US EPA ARCHIVE DOCUMENT

CB

EEE BRANCH REVIEW

DATE: IN _____ OUT _____ IN 4/7/75 OUT 6/24/~~74~~ 75 IN _____ OUT _____

FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE OR REG. NO. _____

PETITION OR EXP. PERMIT NO. 5F1606

DATE DIV. RECEIVED 3/26/75

DATE OF SUBMISSION 2/28/75

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TYPE PRODUCT(S): I, D, (H) F, N, R, S

PRODUCT MGR. NO. 24

PRODUCT NAME(S) CGA 24705

COMPANY NAME CIBA-GEIGY

SUBMISSION PURPOSE Use on field corn

CHEMICAL & FORMULATION 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methyoxy-1-methylethyl) acetamide

1.0 CONCLUSIONS:

This chemical should not be registered at this time because possible hazards have been identified from the data submitted. To properly assess the hazard the following are needed:

1.1 Additional data are needed to determine the hazard to rotational crops. These data may be obtained as follows:

1.1.1 For crops rotated the following year after treatment, the pesticide is to be aged in the soil for one year prior to planting. This should be a radiolabeled study.

When significant residues are found, then actual field studies using non-labeled pesticide are required. Such data must be obtained under actual agricultural practices.

When residues are found in rotational and/or subsequent crops in the field, then a labeling restriction is needed. This restriction will take the form of a time interval from application to planting of rotational crops such that residues will not occur in the rotational crop.

Cover crops can be rotated if label restrictions are such that the cover crop is plowed under and not grazed.

If the agricultural practice is such that a treated crops area is rotated with another crop that will result in another treatment of the pesticide to the same area, residue data will be required on the second crop. The rotational crop is to be grown under actual use conditions.

1.1.2 Data from the above studies must be collected at appropriate intervals to permit the determination of a proper rotation interval needed to reduce hazards in subsequent crops. A crop rotation restriction of 18 months would reduce the likelihood of hazards to rotational crops.

1.2 Data from the following studies may be submitted after registration:

1.3 Tank Mixtures

1.3.1 In addition to the environmental data needed for registration of pesticides the following are also needed to support tank mixtures.

a. Laboratory study using cold chemicals applied to two soils as recommended in the proposed use. A light and heavy soil will be adequate.

b. Analysis through two half-lives of each pesticide applied as a mixture and separately. The same soil types are to be used for the comparison of the mixture vs. individually applied chemicals. Sampling depth should be to bottom of container (pot) or 6 inches.

1.4 Long Term Studies for Highly Persistent or "Bound" Pesticide Products:

In the event a pesticide is very persistent, leads to highly stable decomposition products or to significant quantities of "bound" material; special studies to determine buildup of these substances may be required. Usually, this would represent selection of test fields where the application rate and number of treatments were the maximum allowable, according to the label instructions, for a succession of growing seasons. Analyses would be preferable for substances having a demonstrated potential for buildup. Test areas would be selected for climatological conditions showing the most likelihood for stability of the parent compounds. These studies should be carried on until (1) it is clearly demonstrated that a "plateau" level or equilibrium is reached, (2) or until the rate of increase due to added increments of pesticide is established. Current residue test requirements are open ended and determined on a case by case basis.

1.5 A chronic fish bioassay study supported with residue analyses will be required on CGA 24705. We will give registrant 2 years to obtain the data. See Environmental Safety comments for the type study we will require.

We will inform C&ED that registration action was taken.

1.6 If other uses of CGA-24705 are proposed, additional environmental chemistry data on possible hazards to the environment may be needed.

2.0 INTRODUCTION

2.1 This has been previously reviewed on 3/5/75 for PP#5G1553.

2.2 This use is for weed control in corn.

2.3 CGA-24705 6EC is 66.7% active ingredient.

2.4 6.0 lbs active ingredient for gallon.

3.0 DIRECTIONS FOR USE

3.1 Apply mixed in a minimum of 15 gals of water per acre.

Broadcast Rates: CGA-24705 6EC Applied alone

	Less than 3% O.M	3% or more O.M.
Coarse: sand, loamy sand, sandy loam.	2 2/3 pts *	2 2/3 pts
Medium: Loam, silt loam, silt	3 1/3 pts	3 1/3 pts
Fine: Silty clay loam, sandy clay loam, silty clay, sandy clay, clay loam, clay.	3 1/3 pts	4 pts

Dosage range is 2 to 3 lbs ai/acre

* Previous review gave pound rates as 1-2, 1.~~4~~5-2.5 and 2-3 lbs. for coarse, medium and fine, respectively, at less than 3% O.M. Corresponding rates for 3% or greater O.M. were 1-2, 2-2.5 and 2-3 lbs.

3.2 Tank mix rates:

	Less than 3% O.M.		3% or more O.M.	
	CGA-24705	AATrex	CGA-24705	AATrex
*Coarse	1 2/3 pts	1.25 lbs or 2 pts	1 2/3 pts	1.5 lbs or 2.4 pts
Medium	2 pts	1.5 lbs or 2.4 pts	2 2/3 pts	2 lbs or 3.2 pts
Fine	2 2/3 pts	2 lbs or 3.2 pts	2 2/3 pts	2.0-2.5 lbs** or 3.2-4.0 pts

* See texture designations for Broadcast rates of CGA-24705 above.

** Apply 2.5 lbs or 4 pts AATrex with 2 2/3 pts CGA-24705 for velvet leaf and yellow nutsedge on fine soil.

3.4 Precautions and restrictions.

3.4.1 Rotational crops.

3.4.1.1 Do not make a second broadcast if crop lost and then immediately replanted. If replanted in untreated row middles, a second band application can be made.

3.4.1.2 For CGA-24705 alone: Rotate full seeded small grains after corn harvest. Rotate any crop the following spring.

3.4.1.3 For tank mix: Do not plant to any crop except corn until the following year. Do not plant sugar beets, tobacco, vegetables, spring seeded small grains or small seeded legumes and grasses the following year. Do not rotate to anything but corn or sorghum the next year if treated after June 10 of the first year. Do not use in High Plains or Intermountain areas where low rainfall occurs or irrigation is required unless corn or sorghum follow corn or untreated corn or sorghum precede other rotational crops. Soybeans may be injured if rotated the following year on calcareous soils in the North Central regions including portions of Minnesota, South Dakota, Iowa and Nebraska.

3.4.1.4 Note: The above restrictions for tank mixes are derived from accepted AATrex labels which were never routed for 70-15 review.

4.0 DISCUSSION OF DATA

4.1 Analytical methods

4.1.1 Plant and animal radioactive metabolite were characterized by ion exchange chromatography (AG-156).

4.1.2 Total organic ^{14}C in soil was measured by combustion (AG-218)

4.1.3 CGA-10832 metabolite was extracted from soil using methanol/water (90/10) mixture and shaking for 15 minutes (AG-254).

4.1.4 Humic and fulvic fractions were extracted from soil having non-extractable ^{14}C - residues using 1N NaOH (shaking 6 hrs). Humic acid is precipitated out with HCl and the supernate partitioned with methylene chloride for fulvic acid. (AG-268)

4.1.5 An improved analytical method for residues of CGA-24705 as CGA-37913 and CGA-49751 was described in AG-277. Levels in corn down to 0.03 ppm (as CGA-37913 [2-(2-ethyl-6-methylphenyl)aminopropanol] or 0.1 ppm (as CGA-49751 [4-(2-ethyl-6-methylphenyl)-2-hydroxy-5-methyl-3-morpholinone] were possible. CGA-24705 is converted to the other two by overnight refluxing with 6N HCl with the acid extract partitioned with dichloromethane to give CGA-49751 in the nonaqueous phase. The aqueous phase is made strongly basic with 50% NaOH and steam-distilled and partitioned into isooctane. Cleanup for CGA-37913 is by alumina column and analysis is by GC using electrolytic conductivity detector, N specific, CGA-49751 is partitioned with 5% sodium carbonate and also cleaned up using alumina. Conversion to chloroethanol-react with BCl_3/2-chloroethanol @ 90°C for 15 min. followed by hexane partition and cleanup using silica gel followed by alumina. Analysis is by GC using Cl specific microcoulometric detector.

4.1.6 An earlier technique involved extraction with acetonitrile for grains, methanol for plant material and methanol in a hot extractor for soil. Cleanup of grain was with acetonitrile/Hexane followed by acetonitrile-water/hexane partitioning. Soil and plant material extracts were cleanup by water-methanol/hexane partition. Final cleanup is by alumina column and analysis by either N specific or microcoulometric detector GC. Technique will detect as low as 0.04 ppm (Basle REM 12/73).

4.2 Soil persistence. (#GAAC 75022)

4.2.1 A field persistence study was performed using CGA-24705 (ring labeled) at 2 lbs/acre on a silt loam soil. Samples were obtained from 4-52 weeks after application. Analysis was by the AG-254 and AG-218 methods described earlier. Humic acid was preformed by AG 268.

The rate of loss of total ^{14}C activity was such that a half life was about 14 weeks and only 70% was degraded after one year. Very little change occurred between 16 weeks and one year. Non-extractables increased from 32 to 80% of the total between 4 and 16 weeks and remained constant thereafter. Undegraded CGA-24705 was not detected at 16 weeks or after. It was 35% of the total at 4 weeks. A decrease in total activity and in extractables was observed throughout the test. It was concluded that the non-extractables fraction was a reservoir which permitted an equilibrium to exist between bound and nonbound materials. Any loss that occurred after 30 weeks in the 3" layer was presumed due to leaching.

Conclusions

It does not appear as if the degradation of parent under field conditions is well defined. Radioactive products persist for a long time. Though it is claimed that parent is not found after 16 weeks, data to support this is not supplied. Analysis of Total ^{14}C residues shows very little loss from 16 weeks on. Leaching may be the primary mode of loss. A buildup after several years application is possible.

4.2.2 Sterile vs. nonsterile degradation (Study ABC).

A comparison of degradation under sterile and nonsterile conditions showed that no significant degradation occurred in 60 days under either condition.

TABLE 1

COMPARISON OF DEGRADATION OF CGA - 24705 IN STERILE AND NONSTERILE SOILS

Day Sampled	Sterile			Nonsterile		
	Mean (µg)			Mean (µg)		
	Extracted	TLC*	Combusted	Extracted	TLC	Combusted
0	190	185	176	186	184	183
2	188	183	177	190	180	180
4	188	185	188	184	188	178
8	195	201	195	184	188	189
16	181	180	194	170	170	187
32	164	150	195	160	151	183
64	181	170	182	174	159	177

* Extracted parent verified by TLC and corrected for 100% TLC recovery.

4.3 Photodegradation.

Two studies were performed, one using soil slides exposed to sunlamps and natural sunlight and the other in aqueous solution.

The first study (GAAC-74102) exposed sterile soil treated with the equivalent of 4.6 lbs/acre to an undescribed artificial light source and to sunlight of 3000 Langleys (≈375 L/day) over eight days.

TABLE 2

PHOTOLYSIS OF CGA-24705 ON SOIL SLIDES

Exposure Conditions	CGA-24705, %[a] Covered	CGA-24705, %[a] Exposed	% Photolysis
Artificial sunlight exposure			
Hours			
0 (initial)	100	100	0
2	100	93	7
6	100	85	15
24	97	76	21
48	100	60	40
144	80	38	42
168	82	30	52
Natural sunlight (days)[b]			
0 (initial)	100	100	0
1	85	92	0
2	96	88	8
3	80	69	11
6	80	48	32
8	80	30	50
14	85	11	74

[a] Based on CGA-24705 content of the initial slides. Samples analyzed by GLC.

[b] One-day exposure is equivalent to about 375 langley units.

Both exposures show a half-life for CGA-24705 of about 7-8 days. Initial degradation was much quicker under artificial than natural light situations. Four degradation products were revealed by TLC but only one, N-propen [? propan]-1-ol-2-yl-N-chloroacetyl-2-methyl-6-ethylaniline, a demethylated parent, was identified. It accounted for about 6% of the artificial and 4% of the sunlight products. Parent was 24-33% of the remaining ^{14}C residues. Much of the loss of ^{14}C was attributed to volatilization.

Report GAAC-75021 was a follow-up of a study where the parent was exposed to light in aqueous solution (See review of 5G1553 on 3/5/75 for details). In this study 42% of the original was parent after exposure, 23% were unknowns in the aqueous phase and 17% were organic phase unknowns found at the origin. This study attempts to separate the components in the last two categories using chloroform: methanol (9:1)Identification of different zones involved use of diazonium fluoroborate or chromotropic acid sprays. Seven zones were observed, but none of the compounds were identified. Some zones had more than one compound.

4.4 Crop rotation studies.

The bulk of the reports submitted in this application and not previously reviewed are crop rotation studies. Some of these studies are field observations following crops rotated after corn treated at 2 lbs/acre (AG-A's 3150,3244,3282,3283 and 3554). Others involved testing of rotational crops planted in treated (2lbs/acre) soil aged for 6-9 months (GAAC's 74056,74057,74058,74071,74085, 74112 and 74113). Rotational crops involved were soybeans (GAAC 74056 and 74113,AG-A 3244 and 3283), carrots (GAAC 74057, 74112), winter wheat (GAAC 74058, 74071 and AG-A3554), oats (AGA 3150 and GAAC 74085), and sugarbeets (AGA 3282). Residues were found in many of these crops.

TABLE 3

Crop	Soil Treatment if any	Residue Amount	Residue Type	Treatment Planting Interval	Treatment Sampling Interval	Report
Carrots (tops)	extracted*	0.15ppm	^{14}C	32 wks	36 wks	GAAC 74057
	--	0.03	^{14}C	36 wks	48 wks	GAAC 74112
"(roots)	--	0.02	^{14}C	36 wks	48 wks	GAAC 74112
Sugarbeets	--	<0.03/0.04	CGA-24705	307 days	372 days	AGA 3282
Wheat	extracted	0.13ppm	^{14}C	32 wks	36 wks	GAAC 74058
" grain	following	0.03ppm	^{14}C	24 wks	39 wks	GAAC 74071
" straw	corn "	0.60ppm	^{14}C	24 wks	39 wks	"
" forage	"	<0.03	CGA-24705	?	336 days	AGA 3554
" fodder	"	<0.03/0.07**	" "	?	412 days	AGA 3554
" grain	"	<0.03	" "	?	412 days	" "
Oats forage	"	0.04/0.05**	" "	134 days	203 days	" 3150
" fodder, grain	"	<0.03	" "	134 days	370 days	" "
Oats grain	"	0.05	^{14}C	36 wks	50 wks	GAAC 74085
straw	"	0.27	^{14}C	36 wks	50 wks	" "
Soybeans	extracted	0.18	^{14}C	32 wks	36 wks	GAAC 74056
" stalks	following	0.07	^{14}C	36 wks	48 wks	" 74113
" beans	corn "	0.04	^{14}C	36 wks	48 wks	" "
" meal	"	0.05	^{14}C	36 wks	48 wks	" "
" oil	"	<0.01	^{14}C	36 wks	48 wks	" "

TABLE 3 (cont.)

Crop	Soil Treatment if any	Residue Amount		Residue Type	Treatment Planting Interval	Treatment Sampling Interval	Report
Soybeans fodder	Following corn	<0.03		CGA 24705	286 days	540 days	AGA 3244
" grain	"	<0.03		CGA-24705	286 days	540 days	AGA 3244
" forage	"	0.06	0.06**	"	358 days	405 days	AGA 3283
" fodder	"	0.04	0.05**	"	358 days	405 days	AGA 3283
" grain	"	<0.03	<0.03	"	358 days	405 days	AGA 3283

* Extracted with methanol to remove non-bound metabolite

** 4lbs/acre treatment

Soil persistence data accompanying the GAAC reports support other soil persistence studies which show virtually no dissipation following several months aging. In each case studied, whether the soils were extracted or not, very little change was noted in amounts of radiolabeled material in the soils from the time the rotation crop was planted to the harvest of that crop. Occasionally, greater amounts of residue were found in the soil on dates midway through the rotational crop studies, than at the beginning of those studies.

Conclusions:

Some residues were found in most crops tested. Cold studies revealed some detectable residues in soybeans at both 2 and 4 lbs/acre treatment at 400-500 days, in oat forage from 2 and 4 lb treatments at 200 days and in sugarbeets (370) days and wheat fodder 412 days from 4 lb treatments. These cold studies were reinforced by detectable radioactive residues in almost all crops at times between 36 and 50 weeks after treatment. Since companion soil dissipation studies show almost no dissipation from aged soils and the establishment of an apparent equilibrium between bound and nonbound residues, it would appear as if residues would be available for uptake to rotational crops for at least one year and possibly longer.

4.5 Fish Accumulation Study (Bionomics Report).

A fish accumulation study was performed by Biononics laboratories. This was a dynamic flow bluegill study at nominal 1000 and 10ug/L. concentrations. Tests were run for 70 days accumulations and 18 day depuration:

TABLE 4

RESIDUE ACCUMULATION IN BLUEGILL SUNFISH

HIGH LEVEL

Day Sampled	Concentration Water (µg/L)	Tissue (mg/kg) Edible	Tissue (mg/kg) Non Edible	Bioconcentration Ratios	
1	760	9.92		13.05	
3	990	11.67		11.79	
7	1430	12.58		8.80	
10	1400	10.88		7.61	
14	1150	13.00		11.30	
21	1200	14.00		11.66	
28	1425	12.83		9.00	
35	1150	21.00	(679.00)	18.26	(590.4)
42	1453	23.25	(581.00)	16.00	(399.9)
49	1075	16.00	(497.00)	14.88	(462.32)
56	1010	21.52		21.31	
63	845	24.17		28.60	
70	825	21.46	(583.20)	26.01	(706.91)
71*	0	13.28	385.80	--	--
73	0	16.75	155.00	--	--
77	0	14.33	73.80	--	--
80	0	19.83	25.60	--	--
84	0	14.50	15.12	--	--
91	0	14.38	--	--	--
98	0	11.69	12.52	--	--

*Withdrawal

TABLE 5

RESIDUAL ACCUMULATION IN BLUEGILL SUNFISH

LOW LEVEL

Day Sampled	Concentration Water (µg/L)	Tissue (mg/kg) Edible	Non Edible	Bioconcentration Ratios	
1	6.75	0.25		3.70	
3	8.85	0.39		4.41	
7	11.00	0.54		4.91	
10	9.30	0.45		4.84	
14	8.50	0.57		6.71	
21	8.70	0.89		10.47	
28	9.20	0.107		11.63	
35	9.30	0.126	(4.54)	13.55	(488.2)
42	10.20	0.142	(5.74)	13.92	(562.7)
49	9.08	0.152	(4.12)	16.74	(453.7)
56	11.09	0.177		14.87	
63	8.52	0.188		22.07	
70	9.73	0.187	(4.54)	19.22	(466.6)
71*	0	0.139	3.30	--	--
73	0	0.168	2.67	--	--
77	0	0.130	0.78	--	--
80	0	0.132	0.75	--	--
84	0	0.108	0.33	--	--
91	0	0.108	--	--	--
98	0	0.083	0.14	--	--

*Withdrawal

These results show an apparent plateau in the non-edible tissue at the low concentration exposure but no true plateaus are apparent in the other cases. In addition, withdrawal from the edible tissue did not exceed half the claimed plateau level for both exposures. Loss from the non-edible tissue was significant in each case, however. Bioconcentration ratios for non-edible tissue were often 30-40 times those of the edible tissue which is a surprisingly high difference.

Conclusion

a. The accumulation of this pesticide in fish is not completely defined. A lack of a true plateau and an unusually high non-edible/edible residue ratio indicates a need for additional study.

b. Residues in edible portion was extracted in hexane and MeOH (51 and 49% recovered respect.) at high level and 37% and 63% at low level.

Conclusions

1. CGA-24705 is a moderately persistent pesticide which does not degrade completely (90%) prior to the next growing season. Residues appear to bind readily in soil and certain studies seem to point to an equilibrium between bound and non-bound residues after 16 wks. A buildup in soil residues after repeat applications may occur but data is lacking in this area to assess hazards.

2. Residues appear in rotated crops sampled up to 500 days following application. The amount of residue determined as CGA-24705 is generally just above the limits of detection but radioactive residues as high as 0.3 to 0.6 ppm are found in small grain straw at 40-50 weeks after application. Hazards to rotational crops can occur.

3. Loss of residues from soil during crop rotation studies is attributed primarily to leaching.

4. CGA-24705 does not appear to be degraded by microbial activity.

5. CGA 24705 is photodegraded slowly but not all important products have been determined

6. A fish accumulation study showed low residues in edible tissue (a BR of about 15-25) but significant accumulation in non-edible tissue (400-700 BR) occurs. The concentration in

non-edible tissue is 25 to 40 times that of edible tissue, which is an unusual ratio. Withdrawal is rapid from non-edible tissue until it reaches a level 1-2 times as great as edible tissue. However the level following withdrawal in edible tissue is more than 50% that of the so-called plateau. A true plateau does not appear to have been reached except possibly in the case of low level exposure in non-edible tissue. Hazards cannot be assessed.

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