Shaughnessy Number: 080804
Date Out of EFGWB: MAY 21 1991

TO: Mr. Thomas Luminello
Special Review and Registration Division (H7508C)

FROM: Elizabeth Behl (H7507C)
Acting Head
Ground Water Section
Environmental Fate & Ground Water Branch/EFED

THRU: Henry Jacoby, Chief (H7507C)
Environmental Fate & Ground Water Branch/EFED

Attached, please find the EFGWB review of:

Reg./File #: 2545

Chemical Name: Prometon

Type Product: Nonselective Herbicide

Company Name: Ciba-Geigy Corporation

Purpose: Review proposed protocol for Small-Scale Prospective Ground Water Monitoring Study in the place of a Small-Scale Retrospective Monitoring Study.

Date Received: 01/09/91 ACTION CODE: 660

Date Complete: 04/09/91 EFGWB #(s): 91-0321

Monitoring Study Requested: x Total Review Time: 8 Days

Monitoring Study Voluntary: _____

Deferrals To: _____ Biological Effects Branch

_____ Science Integration & Policy Staff, EFED

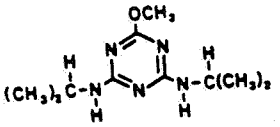
_____ Non-Dietary Exposure Branch, HED

_____ Dietary Exposure Branch, HED

_____ Toxicology Branch, HED

REVIEW OF SMALL-SCALE PROSPECTIVE GROUND WATER MONITORING STUDY

1. CHEMICAL:
Chemical name: Prometon
Common name: Pramitol®
Trade name: Pramitol®
Structure:



Physical/Chemical Properties:

Chemical Formula	$C_{10}H_{19}N_5O$
Molecular Weight	225.34
Water Solubility	620 mg L^{-1} @ 20°C
K_d	0.4 to 2.9
K_{oc}	48 to 100
Vapor Pressure	3.1 x 10^{-6} Torr
Log Octanol/Water Partition Coefficient	4.03 @ 20°C
Field dissipation half-lives	139 to 2058 days
Aerobic soil metabolism	> 365 days @ 25°C
Anaerobic soil metabolism	Stable at 90 days

2. TEST MATERIAL:
Not Applicable.

3. STUDY/ACTION TYPE:
Review proposed protocol for small-scale prospective ground-water monitoring study in conjunction with supportive information and justification and request for change in study type.

4. STUDY IDENTIFICATION:
Title: Study Protocol: A Modified Small-Scale Prospective Ground-Water Monitoring Study for Prometon.

Author(s): Blasland & Bouck Engineers, P.C.
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Suite 210W
Syosset, New York 11791

Submitted by: Agricultural Division
Ciba-Geigy Corporation
P. O. Box 18300
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Identifying No: 080804-000100
Case: 813912
Submission: S388516

DP Barcode: D159980
Action Code: 660
Date Sent to EFED: 12/21/90
Date Received by EFED: 12/28/90

5. Reviewed by:
James K. Wolf
Soil Scientist
OPP/EFED/EFGWB/GWTS

Signature: James K Wolf
Date: APR 23 1991

6. Approved by:
Elizabeth Behl
Acting Head
OPP/EFED/EFGWB/GWTS

Signature: Eliz Behl
Date: May 15, 1991

7. CONCLUSIONS:

The objectives of this review were to assess the registrants request to conduct a small-scale prospective ground-water study instead of the previously required small-scale retrospective ground-water study and the STUDY PROTOCOL: A Modified, Small-Scale Prospective Ground-Water Monitoring Study for Prometon submitted by Ciba-Geigy Corporation. This Protocol has been submitted to take the place of a retrospective study for this compound.

The ground-water study design outlined in the protocol is not acceptable in its present form as several areas are deficient and will require some modification. A major problem with the protocol is that it is too general, thus a thorough review is not possible. More specific detail, rather than referring to a guideline or some Standard Operating Procedure (SOP), is necessary to clearly define the information to be obtained from the study. Half-lives have been found to range from less than a year to more than six years. Therefore, the duration of the ground-water monitoring study must also be long enough to adequately characterize the fate of prometon.

The proposed study site will require EFGWB approval prior to initiation of the study. Additionally, study protocol will require EFGWB approval and should reflect site specific conditions present at the proposed study area.

The monitor well clusters should be located inside the subplot boundaries. Soil samples (initial and temporal) should be randomly sampled from in the subplot. Suction lysimeter clusters should be randomly distributed throughout the subplots rather than having all three sets of lysimeter clusters placed systematically in a row. The protocol calls for the installation of 9 monitor wells (8 adjacent to the plot and 1 up gradient), 4 piezometers (at the corners of

the 2 acre plot), and 20 suction lysimeters (15, 5 per subplot, and 5 up gradient) plus an on-site weather station.

8. RECOMMENDATIONS:

1. The request by the Registrant to conduct a Prospective Study in place of a retrospective study appears to be a valid request and is acceptable.

2. The reason(s) for narrowing the site selection to the Southeastern United States should be justified. Pesticide use information and prometon detections in ground water indicate that other regions should also be considered.

3. Final site approval by EFGWB will be required prior to initiation of the study. Supportive data used for site selection should be submitted for review by EFGWB. This should included information for all candidate sites evaluated and reasons why sites were eliminated from consideration. If a site is chosen which does not meet all "ideal" conditions, the use of such site should be justified.

4. Characterization of Candidate Sites, Study Protocol document, page 11 of 25. Soil sampling methods (sample increments, etc.) should be specified in the protocol document. This may include the Blasland and Bouck SOP. Soil profile descriptions should use SCS methodology. Clay type should also be specified.

5. The protocol should provide specific detail rather than referencing guidelines or an appropriate Blasland and Bouck SOP. A method of dealing with changes in protocol procedures due to unanticipated site conditions should also be specified.

6. Potentially interfering chemicals should be specified (Study Protocol document, page 13 of 25). How will the presence of these chemicals be identified?

7. The study should use Promitol^{R} 25E because Promitol^{R} 5S contains simazine as an active ingredient.

8. The determination of prometon metabolite residues in soil and water will also be required. The analytical methods for prometon and prometon metabolites and detection limits for both water and soil will also need to be specified. This should be included in the reissued protocol, and approved by EFGWB prior to initiation of the study.

9. Hydraulic properties of the aquifer such as: transmissivity, hydraulic conductivity, hydraulic gradient, etc., should be determined in the site characterization phase. A description of the study area should be included. This should describe the regional and local geologic and soil conditions, climate, etc. Also any off-site features that may influence the hydrologic system in the study area should be identified, such as ponds, lakes, streams, recharge or discharge zones, irrigation wells and pesticide loading or storage activities.

10. Background characterization of the water quality (i.e. pH, EC, cations, anions, redox, temperature) of the aquifer should determined prior to chemical application and also at the end of the study. The analytical methods should be specified.

11. Monitor wells should be placed inside subplot boundaries and be well inside irrigation coverage limits so as not to locate the monitor wells on a boundary (i.e., irrigated/nonirrigated boundary).

12. The irrigation plans should be better defined. This should include type of irrigation system, anticipated application rate, irrigation pattern, and the source and quality of water. The irrigation duration and distribution efficiency should be determined and be reported. Application rates should be low enough that runoff does not occur unless runoff volumes are measured and samples are collected and analyzed. The registrant must demonstrate that pumping the irrigation well does not affected the flow system in the target aquifer at the study site.

13. Water and soil sampling should continue for at least two years and may be longer depending on persistence at the study site. This may be necessary, as field dissipation half-lives are highly variable and have been documented up to six years. Sampling can <u>not</u> be discontinued until EFGWB concurs and written approval to discontinue sampling has been obtained from EPA/OPP.

    Soil sample preservation and storage methods should be specified. This should be reflected in the protocol. Soil should be sampled monthly for a minimum of two years. A reduction in sampling frequency can be requested by the registrant based upon interim data results.

14. Soil samples should not be composited (Study Protocol Document, page 23 of 25). Compositing does not allow

for the determination of field variability. Split samples should be routinely included in the analytical programs to assess laboratory precision.

Because pesticide and metabolite residue distributions within the root zone and vadose zone is one of the primary objectives of a prospective study, soil sample increments should be 6 inches in the 0 to 2 foot depth and 12 inches in 2 to 5 feet depth and not exceed 2 feet below the five foot depth.

15. Methods of soil preservation, preparation and analysis should be defined in the Study Protocol. Volumetric soil water content should be determined for all soil samples collected. Soil and vadose zone hydraulic conductivity should be measured at the study site. Instruments such as the Guelph permeameter are easy to implement in the field and can provide saturated hydraulic conductivity values and estimates of unsaturated hydraulic conductivities. Hydraulic conductivity versus water content or matric potential (unsaturated soils) should also be determined. Adsorption isotherm values (Kd) should be determined for the soil and vadose zones. These additional information will enable simple computer models to be calibrated to the study site.

16. What meteorological measurements will be collected by the weather station (Study Protocol document, page 20 of 25) at the study site? It is recommended that a backup raingauge be located on the study site to insure that precipitation is measured on-site.

17. An idealized study site map should also submitted which delineates all anticipated instrumentation and sampling locations. This should include the 2 acre area with piezometers, up gradient monitor well, monitor wells, suction lysimeters and piezometers, weather station, and the half-acre treatment area with all corresponding instrumentation. Also a downgradient sample staging and decontamination area should be delineated. After the instrumentation and pre-sampling program is completed an actual map should be submitted.

18. A thick (> 20 feet) aquifer may require a third monitor well in each well cluster. The protocol should address conditions when a third well would be added. The upper screen should be placed to sample at the water table surface. If a large seasonal fluctuation is expected this may also necessitate more than two wells per cluster.

19. A schedule for reporting interim and final study results should be specified.

20. During purging (Study Protocol document, page 20 of 25) of ground-water monitoring wells prior to sampling, how and where will the water be disposed of? Will dedicated samplers and sampling pumps be used for each monitor well? If not how will samplers and pumps be decontaminated?

21. All necessary state and local permits should be obtained for the monitor wells and piezometers.

9. BACKGROUND:

Prometon is a nonselective pre-emergence and post-emergence industrial herbicide used for weed control on non-cropland at rates between 0.5 to 2 lbs 100 ft^{-2}, or 5 to 100 gals $acre^{-1}$. Highest rates of use is for hard-to-kill weeds such as johnson grass, bindweed, and wild carrot. Prometon is an s-triazine compound which is stable, persistent and mobile in soil. The environmental chemistry and fate characteristics (Table 1) indicate that the herbicide has the potential to leach to ground water.

Prometon has been detected in 36 of 746 ground-water samples (STORET, 1988). Samples were collect from 250 wells and prometon was detect in 12 states. The presence of prometon in ground water was also confirmed in 4 of 80 samples by the Pesticides in Ground Water Data Base (Williams et al., 1988). Prometon levels ranged from 5.2 to 29.6 ppb with a mean of 16.6 ppb. The National Pesticide Survey (NPS, 1990) found prometon in 1 of 564 (0.2%) community water systems and 4 of 783 (0.5%) rural domestic drinking water wells. Prometon levels for this study ranged from detectable to 0.57 ppb.

An initial review of environmental chemistry, fate and ground-water monitoring data was conducted by M.R. Barrett, EFGWB/ Ground Water Section, under combined EAB #(s) 70730 and 70747, date 6/09/88, which stated the need for a small-scale retrospective ground-water monitoring study.

The Study Protocol reviewed was submitted by Ciba-Geigy Corporation with a transmittal date of December 21, 1990. A letter to Mr. Thomas Luminello, EPA, from Mr. Thomas J. Parshley, Ciba-Geigy Corporation accompanied the submittal. This letter stated that the subjects of the submittal would deal with the following topics: the submission of amendment request, site selection reports, the revised protocol for

Prometon ground-water monitoring study, and the reregistration of Prometon (Case 2545).

The following is a summary of events concerning Prometon, according to the submission letter to Mr. Tom Luminello, EPA, from Thomas J. Parshley, Ciba-Geigy Corporation, dated December 21, 1990:

Ciba-Geigy was required during a September 28, 1988 Ground-Water Data Call-In notice to conduct a small-scale retrospective ground-water monitoring study. Parshley further stated that Ciba-Geigy committed to conducting a small-scale retrospective ground-water monitoring study on February 9, 1989. Ciba-Geigy also indicated that a protocol was submitted to EPA on May 10, 1989 for review and comments. Parshley indicated in the December 21, 1990 letter that no comments were received from the Agency concerning this protocol. No record or review of this protocol was found in EFGWB files.

In response to the Data Call-In, a small-scale retrospective ground-water monitoring study, prepared by Diane Miller of Roux Associates, Inc., dated October 8, 1990, was included in the December 21, 1990 submittal by Ciba-Geigy.

Ciba-Geigy indicated that they were unable to find suitable cooperators willing to make available any land for a study site(s). Therefore, the Registrant proposed conducting a small-scale prospective ground-water monitoring study rather than a retrospective study per 11/21/90 telephone conversation with the J.H. Jordan (refer to Discussion Section of Jordan review, 1990). This retrospective study protocol and suggested change in study type was review by J.H. Jordan, EFGWB, on 12/07/90, EFGWB# 90598. Deficiencies were noted in the retrospective study protocol. However, it was recommended by EFGWB (Jordan, 1990) to waive the retrospective study requirements in favor of the prospective ground-water monitoring study, because of difficulties in finding suitable retrospective study sites.

The request to considered changing the ground-water monitoring study from a retrospective to a prospective was formally made in the December 21, 1990 letter from T.J. Parshley to T. Luminello. Supporting documentation for this request was included in Volume 2 of 4: Site Investigation for a small-scale retrospective ground-water monitoring study of Prometon. Ciba-Geigy indicated that protocol for a small-scale prospective ground-water monitoring study would be submitted for review in January 1991.

This review addresses the change in study type and the draft small-scale prospective ground-water monitoring study

protocol submitted on December 21, 1990 per data review package instructions.

10. DISCUSSION:

The Ciba-Geigy transmittal document, dated December 21, 1990, indicates that the submittal consisted of four volumes:

> Volume 1 of 4: Transmittal Document
> Volume 2 of 4: Site Investigation for a small-scale retrospective ground-water monitoring study of prometon (Blasland and Bouck Engineers).
> Volume 3 of 4: Small scale retrospective ground-water monitoring study for prometon (Roux Associates).
> Volume 4 of 4: Pramitol 25E and Pramitol 5PS 1990 usage survey.

However, a fifth document was included in the submittal "Study Protocol: A Modified, Small-Scale Prospective Ground-Water Monitoring Study for Prometon" which was prepared by Blasland and Bouck Engineers.

The Site Investigation for a Small-Scale Retrospective Ground-Water Monitoring Study of Prometon (Volume 2 of 4) document demonstrates the inability of the Registrant to locate suitable study sites for a retrospective study because of a lack of willing cooperators. This document supports the contention that the Registrant was unable to find suitable study sites for retrospective studies. Based upon the information supplied by the Registrant, the request to conduct a Prospective Study in place of a retrospective study appears to be a valid and acceptable. Therefore my review is based upon the fifth document, "Study Protocol: A Modified, Small-Scale Prospective Ground-Water Monitoring Study which was for Prometon" which was prepared by Blasland and Bouck Engineers. The retrospective study was <u>not</u> reviewed as the Registrant is requesting to conduct a prospective study.

<u>Discussion on Protocol</u>

The overall objective seems to adequately define the intended goal of the study, but the protocol is too general. More specifics should be included concerning soil sampling procedures and analytical procedures and suction lysimeter and monitor well installation. Specifically, the protocol calls for the installation of 9 monitor wells (8 adjacent to the plot and 1 up gradient), 4 piezometers (at the corners of the 2 acre plot), and 20 suction lysimeters (15, 5 per subplot, and 5 up gradient).

Site Selection Criteria

The site selection is a very important consideration any ground water monitoring study whether it is prospective or retrospective in nature. Because of the types of uses for prometon, I question whether a relatively flat topography site is what is desired. Many of the areas where prometon is applied (roadways, pipelines, drainage ditch banks, etc.) may result in a concentration of flow as surface runoff, i.e. in a borrow ditch along a road. This concentration of runoff water in topographic lows (i.e., borrow ditch) may concentrate prometon and thereby increasing the likelihood of reaching the ground water in measurable concentrations. This should be considered in the site selection process.

The soil textural criteria listed on page 9 (Study Protocol) indicates that sand content should be greater than 70% and the clay content should be less than 20%. Previously conducted ground-water monitoring studies have indicated that sand contents should be greater than 80 to 90% and clay should be less than 10 to 15%. This is especially important in the root zone as the majority of microbiological activities and highest adsorption capacities occur in this zone. These changes in soil textures should be included in the search criteria.

It is also preferable that the study site have an unconfined aquifer closer to 20 feet below the land surface rather than 30 feet (Study Protocol document, page 10 of 25).

Sampling Methodology and Instrumentation

Soil profile descriptions should utilize USDA SCS methodology and criteria (USDA SCS Handbooks 18 and 436) including such information as Munsell soil colors, soil structure type and size. This may require some adjustment, because of sampling by a specified increment (i.e. 0 to 6", 6" to 12"), to stay within soil horizons so that physical and chemical data are available to aid in correlating soils at candidate sites to soil series.

The data to be collected by the on-site weather station (Study Protocol document, page 20 of 25) is not specified. It is strongly recommended that in addition to rainfall, that wind speed, relative humidity, maximum and minimum daily temperatures, and pan evaporation be measured. This information then can be used to estimate the water balance for the site.

The protocol should specify whether the water potential used for field capacity will be 1/3 or 1/10 atmospheres. Measuring a soil water content in the laboratory at a

specified tension and then using this value as field capacity is a controversial concept and care must be used when evaluating the significance of the value. Laboratory measurements of field capacity can result in erroneous values by using disturbed samples rather than an undisturbed sample.

This reviewer has had some field experience with suction lysimeters. Therefore, it is suggested that the suction lysimeters be installed as soon as possible, after a site is selected and OPP approval obtained, and to start collecting water samples as soon as possible to make sure that the lysimeters are operating properly, prior to chemical application.

It is not explicitly clear, but it is assumed that well elevations will be surveyed to at least one-hundredth of a foot. Relative elevation will be adequate, but actual elevation with a latitude and longitude would be better.

Data Presentation

Maps should have, at a minimum, the following information: a complete legend; north arrow, scale, symbol key, title, plus State, County, Section number, Range and Township, etc. A location map on a U.S.G.S. Quadrangle Map should be included. Aerial photographs (photo-pair) would be of considerable use.

Environmental Fate

Field dissipation studies of prometon by Balcomb and Honeycutt (1986a, b,c) which were summarized by Barrett (1988) indicated parent dissipation half-lives ranging from 200 to 400 days in California, 531 to 2058 days in New York, and 139 to 2227 days in Nebraska. Significant leaching was also evident to the maximum depth (18 inches) of sampling. Because of variability in field dissipation half-lives, it is inappropriate to limit sampling to one year after application. Discontinuation of monitoring at a study site is contingent upon results of the monitoring data and other factors. Sampling should continue for at least two years. If EFGWB is satisfied that of the chemical has been adequately characterized, monitoring may be discontinued upon written approval from EPA/OPP. This should be reflected in the protocol.

Field dissipation half-lives are highly variable may indicate that climatic factors need to be considered in site selection. For example, California (200 to 400 days) suggest a warm climate and warm soils while Nebraska and New York (139 to 2227 days) suggest cooler climate and soil

conditions. Therefore one site in the southeastern United States may not be adequate and a second site may need to be considered. It also may be beneficial to consider where prometon has been detected in ground water, such as California, Florida, Iowa, Massachusetts, Oklahoma, and Texas, and also high use states should also be considered.

TABLE 1. Related environmental chemistry and fate characteristics for Prometon compared with those of some pesticides that have been found to leach.

Name of Characteristics	Prometon Characteristics	Known leacher[1] Characteristics
Kd	*0.4 to 2.9 in 5 soils from sand to silty clay loam and OM** % between 0.8 and 5	< 5, usually less than 1 or 2
Koc	*48 to 100	< 300 to 500
Kw (mg L^{-1}) Water solubility	*620 @ 20°C	> 30
Henry's Law Constant (atm mol^{-1})	*1.5×10^{-9}	< 10^{-5}
Photolysis, $t_{1/2}$ (days)	*In water, >>30	> 7
Photolysis, $t_{1/2}$ (days)	*In soil, 357	> 14 to 21
Hydrolysis, $t_{1/2}$ (days)	* > 365	> 175
field dissipation $t_{1/2}$ (days)	139 to 2227	
leaching depth	***45 cm	90 cm

[1] Cohen et al., 1984.
* Trigger factors
** OM is organic matter.
*** 45 cm - Prometon residues were present a the maximum depth of sampling, 45 cm.

REFERENCES

Balcomb, R.T. and R.C. Honeycutt. 1986a. Field dissipation studies on prometon (Pramitol 25E) Fresno, California. Report EIR-86013 submitted by Ciba-Geigy Corporation, Greensboro, NC.

Balcomb, R.T. and R.C. Honeycutt. 1986b. Field dissipation studies on prometon (Pramitol 25E) Columbia, New York. Report EIR-86014 submitted by Ciba-Geigy Corporation, Greensboro, NC.

Balcomb, R.T. and R.C. Honeycutt. 1986c. Field dissipation studies on prometon (Pramitol 25E) York, Nebraska. Report EIR-860018 submitted by Ciba-Geigy Corporation, Greensboro, NC.

Barrett, M.R. 1988. Ground-Water Data Call-In Review. Date 06/09/88, EAB#,s 70730, 70747.

Jordan, J.H. 1990. Review proposed Pramitol small-scale retrospective ground-water monitoring protocol. 12/07/90. EFGWB# 90598.

NPS (National Pesticide Survey) 1990. U.S. Environmental Protection Agency. Washington D.C.

STORET. 1988. STORET Water Quality File. Office of Water. U.S. Environmental Protection Agency.

Williams, W.M., P.W. Holden, D.W. Parsons, and M.N. Lorber. 1988. Pesticides in Ground Water Data Base. OPP/EFGWB U.S. Environmental Protection Agency. Washington, DC.