EEE BRANCH REVIEW

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DATE: IN 3/23/79 OUT 10/1/79 IN _____ OUT _____ IN _____ OUT _____

FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE OR REG. NO. 100-LOO, LOI

PETITION OR EXP. PERMIT NO.

DATE DIV. RECEIVED 3/20/79

DATE OF SUBMISSION

DATE SUBMISSION ACCEPTED

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

DATA ACCESSION NO(S). 237827 237826

PRODUCT MGR. NO. 16

PRODUCT NAME(S) CURACRON 6E

COMPANY NAME CIBA - GEIGY

SUBMISSION PURPOSE Resubmission with data

CHEMICAL & FORMULATION CURACRON 90%

100.1 Pesticide Use

For use as an emulsifiable insecticide in cotton

100.2 Formulation Information

Curacron 6E; 59.6% ai; 6 lbs ai/gal

100.3 Application Method/Directions/Rates/Pests

Cotton bollworm, tobacco budworm, and cotton leafperforator - Apply on a 5-7 day schedule when larvae appear. Use 2/3-1 pt. per acre (0.5-0.75 lb ai) on light to moderate infestations and 1-1 1/3 pts. per acre (0.75-1.0 lb ai) on moderate to heavy infestaions.

Beet armyworm (Eastern U.S. only) - Apply on a 5-7 day schedule when larvae appear. Use 2/3-1 pt. per acre on light moderate infestations and 1-1 1/3 pts. per acre on moderate to heavy infestations.

Cotton boll weevil - Apply 2/3-1 1/3 pts. of Curacron 6E plus either 1/2-1 pt. of Guthion^{R} 2L or 1/2-1 pt. of methyl parathion 4E per acre. Use the low rate of either Guthion or methyl parathion for light to moderate infestations and the high rate for moderate to heavy infestations.

Apply in a minimum of 5 gals. of spray per acre with ground equipment or in a minimum of 1 gal. of spray per acre by air.

Note: Do not apply more than 4 qts. (6.0 lb ai) of Curacron 6E per acre per season nor apply within 14 days before harvest.

Refer to the Guthion 2L and methyl parathion 4E labels for further directions, limitations and precautions.

100.4 Precautionary Labeling

This pesticide is toxic to fish and wildlife. Use with care when applying to areas frequented by wildlife or adjacent to any body of water. Keep out of lakes, streams, or ponds. Do not apply when weather conditions favor drift from treated areas. Apply this pesticide only as specified on this label. Do not contaminate water by cleaning of equipment or disposal of wastes.

This product is highly toxic to bees exposed to direct treatment or residues on crops or weds. Do not apply this product or allow it to drift to crops or weeds on which bees are foraging. Additional information may be obtainded from your Cooperative Agricultural Extension Services.

direct treatment or residues on crops. Protective information may be obtained from your Cooperative Agricultural Extension Service.

Refer to Guthion 2L and methyl parathion 4E labels for further directions, limitations, and precautions.

101.1 Chemical name

0-(4-Bromo-2-chlorophenyl)-0-ethyl-S-propyl phosphorothioate

101.2 Common name

Curacron

101.3 - 101.6.3 See Previous reviews by H. T. Craven

102.0 Behavior in the Environment

The following is an abstract from Environmental Chemistry's 5/26/78 review of Curacron.

A. Hydrolysis

Curacron degrades more rapidly at basic pH's and increasing temperature. Halflives at 30°C at pH's 5, 7 and 9 are 670, 120 and 2 hours, respectively. Hydrolysis in basic solution is rapid yielding the 4-bromo-2-chlorophenol (CGA-55960 or BCP) and in acidic solution the following intermediates to BCP formation are identified;

CGA-47197 0-(2-chloro-4-bromophenyl)-n-S-propylthiophosphate

CGA-47196 0-ethyl-0-(2-chloro-4-bromophenyl)-phosphate

CGA-47195 0-(2-chloro-4-bromophenyl)-phosphate

BCP is stable to acid and basic hydrolysis.

B. Photolysis in Water and Soil

Under a mercury vapor lamp (radiation <290 nm absorbed and 173 Langleys/hr. or 2000±300 joules/m^2/sec), curacron degrades in water with a halflife of 27 hours with 62% of the initial material volatilizing in 72 hours.

No data on soil photolysis of curacron have been submitted with this or previous submissions. However, judging from the fate in soil, where formation of bound residues is rapid with some release of CO_2, a study on curacron volatility from soil showing 3% of the fortification (8:1 BCP: parent) volatilizing/hour for the first day, the photolytic fate in water where volatile debrominated parent is formed and the lab fate on cotton leaf surfaces when the parent volatilized, provide sufficient information for the soil photolysis study not to be required for this use.

C. Aerobic Soil Metabolism

Over 4 weeks, ^{14}C ring labeled curacron is degraded in soil under aerobic conditions to primarily (73%) non-extractable material and 17% of the initial activity is released as $^{14}CO_2$. Only 1.6% remains as parent and 1.8% as 4-bromo-2-chlorophenol.

There is a clear correlation between the sharp drop in extractable residues and the sharp increase in bound residues. There is also greater degradation of the parent and formation of bound residues with increasing pH. The bound residues formed may be available for uptake by rotational crops and run-off into natural waters.

In soils between pH 5.6 and 7.5 the halflife of the parent is less than 4 weeks. The only degradation product identified is 4-bromo-2-chlorophenol which is never greater than 8% of the initial material applied and drops with increasing time after day 0.

D. Anaerobic Soil Metabolism

Although only a 4 week anaerobic sample was taken and an anaerobic control was not run, we can conclude that anaerobic soil conditions will not change patterns of degradation of curacron from those under aerobic conditions.

E. Effects on Microbes

It is difficult to determine if CGA-15324 and bromo-chlorophenol significantly inhibit microorganisms involved in biogeochemical transformations occurring in soil and aquatic habitats because of the many discrepancies found between the studies submitted. In a recently submitted study by C. D. Ercegovich (2/15/78), CGA-15324 and bromochlorophenol at 5 ppm significantly inhibited one bacterial population out of nine and six fungal populations out of fourteen tested.

The results from this study do not agree with a previously reviewed study by Graham and Lawson, 6/7/76 (Bioresearch Labs) where no effects were observed on bacterial, actinomycetes, or fungal populations in soil at rates as high as 250 ppm.

F. Effects of Microbes.

Soil metabolism studies using sterile vs. non-sterile soil showed that microorganisms may contribute to the degradation of CGA-15324.

G. Leaching

This information is acceptable and shows that soils low in organic matter and high in sand permit minor leaching of curacron.

H. Field Soil Dissipation

The studies submitted and reviewed showed curacron residues to be not detectable after

15-40 days down to 12 inches in the soil.

We note from the aerobic soil metabolism studies that most of the soil applied curacron becomes bound in 2-4 weeks and would not be detected by the analytical methods used in these field dissipation studies. Therefore, the data are acceptable.

I. Rotational Crops

Cotton treated at 1x and 2x (6 and 12 lb. ai/A) the maximum rate for 1 and 2 consecutive seasons with non-labeled curacron and then planted to rotational crops showed no detectable uptake (<0.05 ppm) of curacron residues containing the 4-bromo-2-chloro-phenol (BCP) moiety.

J. Fish Accumulation

Although five studies were reviewed, only two have been abstracted.

The flow-through exposure systems using bluegill showed varying results. In one experiment where fish were exposed *1ppm ^{14}C-CGA-15324, muscle tissue exhibited bioconcentration factors of 17x, head portion 24-42x, visceral portion 320-676x and whole fish 60x. Within 24 hours of depuration bluegill had eliminated 90% of radioactivity in the muscle tissues. Within 72 hours after transfer, bluegill had eliminated 95% of ^{14}C residues in viscera and whole fish.

* If 1ug/L was added to the tank, the value should be 1 ppb.

In a second flow-through experiment where bluegills were exposed to 30 ppb CGA-15324, fish began to die by the ninth day. Bioaccumulation levels reached 1900x in the viscera, 230x in the head and 120x in the body. Parent compound and 4-bromo-2-chlorophenal represented 28% and 14% of the total ^{14}C-residues in viscera and 62% and 12% in the fish body.

In three experiments where fish exhibited chemical toxicity, muscle tissue concentrations of CGA-15324 were not reported. Nevertheless, the data that were reported indicate a potentially serious hazard to nontarget aquatic organisms and contamination of the food web at very low concentrations of CGA-15324.

K. Tank Mix Data

When considered together, the different tank mix studies are acceptable. They show curacron to degrade with a halflife of less than 2 weeks when applied alone or tank mixed with Guthion and to degrade with a halflife of less than a month when applied alone or tank mixed with methyl parathion.

L. Dislodgeable Residues on Cotton

Cotton, of an unspecified age was treated with curacron at 1 lb./A/application eight times between September 4 and November 3, 1976 by ground application in Maricopa County, Arizona. Leaf samples were collected for residue analysis at various intervals (0-120 hrs.) following the eighth application. The pretreatment sampling produced an average residue of 5.0 ppm. Immediately upon application extractable residues were 37.5 ppm. The Environmental Safety Section developed a residue decline curve to determine a potential half life value for curacron on vegetation. (See print out). A 1/2 + value of 63.3 hours was determined.

103.0 Toxicological Properties

(See review by H. T. Craven for Reg. of Tech. 5/3/78)

Personal communication with D. Ritter revealed previously abstracted acute and subacute data are considered acceptable.

103.1.2 -
103.1.4 See review by H. T. Craven 5/3/78

F. Report 80:

Material: CGA-15324 (Curacron)

Author: E. L. Atkins

Test species: Honeybee (Apis mellifera)

Registrant: CIBA-GEIGY Corporation

Date of test: 1976

Results:

Laboratory testing showed the LD_{50} of CGA-15324 to be 3.462 micrograms per bee, which is moderately toxic.

104.0 Hazard Assessment

104.1 Discussion

The use of Curacron as an insecticide to control bollworm, budworm, boll weevil, leafperforator and beet army worm on cotton will produce the opportunity of environmental exposure to a wide variety of non-target species and ecosystems. In 1976 the estimated geographic area in the United States planted to cotton was greater than 11,610,000 acres scattered in 19 states. These states could generally be classified as the Southern tier of agricultural effort. The land utilized in this type of agriculture can be of varying soil types, from flood plain allivial soil to upland soil types. The agricultural practices can vary from state to state but with a sizable amount of mono-culture involved. This type of agriculture is characterized by large dependance upon irrigation and aerial spraying of persistant chlorinated hydro-carbon compounds to control pests. This type of agricultural utilization of artificial control of pests has ~~also~~ been credited historically with many of the fish kills that have occurred in these states.

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104.2 Likelihood of Adverse Effects to Non-Target organisms (including exposure and toxicity)

Aerial application of Curacron as an insecticide will result in exposure of myriad species of birds and mammals. The major exposure will occur on field edges rather than in the cotton itself where residues will occur as a result of drift.

Based upon currently available acute and sub-acute data, Curacron is highly toxic to fish and birds, and very highly toxic to aquatic invertebrates. Lastly, a single eye irritation study in rabbits showed lethality resulting from exposure to 0.1 ml.

A summary of some data is presented below:

Organism	Test	Toxicity
*black bullhead	96 hr. LC_{50}	20 ppb
*Bluegill	96 hr. LC_{50}	300 ppb
*Rainbow	96 hr. LC_{50}	80 ppb
Daphnia	48 hr. EC_{50}	1.06 ppb
Bobwhite quail	8-day dietary	201 ppm

*Unacceptable studies

The above values are based upon studies conducted utilizing the technical A.I. In addition to the above fish studies flow through fish accumulation studies with bluegills caused mortality at 30 ppb in nine days.

Curacron may adversely effect non target vertebrates by removal of insect biomass and the resultant impact upon species of insectivores that are trying to produce broods at this time. Futhermore, the repeat applications of Curacron will cause a continual removal of biomass throughout the growing season and may cause natural predator populations to be suppressed.

Data does not exist regarding chronic toxicity to birds, fish or aquatic invertebrates.

Direct contamination of aquatic areas adjacent to cotton fields would expose game and commercial fish species to possible acute and chronic effects. Areas of greatest concern will be: *1) wooded swamps in S. Carolina and Georgia, *2) the Mississippi and its tributaries in Arkansas and Mississippi and 3) lakes and ponds in any of the cotton growing states.
[*Wetlands of the United States - FWS #39]

In order to estimate the amount of Curacron residues fish and wildlife will be exposed to from aerial application to cotton, several approaches have been taken.

Environmental Fate Branch does not review residue data for the following substrates:
Leafy crop
Short range grass
Long range grass
Forage

This is gratuitous and misleading.

Excluding any input from Environmental Chemistry, relying only on nomographs used by Environmental Safety the residues are as follows:

Curacron Residue Profile Immediately upon the initial application

Application rate (lb ai/A)	Substrate				
	6"H_2O	Leafy Crop	Short Range Grass	Long Range Grass	Forage
0.5	367 ppb	63 ppm	120 ppm	55 ppm	29 ppm
1.0	734 ppb	125 ppm	240 ppm	110 ppm	58 ppm

These values are altered by repeat applications and Environmental Chemistry studies--primarily photolysis (conducted in water), hydrolysis, dislodegable residue and rotational crop studies. The first two studies yielded half lives of 27 hours and 120 hours (pH 7, 30°C) respectively. The results of these two studies were intergrated by R. Holst into a half life of 36 - 48 hours for water. A half life of 63 hours was derived from the data on dislodgeable residues using the Imidan half life program contained in the Environmental Safety TI 51 calculator. (See file for printout).

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A residue profile depicting levels over time in vegetation bordering cotton fields is shown on the accompanying graph. Note that short range grass was considered representative of vegetation adjacent to cotton fields. However rather than assuming the maximum hazard would result from 1.0 lb ai/A equalling 240 ppm it was based on 0.296 of that 240 ppm. (This 0.296 factor equals the factor derived from the dislodgeable residue study on cotton (1.0 lb ai/A =37.5 ppm) and the nomograph value for leaves = 125 ppm. Birds and mammals will be exposed to the following average minimal residues:

1. 1.0 lb ai/A = 24 ppm for approximately 30 days, and

2. 0.5 lb ai/A = 10 ppm for approximately 60 days.

Estimating the environmental concentration of Curacron in water is extremely difficult--even with environmental Chemistry data. A suggested approach is as follows: Truly gratuitous

Determined the maximum allowable residues based upon LC_{50} to most sensitive fish. An invalid trout study gave a 96 hr. LC_{50} value of 80 ppb. Therefore for Curacron 40 ppb (1/2 LC_{50} = RPAR level) "might be" considered an acceptable level. The accompanying graph illustrates (with different half lives) what multiple applications, each contributing 40 ppb from drift alone, may result in over time.

Half Life (hours)	Residues of Curacron in 6" H_2O Minimum residues
36	~ 4 ppb (a)
48	~ 8 ppb (a)
120	~38 ppb (b)

(a) after 5 days for up to approximately 60 days.

(b) after 20 days for up to approximately 60 days.

Minimal residues in water when are 36,

The half life values ~~for~~ 48 and 120 hours support the need for at least a partial chronic fish and chronic invertebrate study. The likelihood of 40 ppb entering into the water from drift alone, not including runoff, leaching or volatilization is discussed in this next statement by R. Holst:

> Aerial application of Curacron at no less than 1 gal/A would most likely result in a droplet size with a vmd of 100 to 200 μ with a few droplets less than 50 to 70μ assuming "normal" nozzle and pressure in use. Assuming a release height of 10 ft. in a 5 mph cross wind with no additional turbulence, a 100μ droplet would drift 87 ft with relative humidity equal to 100% or only 60 ft before it evaporated at 50% RH while a 200μ droplet would travel only 31 ft regardless of RH.
>
> One and one third pint Curacron 6EC per A equals 1 lb ai/A or about 736 ppb in 6" of water if applied directly. A safe limit to non-endangered fish species is considered 40 ppb or approximately 5% of the total application. Allowing no more than 5% of the application from a single pass to reach an aquatic system, the system would have to be about 250 to 300 feet downwind. This assumes that the droplet distribution is such that 5% of the total droplet volume is in the less than 70μ size. (50μ droplets drift 300 ft when released at 10 ft in a 5 mph wind.)

HTC

*For a more sensitive fish species such as catfish (LC_{50} = 20 ppb), the safe limit is 10 ppb. Assuming no turbulence or evaporation (RH = 100%), and allowing for no more than 2% of the total application volume to reach the aquatic system, the aquatic system would have to be 750 ft. To try to account for no-effect levels in the drift assessment for endangered species, a safe limit could be as low as 1 ppb. With the above assumptions and allowing for no more than 0.1% to reach the aquatic system (1/20 of the catfish LC_{50}), the safe distance would have to be 750 ft.

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*Note: This LC_{50} is considered supplementary. Conceivably the LC_{50} is lower and the corresponding LC_{50} will be used to estimate hazard to endangered species.

However, in most cases the droplets would be subject to evaporation. At 70% RH the 100μ droplets would travel only about 100 ft while at 50% RH they would travel only about 60 ft. Smaller droplets would evaporate faster and not travel as far.

Side by side swath application (approximately 50 ft centers) will have some affect on the total quantity that will reach the 250 to 300 ft mark but not an appreciable amount. It would most likely substantiate the need to use 300 ft rather than 250 ft buffer zone regardless of evaporation.

Operative Statement

It must be remembered that where updrafts or turbulence occurs, the pesticide could be carried further. However, determination of the extent under even "normal" conditions can not be made at this time.

As stated previously, one can expect contamination of areas adjacent to cotton fields primarily as a result of drift. Curacron is acutely toxic to fish and daphnia. This reviewer has a concern for Curacron's effect on estuarine invertebrates.
*USDA 1964 map of cotton harvest locations shows only a S. Eastern portion of the Texas coast as fringing on an estuarine area. Although cotton is grown extensively along the Mississippi the reported behavior of Curacron in water suggests little or no levels would reach the La.-Miss. coast to contaminate shrimp, crab and oysters.

*Wetlands of the United States - FWS # 39
*Usual planting and harvesting dates - USDA #283

104.2 Phytotoxicity

Curacron is applied by aerial methods, and is therefore susceptable to aerial drift. The extent of drift was not determined. The phytotoxic effect

of Curacron to non-target plants was also not determined.

If Curacron can cause a leaf reddening and early maturing to cotton, it may cause such effects which may be detrimental to non-target plants, both crop and non-crop.

The persistance of Curacron has not been determined or at least made known to this reviewer. With repeat applications (up to possibly 12) and up to 6 lbs ai/A total per year, and with a relatively long persistence, phytotoxic conditions may build up in non-target areas.

104.2 Beneficial/Non target Insects

Data from laboratory, screenhouse, and field tests show that Curacron has the potential to significantly reduce populations of non-target insects in cotton. Populations of the following insects, exposed to direct treatment or residues on crops, were significantly reduced by one application of Curacron at 0.75 - 1.00 lb. a.i. per acre:

Orius sp., Geocoris sp., and Nabis sp. (hemipteran predators); Chrysopa sp. (lacewing); Collops sp. (predaceous beetle); Apis mellifera (honeybee); Megachile pacifica (leafcutting bee); Nomia melanderi (alkali bee).

In addition, other screenhouse and field tests showed Curacron toxic to Hippodamia convergens (convergent lady beetle) and Trichogramma pretiosum (parasitic wasp). Data from these particular tests are, however, subject to question.

Due to Curacron's high toxicity to bees, the proposed bee precaution labeling should be revised to read as follows:

> This product is toxic to bees exposed to direct application. Do not apply when bees are actively visiting the treatment area. Time applications to coincide with periods of minimum bee activity.

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In regard to non target insects other than bees, it should be noted that all the field data are based on the effects of a single application of Curacron, these effects being monitored only for a period of several days following application. Proposed use directions would allow for a maximum of 12 applications of Curacron in one season, applications being made on a 5 - 7 day schedule. In addition, proposed use directions allow for combination of Curacron with Guthion or methyl parathion for control of cotton boll weevil. Long-term effects (from a series of Curacron applications) have not been evaluated. Effects of Curacron-Guthion and Curacron-methyl parathion combinations on non-target insects have yet to be evaluated, as well.

In addition, effects of Curacron on aquatic insects have not been evaluated. This type of information is needed in cases where aquatic contamination is a possibility.

In summary, the following tests are needed prior to making a complete non-target insect hazard evaluation:

1. long-term field test, to show effects on non target insects from a series of Curacron applications to cotton;

2. tests to show effect of Curacron-Guthion and Curacron-methyl parathion combinations on non target insects; and

3. tests to show at least the short-term effects of Curacron on non target aquatic insects.

104.3 Endangered Species Consideration

Endangered Species have been initially screened by N. Cook (birds) L. Turner (mammals) and R. Balcomb (fish) for potential exposure to pesticides applied in the following cotton growing states:

Alabama	Georgia	Tennessee
Arkansas	Florida	Virginia
Arizona	Nevada	North Carolina
California	Kentucky	South Carolina
Texas	New Mexico	Missouri
Louisiana	Oklahoma	

Species with Hich likelihood of exposure:

Bald Eagle/Southern Bald Eagle-- All states

American Perigrine Falcon -- AK, NM

Red Cockaded Wocdpecker -- AL, AK, FL, GA, KT, LA, MI, VA, TN, SC, OK, NC

Mexican Duck -- NM, AR, TX

Attwater's Prairie Chicken -- TX

Gray bat -- AL, TN, GA, FL, OK, MO, AK

San Joaquin Kit Fox -- CA

Blackwater darter -- AL

Gila Topminnow -- AR

Bayou Darter -- MI

Pahrump Killifish -- NV

Alabama Cavefish -- AL

Leopard Darter -- OK

Comanche Spring Pupfish -- TX

Pecos Gambusia -- TX

Shortnose Sturgeon -- GA, SC

Species with possible likelihood of exposure:

Yuma clapper rail -- AR, CA

Whooping crane -- TX

Aleutian Canada Goose -- CA

California condor -- CA

Brown Pelican -- CA

Masked bobwhite -- FL, LA, GA, NC, SC, TX

Indiana bat

Eastern cougar

Species with little or no likelihood of exposure:

Bachman's warbler
Eskimo curlew
San Clemente sage sparrow
San Clemente Loggerhead shrieke
Santa Barbara Sparrow
Rusky Seaside Sparrow, Cape Sable Sparrow
Florida Everglad Kite
Ivory-billed Woodpecker
California Clapper Rail
Light-footed Clapper Rail
California Least turn
Mississippi Sandhill crane
Thick-billed parrot
Black Footed Fenet
Red Wolf
Sonoran pronghorn

Until the results of field and reproductive studies have been submitted formal consultation with the Office of Endangered Species will not be requested.

104.4 +.5 See conclusion

105.0 + 106.0 NA

107.0 Conclusions

107.1 Environmental Fate and toxicology Acknowledgement

D. Ritter of toxicology and S. Creeger and R. Cook have been consulted for this review.

107.2 + 107.3 NA at this time.