed by an ethanol extraction removed 17% of the total radioactivity. Six percent of the total actity was unchanged ^{14}C-CGA-24805, as shown by thin layer (TLC) analysis of the MeOH/H_2O extractables. The wheat grown in the extracted soil (containing only bound residues) took up 0.13 ppm total activity when analyzed 28 days after germination.

Less than 10% of this residue was chloroform extractable. When expressed as either H_2O/MeOH extractable vs. non extractables the percentages were 85% and 15% respectively. As can be seen in Table II, the major components in the polar (H_2O/MeOH extractable fractions) were acidic compounds (40%) and neutral compounds 17%.

Table 1: Analysis of Radioactive Residues of ^{14}C-Metolachlor Treated Soil Used to Grow Winter Wheat[b/]

Time Interval	Total ppm[a/]	Balance %		
		MeCH Extractable	Ethanol Wash	Nonextractable
Before Extraction	.34	10%	7%	80%
Immediately after extraction	.27	0	-	100%
28 days after extraction(no plants grown)	.28	14		86
28 days after extraction (with plants)	.28	11		75

a/expressed as ppm equivalent to ring labeled ^{14}C metolachlor.

b/soil treated with 2 lbs/acre of ^{14}C metolachlor ring labeled - 32 weeks before extraction with methanol

Table 2: Radioactive Metabolites Present in Winter Wheat Grown in Soil Containing Non-extractable Soil Metabolites of ^{14}C-Metolachlor [a/]

Interval between soil treatment and extraction with methanol/water and ethanol	8 months
Interval between extraction to remove non-bound residues and planting of wheat	0 days
Interval between germination and harvest	28 days
Total ppm, expressed as CGA-24705 equivalents	13
Balance	
a. $CHCl_3$ extractables	10%
b. H_2O/MeOH extractables	85%
c. Non-extractable	15%
Ionic Characterization of H_2O/MeOH Solubles	
a. Neutrals	17%
b. Acids	40%
c. Bases	3%
d. Amphateric Compounds	5%

[a/] Soil treated with ring labeled ^{14}C-Metolachlor, 32 weeks prior to extraction with methanol followed by planting to wheat.

[b/] Total ppm for plants harvested 7 and 21 days after germination was .03 and .09 respectively.

CONCLUSIONS:

1. Winter wheat grown in soil containing aged and unextractable residues of ^{14}C ring labeled CGA-24705 is able to take-up some of these unextractable residues. Winter wheat grown for 28 days in soil from which all extractable residues had just previously been removed by methanol, prior to planting, contained radioactivity equivalent to 0.13 ppm of ^{14}C-metolachlor. Unextractable residues in this soil at the day of planting were 0.27 ppm. During this 28 day growing period no significant change in total soil residues occurred. However, soils in which wheat plants were growing as well as control soils, without plants increased from 0% MeOH extractable residue on day 0 (from planting of wheat) to 11% and 14% respectively at the end of the 28 day period. The registrant suggested "that rehydration followed by an aging period established an equilibrium which allows release of the same percentage of the soil radioactivity as the originial extraction. This probably represents the radioactivity available to the plant".

2. The majority of the .13 ppm residues in the wheat plant is extractable with H_2O/MeOH (85% of the total) but was not well characterized. Up to 17% of the H_2O/MeOH extractable is classed as "neutrals", in addition to reported 10% chloroform extractable (non-polar compounds such as the parent molecule). Until further clarified, it must be assumed that residues of metolachlor were detected in wheat grown on soil previously treated with metolachlor eight months earlier.

DISCUSSION:

1. Six percent of the total 17% extractables from soil treated 8 months previously with 2 lbs/acre metolachlor was found by TLC to be undegraded metolachlor. The remaining 11% was only identified as "unknown extractables" with no comment on their R_f values (relative polarity). Information on the TLC characteristics of these unknowns is necessay to fully evaluate the significance of the 17% neutral (.02 ppm metolachlor equivalent) residues found in the .13 ppm total residues of 28 day wheat.

2. Only ring labeled ^{14}C metolachlor was used. Due to the nature of the N-dealkylation products the uptake is therefore only partially defined.