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TO: Lois Rossi
 Product Manager # 70
 Special Review and Reregistration Division (H7508W)

FROM: Elizabeth Behl, Head
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THRU: Henry Jacoby, Chief
 Environmental Fate & Ground Water Branch/EFGWB (H7507C)

Attached, please find the EFGWB review of...

Reg./File # :

Common Name : Bromacil

Product Name : Hyvar, Krovar I, Krovar II

Company Name : Dupont Agricultural Products

Purpose : Review Progress Report of Small-Scale Retrospective Ground-Water Monitoring Study

Type Product : Herbicide

Action Code : 627 EFGWB #(s): 92-0648, 92-0663 Total Review Time = 10 days

EFGWB Guideline/MRID/Status Summary Table: The review in this package contains...

161-1	162-4	164-4	166-1
161-2	163-1	164-5	166-2
161-3	163-2	165-1	166-3
161-4	163-3	165-2	167-1
162-1	164-1	165-3	167-2
162-2	164-2	165-4	201-1
162-3	164-3	165-5	202-1

Y = Acceptable (Study satisfied the Guideline)/Concur P = Partial (Study partially satisfied the Guideline, but additional information is still needed)
 S = Supplemental (Study provided useful information, but Guideline was not satisfied) N = Unacceptable (Study was rejected)/Non-Concur

1. CHEMICAL:

Chemical name: 5-Bromo-3-sec-Butyl-6-Methyluracil
Common name: Bromacil
Trade name(s): Hyvar, Krovar I, Krovar II
Structure:

2. TEST MATERIAL:

Not Applicable.

3. STUDY/ACTION TYPE:

Review progress report for small-scale retrospective ground-water monitoring study.

4. STUDY IDENTIFICATION:

Title: Memo Regarding the Progress of a Small Scale Retrospective Study on the Effects on Groundwater of the Use of the Herbicide Bromacil in Citrus Groves in Florida

Authors: E.I. Du Pont de Nemours & Company, Inc.

Submitted for: E. I. Du Pont de Nemours
Wilmington, DE

Identifying No.: 0123011
DP Barcode: D175887
Date Sent to EFED: 1/14/91

5. REVIEWED BY:

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Signature: Kevin J. Costello

Date: 9/28/92

6. APPROVED BY:

Elizabeth Behl
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Signature: E. Behl

Date: 9/28/92

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7. CONCLUSIONS:

Bromacil has been detected in three small-scale retrospective ground-water monitoring studies performed in the three major citrus-growing regions of Florida. Concentrations of bromacil in ground water ranged from 1.1 to 156 ppb, significantly above the Health Advisory Level (HAL) of 90 ppb. Bromacil was also detected in private drinking-water wells in Sebring and De Soto City in central Florida at concentrations ranging from 1.3 to 896 ppb.

The highest bromacil concentrations detected in the small-scale retrospective studies were detected in a Polk County citrus grove in the Central Ridge region. Concentrations ranged from 12.4 to 156 ppb, and all wells on the site had bromacil detections. Soils on the site were sands to a depth of at least 54 ft with an depth to the water table of at least 12 feet. Bromacil concentrations at the Flatwoods and Coastal region sites ranged from below the detection level to 147 ppb.

Du Pont suggests that the recent decrease in application rates for bromacil should lower ground-water contamination below the HAL. Based on the information presented in this report, this suggestion is not justified. Evidence for a linear connection between application rate and residues in the ground water is not presented, and is probably not realistic.

The studies produced by Du Pont in conjunction with the Florida Department of Environmental Regulation (FDER) and the Florida Department of Agriculture and Consumer Services (FDACS) have proven that bromacil does leach to the ground water. However, the studies may have given more information about the extent of contamination if they had followed the OPP guidelines for small-scale retrospective studies. Deviations from the guidelines are as follows:

1. The Coastal and Flatwoods region study sites do not adequately address the variation of ground-water contamination with depth, as each has single shallow monitoring wells screened to the same depth, rather than clusters of wells over a range of depths;
2. The monitoring wells at the Flatwoods region study site were installed with 10-foot screens below the top of the water table. Five-foot screens are recommended to avoid sample dilution.
3. The composition of the soil column is unclear, as the description given by Weston in Appendix A of the progress report and the description in the January 14, 1991 "Bromacil Ground and Water Well Studies," are inconsistent. The actual encountered soil profiles were not made clear for any of the three study sites;
4. The report states that "the Central Ridge Site was chosen so that the down-gradient monitoring well cluster is far enough away from the grove to allow sufficient time for measurable degradation of any bromacil residues to occur." Why and how that would be done is unclear;
5. Samples at all sites were taken quarterly, not monthly, perhaps allowing peak concentrations to go undetected;

6. No documentation of past or present bromacil use at or near the study sites was provided. This information would be of great use in interpreting patterns of contamination, especially for the sites bounded by drainage canals.

7. The dates of bromacil application at each of the three Florida sites were not provided.

8. Soil samples were to be "taken after at least 6 to 12 inches of combined rainfall and irrigation has occurred and 2-4 months have elapsed." The reasons for these delays is unclear.

8. RECOMMENDATIONS:

- 1) The registrant is required to conduct a small-scale prospective ground-water monitoring study for bromacil. A study protocol should be submitted to the Agency and approved by OPP's Ground-Water Section prior to study initiation.
- 2) Du Pont should meet with OPP's Ground-Water Section within 60 days to discuss the prospective ground-water monitoring study and questions raised in this review.
- 3) We recommend that application rates for citrus groves in the Coastal region be reduced to at most the 4.0 lbs. ai/acre currently labeled for the Central Ridge region, since detections of bromacil were found in ground-water samples collected from the Coastal Region study site with concentrations comparable to those encountered at the Central Ridge site.
- 4) The final report for the Florida small-scale retrospective study should include maps of the study sites showing exact well locations, location of drainage ditches, and depth to ground-water contours to illustrate direction of ground-water flow. Results of the soil sampling program, including bromacil concentrations in soil and drilling logs depicting the actual observed soil profiles should also be provided, as well as details of the bromacil applications, results of spray drift disk samples, and on-site meteorological data. The input file for the PRZM modeling of bromacil in Florida alluded to in the report should also be provided.
- 5) In the meeting with the Ground-Water Section, Du Pont should provide detailed sales information for Hyvar and Krovar nationwide, especially for the use on pineapples in Hawaii and Puerto Rico.
- 6) In the meeting with the Ground-Water Section, Du Pont should provide details of its carbon filter installation program for drinking water wells contaminated with bromacil, as detailed in the Discussion section.
- 7) Du Pont should revise the ground-water label advisories for Hyvar and Krovar herbicides to meet current standards.

9. BACKGROUND:

Bromacil is the common name for 5¹-Bromo-3-sec-Butyl-6-Methyluracil. It is marketed under the trade names Hyvar X, Krovar I, and Krovar II.

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Bromacil herbicide is used predominantly in the State of Florida, where it is applied on about 95% of the citrus crop grown. Florida citrus is grown approximately equally between the three major growing regions: the Central Ridge, the Coastal, and Flatwoods regions. California and Texas are other major citrus markets for the product. Bromacil is also used for pineapple production in Hawaii and Puerto Rico. Bromacil was also used until recently for non-crop weed control in ditches and right-of-ways. This use has been removed from the product label in response to concerns with surface water contamination.

Bromacil is formulated primarily as a water-soluble powder (80% ai in Hyvar herbicides, 40% ai in Krovar herbicides). The product was applied by continuous band application on the sites chosen for this study. The current label rates of Hyvar application for Florida citrus are 6.4 lbs. ai/acre for the Coastal and Flatwoods regions, and 4.0 lbs. ai/acre for the Central Ridge region. These rates were recently lowered in response to preliminary results of the current study.

Bromacil residues have been detected in previous studies in the ground water of 5 states (FL, CA, TX, OR, and WA). However, according to the Pesticides in Ground Water Database, ground-water concentrations above the HAL have only been encountered in Florida. The database indicates that out of a total of 15,484 wells in Florida, 238 had bromacil detections. Concentrations ranged up to 951.6 ppb. The state with the most detections after Florida is California, which had 46 detections in 1395 wells. Concentrations of bromacil in California ranged up to 20 ppb. To date, ground-water samples have not been taken for bromacil analysis in pineapple groves in Hawaii.

Du Pont, working in conjunction with the Florida Department of Environmental Regulation (FDER) and the Florida Department of Agriculture and Consumer Services (FDACS), chose three citrus-growing sites to conduct small-scale retrospective ground-water studies. These sites were selected to represent the three major citrus-growing regions in Florida. The purpose of the study was to determine if residues of bromacil "have reached the potable groundwater beneath the sites under normal use conditions." OPP was advised in 1986 that this study would be conducted, and has been awaiting reports of study results to determine if additional information is needed. This review summarizes a progress report of the study results.

The lifetime Health Advisory for bromacil is 90 $\mu\text{g/L}$, and it is listed in Cancer Group C (EPA, 4/91), which signifies a possible cancer risk for humans. No Maximum Contamination Level (MCL) has yet been established for bromacil. No health advisory nor MCL has yet been set for the degradates of bromacil, as studies have not yet been performed to determine the possible toxicity or carcinogenicity of the degradates.

10. DISCUSSION:

SITE DESCRIPTION:

Three sites, described below, were chosen for the Du Pont study:

Central Ridge Region Site: The Central Ridge Region site was located in Polk County in central Florida. The surface soil was classified as a Candler sand. The stratigraphy of the site was described as "sand to depth." Ten monitoring wells

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were installed on site, with 9 of the 10 in three clusters of three. The depths of these wells were staggered, covering a range from 14 to 54 feet deep. The depth to ground water was as shallow as 12 feet during the study. Organic matter content for the site was not provided in the current report.

Flatwoods Region Site: The Flatwoods Region site was located in Hendry County in southwestern Florida. Two conflicting descriptions of the site stratigraphy are included in the current submission. The stratigraphy of the site was described in Appendix B of the report as a Wabasso sand from 0 to 5 feet, clay from 5 to 6.5 feet, and limestone bedrock from "6.5 feet to depth." However, in the January 14, 1991 memo, "Bromacil in Ground and Well Water," the stratigraphy is listed as medium-grained sand with some clay from 0 to 4 feet, yellowish-brown coquina from 4 to 6 feet, and light greenish clay with sand and some silt from 6 to 32 feet. Average depth to ground water on-site was approximately 8 feet. Organic matter content was not provided in the current report.

Coastal Region Site: The Coastal Region site was located in St. Lucie County on the east coast of Florida. The soil on this plot has been classified as a Wabasso sand. The stratigraphy of the site was described as "thinly stratified, unconsolidated coarse sand and shell gravel" in the January 14, 1991 memo, but in Appendix B of the report it was described as sand with some clay and limestone fragments from 0 to 7 feet, hardpan from 7 to 8 or 9 feet, and sand with shells from 8 or 9 feet to depth.

Three shallow ground-water monitoring wells were installed on the site, all screened from 5 to 10 feet. The first of these wells, MW-1, was installed at the intersection of two drainage canals that border the site to the west and south. The other two wells, MW-2 and MW-3, were apparently installed in a line equidistant between the two canals. A fourth well, MW-4, was installed later with a screened interval from 50 to 60 feet. Average depth to ground water was about 6.5 feet. Organic matter content was not provided in the current report.

In addition to the three sites described above, Du Pont monitored ground-water concentrations of bromacil at sites in Sebring and De Soto City, in central Florida:

Sebring Site: Du Pont began a quarterly sampling program in July 1987 at a citrus grove near Sebring after samples taken by the FDACS indicated bromacil residues above the HAL in one well. The site is underlain by sandy soils, with depths to water as shallow as 9 feet. Shallow sand-point wells were installed to expand upon the data being collected from existing wells. These wells were also sampled quarterly.

Du Pont Site: Du Pont expanded its sampling program in October 1987 to include domestic wells in De Soto City, a residential area near the Sebring site that is "essentially surrounded by citrus groves." It is not clear from the report whether this action was voluntary, or mandated by the FDACS. Quarterly samples were taken from wells that exhibited an initial ground-water bromacil concentration level of 30 ppb or greater. "Periodic samples" were taken from some of the wells that did not have detections at this level. Depths to ground water were not provided for this site.

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RESULTS:

Ground-water samples were collected from the three sites starting in September, 1987. Sampling was discontinued at the Flatwoods and Coastal region sites after

December, 1989, with the approval of FDACS and the FDER. Data is provided in the current report through September, 1990 for the Central Ridge region site. Results of the ground-water monitoring studies are as follows:

Central Ridge: Bromacil residues were detected in all 10 of the monitoring wells installed on this site. Five of these wells had at least one detection above the HAL of 90 ppb, with the highest detection (156 ppb) occurring in January, 1989 in MW-4. The concentrations of bromacil did not decrease with time in any particular well over the three years of data presented, falling below and then rising above the HAL in wells MW-4 and MW-8. Current and historical bromacil use history might help in the interpretation of these trends, but this information was not provided by Du Pont.

Flatwoods Region: Bromacil residues were detected in all three of the monitoring wells installed on this site, with the highest concentration (21.8 ppb) detected in MW-2. Sampling was discontinued with the approval of the FDACS and the FDER after December, 1989, since none of the concentrations detected were near the HAL. Based on our review of this study EFGWB has concerns with the results from this study, and reservations with the way the site was instrumented. These reservations pertain to the length and placement of the well screens at this site. The wells have 10 foot screens, 5 feet longer than the length preferred by OPP. The concern is that longer screen lengths may allow dilution of the ground-water samples, a concern that may be particularly valid for this site due to the placement of the screens. The wells are either screened totally in "greenish clay" or limestone bedrock, depending on which of the two stratigraphies provided is accurate. Both textures could potentially retard the downward migration of product to the lower five feet of screen.

Coastal Region: Bromacil residues were detected in three of the four monitoring wells, with the greatest concentrations in downgradient well MW-1. Concentrations detected in this well ranged from 26 to 147 ppb. Bromacil concentrations up to 11.5 ppb were detected in the other shallow wells. Du Pont postulated that the high concentrations detected in MW-1 were the result of contamination that occurred during well installation. They attempted to justify this by pointing out that nearby well MW-4 did not have a single detection. However, the concentrations encountered in MW-1 persisted over more than two years, with a detection of 95 ppb as late as May, 1989. It is doubtful that this level of contamination could be maintained by cuttings from a 2-inch diameter well for this length of time. Furthermore, the screened interval for MW-4 was 50-60 feet, offering no means for comparison with the MW-1 screened depth of 5 to 10 feet. The concentrations detected in MW-1 must be considered valid in this light. Sampling was discontinued with the approval of the FDACS and the FDER after December, 1989.

Sebring Wells: Significant bromacil contamination was detected in the water wells for a barn and an office near the citrus grove, with concentrations of 64.5 to 239 ppb in the barn well, and 27.3 to 54.9 ppb in the office well. Carbon filters were installed on both wells, and the barn and office were later

connected to city water. The filtered water was analyzed concurrently with the pre-filtered water starting in September, 1987. Concentrations of bromacil in the filtered office water were reduced to below detection level through the last sample described in February, 1989. However, the filtered barn water concentrations were below detection level only through January, 1988.

Concentrations of 1.1 to 5.5 ppb were detected in quarterly sampling through March, 1990, and in a final sample taken in June, 1990, the concentration was back up to 76.0 ppb.

Significant bromacil contamination was also encountered in the wells at an on-site trailer and mixing/loading area, as well as in sand point wells installed to better characterize the extent of contamination. The locations of these wells are not clear, as Du Pont did not submit a complete map of the grove. Most of these wells had four-foot screens, and were installed near the top of the water table. Concentrations of bromacil exceeded the HAL in 5 of 10 of these wells, with the highest detections over 400 ppb. Four of the other 5 wells had at least one detection above 35 ppb.

Sand point well 6II was installed with one foot of screen to a depth of 16 feet below the water table. This well produced detections above the HAL through more than 2 1/2 years of quarterly sampling, with concentrations between 91 and 313 ppb. This well was installed adjacent to Sand Point Well 6I, which produced a concentration range of 4.5 to 67.2 ppb.

The samples collected at this site were also analyzed for diuron, which is mixed in equal parts with bromacil in the Krovar herbicides. Nine of the 15 wells on site had at least one detection, with the highest diuron concentration of 15.5 ppb detected in Sand Point Well 6II.

De Soto City Studies: Ground-water samples were taken from 85 private wells in De Soto City, adjacent to and south of the Sebring study site. Half of these wells (43) had detectable levels of bromacil residues, with concentrations ranging from 1.2 to 896 ppb. Twelve wells had contamination above the HAL. One of these wells had detections as high as 896 ppb, a concentration almost 10 times the HAL, significantly higher than the range of 90 to 136 ppb detected in any of the other 11 wells. Du Pont considers this well to have been contaminated by a point source, noting that a spray rig was frequently parked near this well.

Du Pont believes that the recent one-third reduction of the maximum label rate, to 6.4 lbs. a.i./acre in the Coastal and Flatwoods regions, and to 4.0 lbs. a.i./acre in the Central Ridge region, will result in a reduction of ground-water contamination to below the HAL. In light of other detections above 136 ppb presented in the current report, the lack of data on historical use rates at the sites monitored or any supporting data, the basis for Du Pont's assumption of a linear response to a change in the maximum label rate is not supportable.

FILTER PROGRAM ISSUES:

The De Soto City and Sebring studies bring up another significant item of concern. Ten wells in De Soto City and two at Sebring were fitted with carbon filters. Bromacil residues could not be detected in the filtered drinking water from these wells in the first samples taken after filter installation. However,

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one of the Sebring wells had 2.7 ppb bromacil contamination within 7 months. After 30 months, the concentration in this well was 76 ppb.

All of the filters were installed on wells that had at least one detection of bromacil above the HAL. However, two wells with detections above the HAL, including the well with the highest concentrations detected, did not receive carbon filters. In addition, none of the wells with detections below the HAL, including one with a detection of 86.9 ppb, received a filter.

In order to protect homeowner health, a consistent and comprehensive carbon filter installation program must be implemented, with a diligent replacement schedule for spent columns. EFGWB is interested to know the details of Du Pont's filter program including:

- criteria for installing filters on private wells;
- criteria for removing filters from private wells;
- methods followed to determine efficacy of filters at removing contaminant of concern;
- methods for filter removal;
- methods for disposal of spent filters;
- approximate number of wells with filters in Florida (by county) installed to mitigate bromacil contamination of ground water.

REFERENCES:

E.I. Du Pont de Nemours and Co. "Memo Regarding the Progress of a Small Scale Retrospective Study on the Effects on Groundwater of the Use of the Herbicide Bromacil in Citrus Groves in Florida". January 8, 1991.

E.I. Du Pont de Nemours and Co. Letter to USEPA, Office of Pesticide Programs, Special Review and Registration Division, October 16, 1990.

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Florida Department of Environmental Regulation, 1990. Impact of Commonly Used Pesticides on the Water Table Aquifer in Collier County, Florida.

Resources For the Future. "Bromacil Use in the United States By State". May 23, 1991.

USEPA, 1989. Environmental Fate and Ground Water Branch, Pesticide Environmental Fate One Line Summary-Bromacil.

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USEPA, 1991. Environmental Fate and Ground Water Branch Review, EFGWB # 91-0632 and 91-0780, October 28, 1991.

USEPA, 1991. Environmental Fate and Ground Water Branch Review, EFGWB # 92-0648, April 24, 1992.

USEPA, 1991. Environmental Fate and Ground Water Branch Review, EFGWB # 92-0663, April 24, 1992.