DP Barcode : D174771
PC Code No. : 081901
EFGWB Out : 1/14/93

TO: Walter Waldrop
Product Manager # 71
Special Review and Reregistration Division (H7508W)

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

David A. Wells for EB

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

Henry Jacoby

Attached, please find the EFGWB review of...

Reg./File # : 081901

Common Name : Chlorothalonil [2,4,5,6-tetrachloroisophthalonitrile]

Product Name : BRAVO 720

Company Name : ISK Biotech

Purpose : Review protocol for small-scale prospective ground-water study.

Type Product : Fungicide

Action Code : 635 EFGWB #(s): 92-0545 Total Review Time = 11 days

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

161-1		162-4		164-4		166-1	D174771
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

DP BARCODE: D174771 REREG CASE #

CASE: 819269
SUBMISSION: S412012

DATA PACKAGE RECORD
BEAN SHEET

DATE: 01/13/93

* * * CASE/SUBMISSION INFORMATION * * *

CASE TYPE: REREGISTRATION ACTION: 635 PROPOSED TEST PROT SUBM
CHEMICALS: 081901 Chlorothalonil 100.00 %

ID#: 081901
COMPANY:
PRODUCT MANAGER: 71 WALTER WALDROP 703-308-8062 ROOM: CS1 3B3
PM TEAM REVIEWER: ANDREW W ERTMAN 703-308-8063 ROOM: CS1 32B5
RECEIVED DATE: 02/05/92 DUE OUT DATE: 05/15/92

* * * DATA PACKAGE INFORMATION * * *

DP BARCODE: 174771 EXPEDITE: Y DATE SENT: 02/21/92 DATE RET.: / /
CHEMICAL: 081901 Chlorothalonil
DP TYPE: 001 Submission Related Data Package
ADMIN DUE DATE: 05/21/92 CSF: N LABEL: N

ASSIGNED TO	DATE IN	DATE OUT
DIV : EFED	02/25/92	/ /
BRAN: EFGB	02/25/92	/ /
SECT: GTS	02/27/92	01/13/93
REVR : JWOLF	08/01/92	09/18/92
CONTR:	/ /	/ /

* * * DATA REVIEW INSTRUCTIONS * * *

Please review the attached protocol for a Ground Water Monitoring study. The registrant, ISK Biotech, is requesting a meeting in 60 days to discuss the Agency's position. Thank you for your expeditiousness.

* * * ADDITIONAL DATA PACKAGES FOR THIS SUBMISSION * * *

DP BC	BRANCH/SECTION	DATE OUT	DUE BACK	INS	CSF	LABEL

REVIEW OF DRAFT PROTOCOL FOR A SMALL-SCALE PROSPECTIVE GROUND WATER MONITORING STUDY

1. CHEMICAL:
Chemical name: 2,4,5,6-tetrachloroisophthalonitrile
Common name: Chlorothalonil
Trade name: Bravo 720, Daconil
Structure: N/A

Physical/Chemical Properties[¶]:

Chemical Formula	$C_8N_2Cl_4$
Molecular Weight	265.89
Water Solubility	1.2 mg/L (1200 µg/L) @25 °C
K_d[§]	3 to 29
Vapor Pressure	2.0×10^{-6} mm Hg @ 25 °C
Log Octanol/Water Partition Coefficient	2.88 (758.58)
Field dissipation half-lives	30 to 60 days
Aerobic soil metabolism	10.3 to 36.5 days (nonsterile)
Anaerobic soil metabolism	

[¶] USEPA One-Liner - 12/14/89; USEPA, 1989; Wauchope et al., 1992.
[§] Values are Freundlich K_{ads}; all 1/n <0.94.

2. TEST MATERIAL:
Bravo 720; chlorothalonil, EPA Registry No. 50534-188

3. STUDY/ACTION TYPE:
Review proposed protocol for Chlorothalonil (Bravo) small-scale prospective ground-water monitoring study in conjunction with supportive information.

4. STUDY IDENTIFICATION/ACTION TYPE:
Title: Protocol Number: Draft-92 Chlorothalonil (Bravo) Small-Scale Ground-Water Monitoring Study.

Author(s): American Agricultural Services, Inc.
P.O. Box 1293
Cary, NC 27512

Submitted by: ISK Biotech Corporation
5966 Heisley Road
P.O. Box 8000
Mentor, Ohio 44061-8000

Identifying No: 0081901
Case: 819269
Submission: S412012
DP Barcode: D174771
Action Code: 635

3

Date Sent to EFED: 02/21/92
Date Received by EFED: 02/25/92

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

Signature: James K. Wolf
Date: November 18 1992

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

Signature: Daniel A Wolf for EE
Date: November 18, 1992

7. CONCLUSIONS:

The protocol submitted by the registrant is incomplete, and is not acceptable in its present form. However, based upon verbal and written responses by the registrant to issues raised by EFGWB during a Registrant/EFGWB meeting, the protocol can be modified through clarification and the addition of supplemental information.

The site-selection process, site-selection criteria, and the historical use of chlorothalonil criteria are acceptable. The registrant proposes select a "realistic worst-case" site within a major use area with vulnerable hydrogeologic conditions in a peanut growing area in North Carolina, where the depth to the water table will be less than 30 feet.

8. RECOMMENDATIONS:

- Study Site Location, Site Characterization, and Use Information

  It is recommended that the study site location and site characteristics be submitted to and meet with EFGWB approval prior to the start of the study to find a mutually acceptable site. The registrant shall submit chlorothalonil use information to justify conducting the study on peanuts. This information was submitted by the registrant pursuant to a meeting held on May 28, 1992 and should be included in the revised protocol.

- Soil Properties

  The registrant should determine the particle size distributions, volumetric soil water content, and organic matter (carbon) content for the soil boring samples (5 to 40 feet). It is also recommended that cation exchange capacity (CEC) be determined for the surface soil material (0 to 60 inches).

- Theoretical Application Verification

  EFGWB requires that the registrant include in the study protocol a methodology to confirm the pesticide application (i.e., application cards, petri dish, etc). EFGWB is concerned that soil analysis after application often results in measured pesticide concentrations much lower than the theoretical application concentration. Low measured values may indicate poor recovery (methodology problems), application rates lower than desired, or a dissipation avenue that has not been account for. This may cause difficulty in interpreting the study results.

- Soil Sampling Schedule

  EFGWB proposes the following modified sampling schedule (Table 4) for the collection of shallow soil samples. Soil samples (3 sectors, 6 depths = 18 samples per interval) should be collected and analyzed prior (-1 days) to the 8 chlorothalonil applications as defined in the protocol (pages 26 to 28). Soil samples shall also be collected and analyzed after each chlorothalonil application from each sector for one (1) depth (0 to 6 inches). After the final chlorothalonil application, soil samples shall be collected and analyzed monthly, following the original sampling plan (3 sectors, 6 depths, 18 samples). This results in 384 soil analyses (rather than 486). Sampling beyond 12 months after the last chlorothalonil application will depend upon study results as does the approval to terminate the study. The protocol should be modified to reflect these changes.

  The protocol is inconsistent in its definition of the timing of deep sampling (page 28 and 29). The bottom of page 28 indicates that the "6-month sampling" will be six months after the last application, whereas page 28 indicates six months after the initial application. This apparent inconsistency needs to be addressed.

- Suction Lysimeter Samples

  The EFGWB does not agree with the registrant's proposal to composite all the suction lysimeter within a lysimeter cluster as proposed by the protocol. Based upon further discussion with the registrant, each suction lysimeter cluster will possess three lysimeters (3, 6, and 9 feet). Samples will be collected and analyzed individually (i.e., 9 samples per sampling interval).

The soil-pore water schedule should be modified. Soil-pore water samples shall be collected for analysis immediately prior (-1 days) to the eight (8) chlorothalonil applications, and 1, 3, 7, 14 days, and 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12-months after the final application. The registrant need not sample soil-pore water immediately after application (0 days). The protocol shall be modified to reflect these changes.

- Ground-Water Sampling Schedule

  EFGWB concurs with the registrant's request to sample ground-water monitoring wells, during the application period, at every other application (≈14 days between applications). The EFGWB will accept the following sampling schedule for the ground-water monitoring wells: water samples from the ground-water monitoring wells shall be collected for analysis prior to application numbers 1, 3, 5, 7, and 8, and then monthly after the last application. The ground-water sampling schedule shall be modified in the protocol.

- Water Sample Volume

  Water sample volumes collected from each suction lysimeter and ground-water monitoring well shall be measured, recorded, and reported for each sampling event.

- Tracer Compounds

  To track the rate at which water recharges the aquifer, a conservative tracer, such as KBr, should be applied with the first chlorothalonil application. The soil cores, soil-pore water and ground-water samples would then be analyzed for Br^-, using the same sampling schedule used for pesticide residues.

- Precipitation/Irrigation

  The registrant's proposed irrigation schedule to supplement precipitation is not acceptable. EFGWB requires that the irrigation requirements be based upon a minimum of 125% of the 30-year monthly averages rather than the 10-year monthly averages. The source of the irrigation water should be specified by the registrant, after the site is selected.

- Progress Reports

  The registrant should submit brief quarterly progress

reports. This allows the registrant and EFGWB to review the progress of the study and to make modifications, if necessary. The progress report shall include analytical data from soil core, soil-pore water, and ground-water samples. It is imperative that the analysis of samples occur in a timely manner (soon after collection) so that the effectiveness of the sampling and analytical methodology can be evaluated. A schedule for the submission of these progress reports shall be proposed by the registrant in the revised protocol.

- Miscellaneous

  The word "should" in line 3 and line 6 of the first paragraph in section 4.4 (page 17) will be assumed by the Agency to be a definite commitment by the registrant to mean "will", rather than the less definitive "should". Therefore, the EFGWB will expect that the soil will be described and ground-water quality characterized as defined on page 17.

9. BACKGROUND:

Chlorothalonil is a broad-spectrum fungicide. Application rates are variable and multiple applications are generally required during the growing season. BRAVO and DACONIL are two major foliar fungicides containing the active ingredient (ai) chlorothalonil. Uses of BRAVO include peanuts, fruits (apricots, cherries, melons, plums, nectarines, watermelon, pumpkins), and vegetables (beans, broccoli, cabbage, celery, onions, potatoes, tomatoes), conifers and turf. DACONIL is broad-spectrum fungicide product which is used on turf grass, broadleaf trees and shrubs, bulbs and flowering plants, foliage plants and conifers.

Peanuts is an important crop that utilizes chlorothalonil receiving on average of eight (8) applications. For example, BRAVO 720 (54% ai) [6.0 lb/gal, or 0.75 lb/pt] has a maximum application rate of 1.5 lb/acre for peanuts and 2.5 lb/acre for soybeans (a row crop), at 10 to 14 day intervals. BRAVO W-75 (75% active ingredient, or ai) is applied to fruits and vegetables at 1 to 3 lb/acre at intervals ranging from 2 to 3 days to 10 to 14 day intervals. BRAVO is be applied to conifers at rates ranging from 1¼ to 5½ lbs/acre at 3 to 4 week intervals.

DACONIL 2787 Flowable Fungicide (40.4% ai) can be applied to turf at 2.09 to 7.3 lb/acre at 7 to 21 day intervals. Wettable powder formulations of DACONIL with 75 and 90% ai can be applied to turf on 7 to 14 day intervals at rates up to 16 and 14 lb/acre, respectively. Other formulations, including DACONIL 2787 (75% ai, wettable powder) and DACONIL 2787 (90% ai, water

dispersible granule) can be applied at rates up to 16 lb/acre depending on crop and formulation.

The EPA has determined that chlorothalonil is a B2 carcinogen, and has a Health Advisory (HA) Drinking Water Equivalent Level (DWEL) of 0.5 mg/L [500 µg/L] (USEPA, 1992a). Health advisory levels have not been established by the EPA for the degradates of chlorothalonil.

Summary of Monitoring Data on Chlorothalonil Residues in Ground Water:

Massachusetts. Chlorothalonil residues were detected (0.22 µg/L, 0.38µg/L) in two shallow ground-water wells by the Cap Cod Golf Course Monitoring Project (Eichner and Carbonell, 1990). The detection limit was reported as 0.015 µg/L. The authors postulate that the detection may be due to contamination resulting from well installation.

New York. Metabolites (DS-3701, DS-19221, DS-46851, DS-47524, and DS-47525) of chlorothalonil (DS-2787) were detected in 16.4 percent (11 of 67 samples) of samples in Suffolk County, New York (Harris and Andreoli, 1988). The concentration of degradates in the New York study ranged from 1.1 to 12.6 µg/L for individual breakdown products. The highest combined concentration of chlorothalonil degradation products was 16.3 µg/L. Contaminants were primarily found in shallow private wells, but also were detected in a 97-foot deep public water supply well. The detection limit was not reported.

An earlier, EPA review (USEPA, 1984) appears to contain a more complete assessment of the data later summarized and reported by Harris and Andreoli (1988), and described above. This review indicates that 24 wells were sampled in Suffolk County, Long Island, New York from September 14, 1981 to October 22, 1981 (R.R. Griffiths. Report Doc. # 561-3AS-82-0065-001 DS2787. Acc. # 253315). From 23 of the 24 wells, five separate analyses were conducted for the analytes DS-3701, DS-19221, DS-46851, DS-47524, and DS-47525. The parent chlorothalonil was also analyzed for in all 24 wells. The parent and degradate DS-47524 were not detected in any of the samples. Degradates were identified in 8 of the 24 wells, and in 11 of 139 (67 + 72) samples. The detections, by degradate, were as follows: DS-3701 (3.6 µg/L), DS-19221 (2.8 µg/L), DS-46851 (5.9, 2.0, 7.9, 12.6, 2.0, 3.9, and 8.5 µg/L), and DS-47525 (2.0, 2.0, and 5.0 µg/L). The reported quantification limit was 2.0 µg/L.

Other States. The Pesticide in Ground Water Database (USEPA, 1991a; 1992e) also reported detections of chlorothalonil residues in ground water in 1 of 25 wells in Florida (0.14 µg/L), 2 of 19 wells in Massachusetts (0.22 -0.38 µg/L), Maine (trace) and 1 of 614 wells in California (0.8 to 1.1 µg/L).

Environmental Fate Data

Chlorothalonil breaks down in aerobic soil with a half-life of 1 to 2 months with the formation of a major degradate, 4-hydroxy-2,5,6,-trichloroisophthalonitrile (SDS-3701), and several other degradates. The breakdown of the parent appears to be primarily due to microbial degradation, as chlorothalonil is relatively stable to hydrolysis and photolysis (USEPA, 1986). The chemical formula of chlorothalonil and primary degradates are listed in Table 1 and the physical and chemical characteristics of chlorothalonil relative to EPA leaching criteria are reported in Table 2. Environmental fate data indicates that the parent is somewhat persistent and moderately mobile in sandy soils, but not very mobile in other soils. The degradate SDS-3701 is both mobile and persistent as demonstrated by results obtain from leaching studies (USEPA, 1991c). These data indicate that the leaching potential of the SDS-3701 degradate is greater than that of the parent.

Table 1. Chlorothalonil and its Degradates

PARENT	
Chlorothalonil	2,4,5,6-tetrachloroisophthalonitrile
DEGRADATES	
1. - (SDS-46851)	3-carboxy-2,5,6-trichlorobenzamide
2. - (SDS-47525)	2-hydroxy-5-cyano-3,4,6-trichlorobenzamide
3. - (SDS-3701)	4-hydroxy-2,5,6,-trichloroisophthalonitrile
4. - (SDS-47524)	3-cyano-2,5,6-trichlorobenzamide
5. - (SDS-47523) isomer of #4	3-cyano-2,4,5-trichlorobenzamide
6. - (SDS-19221)	3-cyano-2,4,5,6-tetrachlorobenzamide

Table 2. Physical and Chemical Characteristics[1] of CHLOROTHALONIL Relative to EPA Leaching Criteria[2].

CHARACTERISTIC	LEACHING CRITERIA	CHLOROTHALONIL PARAMETERS[3]
Water Solubility	> 30 mg/L	1.2 mg/L
Henry's Law Constant	$<10^{-2}$ atm-m^3/mol	$5.83X10^{-7}$ atm-m^3/mol
Hydrolysis half-life	> 25 weeks	pH5 - stable pH7 - stable pH9 - 10% degrade in 30 days
Photolysis half-life	> 1 week (water)	stable
Soil adsorption: K_d	< 5 (usually <1-2) [Freundlich K not K_d]	20 sandy lm-3.5% OM 3 sand-0.6% OM 29 silt-0.8% OM 26 silty lm 3.2% OM OM did not influence mobility in soil
Soil adsorption: K_{oc}	<300-500	1380(USDA)
Aerobic soil metabolism half-life	> 2-3 weeks	<1 to 2.3 sa lm 1.1 to 4.4 si lm 1 to 2.3 peat-lm @80% of FC, 77 to 95 °F
Field dissipation half-life	> 2-3 weeks	4 to 8 weeks in sd lm; 5 weekly applications: total Σ=15 lb ai/A.
Depth of leaching in field dissipation study	> 75-90 cm	degradate DAC-3701 is mobile; parent shows little mobility

[1] One-liner Database (USEPA, 1989); Wauchope et al. (1992).
[2] Cohen et al., 1984.

Indicates exceeds leaching criteria/fate data are not complete

[3] symbols:lm is loam, sd is sand, si is silt; OM is %organic matter; total Σ is total sum applied in pounds active ingredient/acre.

10. DISCUSSION:

References to a specific page number correspond to the consecutively stamped page numbers (1 to 135) rather than the Protocol page number (1 of 53 to 53 of 53). Additionally, minor questions to, or modifications requested of, or key commitments by the registrant are depicted in **"bold with underlining"**.

It is requested that in future submittals that the Table of Contents be expand to include the Appendices, SOP's, and Forms with the appropriate page numbers. This makes the process of locating information easier.

Registration.

The registrant proposes to support the continue registration of Bravo 720, Bravo W-75, Bravo 500, Bravo 90DG, Daconil 2787 WDG, Daconil 2787 Fungicide, and Daconil 2787 Flowable Fungicide.

Study Type and Duration.

The registrant is proposing to conduct one small-scale prospective ground-water monitoring study for chlorothalonil on peanuts in North Carolina. The study is anticipated to begin May 1993 and be completed by February, 1995. However, the actual date of termination will be determined by the EFGWB.

Chlorothalonil Use Information.

The registrant reports (page 10) that the primary uses of chlorothalonil are on peanuts, fruit, and vegetable crops in the Atlantic Coastal Plain, and on turf in the Midwest and Northeast.

No chlorothalonil use (tons/state/county/year) data, were provided by the registrant in the protocol document. However, the registrant indicated in a 28 May 1992 meeting that the largest single use of chlorothalonil in the United States is on peanuts, and the areas with greatest use are in the Atlantic Coastal Plain and Gulf Coast States, and Texas and Oklahoma (USEPA, 1992b,c).

The registrant will document any prior chlorothalonil use on the proposed study sites for the previous five to ten years (pages 14 to 15). **Crop and pesticide history for ten previous years should be provided.**

Irrigation source and application, pages 14, 21 to 24, 36.

The applicant proposes to irrigate to supplement rainfall, to obtain 120% of the 10-year average monthly rainfall or irrigation plus over flow whichever is greatest (page 14). It appears that the registrant is referring to the monthly average. This should be clarified. EFGWB also recommends that the irrigation requirements be based upon a minimum of 125% of the 30-year monthly average rather than the 10-year monthly average. The monthly

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amount of required water applications (precipitation plus irrigation) should be defined.

The registrant will analyze the irrigation water for pH, COD, and suspended solids at the being of the study and chlorothalonil and its principle metabolites at bi-monthly (two month intervals) intervals, if irrigation was applied during the two month period.

The source of irrigation should be clearly defined, when a site is selected, and the chemical quality of the water characterized.

Chlorothalonil Applications, pages 21 to 24.

The application rate specified for Bravo 720 will be 2.25 lb/acre, or 3 pt/acre (2.25 lbs/acre), which is twice the label rate for peanuts (page 22). Maximum label rate is up to 5½ pt/acre for conifers and selected fruit crops. Bravo will be applied eight (8) times, at 14 day intervals, during the study.

EFGWB will require that the registrant include in the application protocol methodologies to confirm the application rate (i.e., application cards, petri dish, etc).

Test Site Selection and Characteristics.

The site-selection process, site-selection criteria, and the historical use of chlorothalonil criteria appear to be adequate (pages 10 to 17). The registrant states (page 15 to 16) that, **"Any proposed deviations to the EPA guidelines will be reviewed with the Agency and special provisions will be included in the final study protocol by Agency permission only"**.

The registrant proposes to conduct a pre-site selection process to identify a "realistic worst-case" county, within a major use area with vulnerable hydrogeologic conditions in North Carolina (pages 10 to 13), and where the depth to the water table will be less than 30 feet. The size of study area will be between 2 and 5 acres, with a surface slope gradient not to exceed 2 percent. Once potential sites are selected a more detailed on-site sampling and soil characterization will occur to evaluate the soil, vadose zone, and depth to ground water for site conditions.

Site Selection Process (page 15 to 17). The proposed site selection process will be comprised of four phases. Briefly, the phase are:

First Phase - The selection of counties having areas thought to be or identified as being sensitive or vulnerable to ground-water contamination.

Second Phase - Identify area within target counties believed

to have the desired hydrogeologic properties based upon soil survey information and ground-water survey reports and information.

Third Phase - Site inspection of most promising sites. A preliminary site evaluation will be conducted. This will include soil sampling to determine soil and vadose zone characteristics and depth to water. At the end of this phase, a primary study site will be identified along with one or two backup sites.

Forth Phase - This phase will include the analysis of soil and water samples for the presence of chlorothalonil and chlorothalonil degradates prior to study implementation. Samples from three bore holes will be in 6-inch increments from 0 to 5-feet, and in 2-foot increments (sub-divided into 1-foot samples for analysis) from 5-feet to ground water.

The registrant will provide the Agency with an interim report prior to final selection of the test sites (page 16).

Soil Characterization and Residue Analysis

The discussion presented in the protocol concerning site selection (site section process, site characterization, soil and vadose zone characteristics, shallow and deep sampling) as outlined by the protocol is somewhat confusing. The confusion involves the redundancy and lack of consistency. **The overall site selection and sampling program presented in the protocol appear to generally be acceptable, but clarification is necessary.**

Soil and Vadose Zone Characteristics (page 12 to 13).

The registrant will locate the study site where soil root zone and vadose (deep soil samples or subsoil) zone consist of loamy sand or sandy loam textural classes (USDA textural classes) with low organic carbon (matter) contents and water holding capacity. Specific values for organic carbon content and water holding capacity were not stated. It should be noted by the registrant that abrupt textural discontinuities with coarse textures (i.e., sand underlying a loam) may also restrict or hinder unsaturated water flow, and should be considered in site selection.

Shallow (root zone) Soil Samples (pages 16-17 and 24-28)

The protocol details the study site characterization which includes soil mapping unit delineations, and soil profile descriptions (0 to 60 inches) which will be described using USDA-SCS methodology (USDA-SCS Handbooks 18 and 436) and include the information listed in Table 3. Samples will be collected with a hand auger. The determination of pre-application levels of chlorothalonil residues in the upper 0 to 60 will also determined from three bore holes.

The word "should" in line 3 and line 6 of the first paragraph in section 4.4 (page 17) will be assumed by the Agency to be a definite commitment by the registrant to mean "will", rather than the less definitive "should". Therefore, the EFGWB will expect that the soil will be described and ground-water quality characterized as defined on page 17.

Soil samples for the post-application analysis will be collected to a depth of 48 inches and analyzed in 6-inch increments from 0 to 24 inches, and 12-inch increments from 24 to 48 inches (Table 3). Two methods are described to minimize or prevent cross contamination during sampling. The original and modified (required) soil sampling schedule (intervals) are summarized in Table 4.

Table 3. Soil Characterization Parameters, Pre- and Post-Application Chlorothalonil and Degradate Determination.

SOIL (SHALLOW SAMPLES) PROPERTY CHARACTERIZATION AND PRE-AND POST-APPLICATION RESIDUE ANALYSIS	
Sampling Increments	6-inch intervals to 60 inches
Particle Size Distribution	% Sand % Silt % Clay
Soil Water	field capacity permanent wilting point available water content soil water content
Chemical Analyses	organic matter (carbon) chlorothalonil residues (parent & degradates
Physical Analyses	bulk density saturated hydraulic conductivity
POST-APPLICATION SOIL (SHALLOW) SAMPLES FOR CYROMAZINE AND DEGRADATE DETERMINATION	
Sampling Increments	0 to 24 inches in 6 inch increments 24 to 48 inches in 12 inch increments
Chemical Analyses	chlorothalonil residues (parent & degradates)

Table 4. Comparison of Original Shallow Soil Sampling Scheme and Modified (required) Soil Sampling Scheme

APPL. NO.	TIME AFTER APPLICATION	ORIGINAL			MODIFIED		
		SECT	DEPTH	# OF SAMPLES	SECT	DEPTH	# OF SAMPLES
1	-1 days	3	6	18	3	6	18
1	0 days	3	6	18	3	1	3
2	-1 days	3	6	18	3	6	18
2	0 days	3	6	18	3	1	3
3	-1 days	3	6	18	3	6	18
3	0 days	3	6	18	3	1	3
4	-1 days	3	6	18	3	6	18
4	0 days	3	6	18	3	1	3
5	-1 days	3	6	18	3	6	18
5	0 days	3	6	18	3	1	3
6	-1 days	3	6	18	3	6	18
6	0 days	3	6	18	3	1	3
7	-1 days	3	6	18	3	6	18
7	0 days	3	6	18	3	1	3
8	-1 days	3	6	18	3	6	18
8	0 days	3	6	18	3	1	3
8	1 days	3	6	18	-	-	--
8	3 days	3	6	18	-	-	--
8	7 days	3	6	18	-	-	--
8	14 days	3	6	18	-	-	--
8	1 months	3	6	18	3	6	18
8	2 months	3	6	18	3	6	18
8	3 months	3	6	18	3	6	18
8	4 months	3	6	18	3	6	18
8	5 months	-	-	--	3	6	18

APPL NO.	TIME AFTER APPLICATION	ORIGINAL			MODIFIED		
		SECT	DEPTH	# OF SAMPLES	SECT	DEPTH	# OF SAMPLES
8	6 months	3	6	18	3	6	18
8	7 month	-	-	--	3	6	18
8	8 months	-	-	--	3	6	18
8	9 months	3	6	18	3	6	18
8	10 months	-	-	--	3	6	18
8	11 months	-	-	--	3	6	18
8	12 months	3	6	18	3	6	18
	Total			486**			384
8	15 months	3	6	18			
8	18 months	3	6	18			

Original (Protocol) 522 samples
Modified (Burton Letter) 288 samples
** Reflects the original sampling plan for the first 12 months (522 - 36 = 486).

Deep (Vadose Zone - Subsoil) Soil Samples (pages 16-17 and 28-30)

The registrant proposes to drill (during ground-water monitoring well installation) three soil borings (hollow stem auger with split-spoon sampler) to about 40 feet at three locations within or adjacent to the study site to describe the soil properties from 5 feet to about 40-feet (Deep Samples: 60 inches to into the water table, also designated by the registrant as Deep Soil Samples). Split-spoon samples will be collected continuously at 2-foot (which are split into two (2) 1-foot samples for analysis) intervals from each boring to the water table and at 5-foot intervals or more frequently as needed to a depth of 20 feet below the water table. Samples will be collected in 1-foot increments from 5-feet to 40 feet for analysis of chlorothalonil parent and degradate residues (pages 17, 29) and particle size distribution (page 29). Deep soil properties proposed by the registrant to be determined are summarized in Table 5.

Tensiometers will be installed by the registrant to determine the direction of water movement below the root zone (vadose zone). [page 22].

The registrant should also determine the bulk density and volumetric soil water content, field capacity, wilting point, and

available water content, and organic matter (carbon) for the deep samples (5 to 40 feet). It is suggested that CEC be determined for the surface soil material (0 to 60 inches).

The bottom of page 28 indicates that the deep soil samples will be six months (6-month sampling) after the last application, whereas page 28 indicates six months after the initial application. This apparent inconsistency needs to be addressed.

The standard soil description form was found in Attachment 5, page 129 rather than Attachment 7 as stated on page 17. A sample core log was found in Attachment 5, page 128 rather than Attachment 7 as stated on page 17. This should be corrected.

Soil color should be measured for subsoil material (5 to 40 feet) using the Munsell Color Charts, and recorded on the sample core logs (page 17 and 128). Soil color is an important physical parameter which much can be inferred about its chemical condition. Additionally, the Munsell Color Charts allows for some consistency in the evaluation of a subjective property such as color.

Table 5. Soil Characterization Parameters, Pre- and Post-Application Chlorothalonil and Degradate Determination for deep soil samples.

VADOSE ZONE, DEEP SOIL SAMPLES (SUBSOIL) PROPERTY	
Sampling Increments (Characterization)	2-foot intervals to water table. 5- to 20-feet below water table
Particle Size Distribution	% Sand % Silt % Clay
Sampling Increments (Pesticide Residues)	1-foot intervals from 5- to 40-feet (top of water table).
Chemical Analyses	chlorothalonil residues (parent & degradates)

Suction Lysimeters and Soil-Pore Water, page 18 to 19.

The protocol document submitted by the registrant called for the installation of three suction lysimeter clusters with nine lysimeters in each cluster (three 3-foot, three 6-foot, and three 9-foot depths). The soil pore-water samples collected were all to be composited, resulting in one sample from each cluster. This was not acceptable to EFGWB, as compositing samples will not allow for assessing chlorothalonil residue leaching patterns. During and following a meeting between the registrant and EFGWB

(USEPA, 1992b,c), considerable dialogue has taken place between EFGWB and the registrant (USEPA. 1992b,c,d) in regards to the suction lysimeter installation and sampling schedule. In addition to the compositing of pore-water samples, EFGWB was concerned that no samples would be collected from the 9-foot (max. proposed) lysimeter depths to the water table (potential up to 30-ft).

The registrant and EFGWB agreed to reduce the number of suction lysimeters to three per cluster (one 3-foot, one 6-foot, and one 9-foot). The registrant, in another study, has been able to collect adequate sample volumes from one lysimeter. This also corresponds to current guideline requirements. Samples will be collected individually from each lysimeter; three lysimeter clusters with three depths (3, 6, and 9-foot) per cluster, resulting in a total of nine samples (and analysis) per sampling event.

The EFGWB in a previous memo (dated 6/25/92) recommended that the soil pore-water and ground water wells need only be sampled prior to (-1 days) to the chlorothalonil applications until the last (8th) application, when sampling would be conducted on 1, 3, 7, 14-days, and monthly after the final application for 12 months, but not immediately after (0 days) applications. This results in a net of 216 soil pore-water samples for analysis and is summarized in Table 6.

The registrant has indicated that the installation of suction lysimeters deeper than about 10 feet is extremely difficult. Additionally, the ability to pump the water out of the suction lysimeters for analysis is difficult, due to physical limitations. The EFGWB concurs that these are both realistic limitations of deeper placement of the suction lysimeters.

EFGWB agrees that the installation of suction lysimeter deeper than the proposed 9 feet may not realistic and concur with the registrants request. However, a concern still remains as to how to monitor pesticide residues below the depth of suction lysimeters and above the water table (10 to 30 feet).

The protocol calls for collecting soil samples from the surface to the water table six months after the last (or first application) chlorothalonil application. **Deep soil sampling can be used address this concern, but the specific sampling frequency will depend upon the conditions of the site selected.**

Table 6. Soil Pore-Water Sampling Frequency and Intensity.

Appl. No.	Sampling Interval	Sectors	Depths	# of Samples
1	-1 day	3	3	9
2	-1 day	3	3	9
3	-1 day	3	3	9
4	-1 day	3	3	9
5	-1 day	3	3	9
6	-1 day	3	3	9
7	-1 day	3	3	9
8	-1 day	3	3	9
8	1 day	3	3	9
8	3 day	3	3	9
8	7 day	3	3	9
8	14 day	3	3	9
8	1 month	3	3	9
8	2 month	3	3	9
8	3 month	3	3	9
8	4 month	3	3	9
8	5 month	3	3	9
8	6 month	3	3	9
8	7 month	3	3	9
8	8 month	3	3	9
8	9 month	3	3	9
8	10 month	3	3	9
8	11 month	3	3	9
8	12 month	3	3	9
Total				216

Piezometers and Bore holes (page 18).

The bore holes will be converted into temporary piezometers and top-of-casing elevations will be determined by a surveyor (page 18). Piezometer installation will be according to state guidelines and generally appear to be adequate. **It is however recommended that before adding the bentonite seal, an additional layer of a different grain size be added above the primary sand to create a layer several inches thick. This will prevent or minimize figuring of bentonite into the primary sand layer as the bentonite is added to the well boring. This procedure should also be considered for the ground-water monitoring wells.**

Ground-Water Quality and Aquifer Characterization

The following parameters will be analyzed to characterize the ground water: pH, EC, suspended solids, redox potential, temperature, NO_3^{1-}, SO_4^{2-}, Ca^{2+}, Mg^{2+}, and Na^{1+}, and chlorothalonil parent and degradate residues.

The aquifer characterization will include water level elevations and water level map(s), hydraulic gradient of the water table and vertical flow gradients, hydrologic characteristics will be determined (slug test, or aquifer test), season fluctuations, and approximate ground-water flow velocity (page 18 and 49).

The registrant proposes to install three well clusters, each consisting of three monitor wells with 5-foot well screens. The well screens will be placed to cover the upper 12.5 feet of the aquifer, the remaining 2.5 feet will be above the water table to account for water table fluctuations. One cluster will be located upgradient and two downgradient with reference to the direction of ground-water flow. Monitoring well installation is acceptable.

Ground-Water Monitoring

Pre-sampling well purging is defined by the registrant and is acceptable.

Page 41, Section 15.2 indicates that 18 ground water samples will be collected at each sampling interval. This number reflects the collection of a primary sample for analysis plus a duplicate sample; only the primary sample is to be analyzed. Therefore, each sampling event will net 9 samples (three clusters with 3-wells per cluster) for analysis. This should be clarified in the protocol.

Sample volumes collected from each suction lysimeter should be measured, recorded, and reported for each sampling event. It is also recommended that the volume of well-water samples be measured, recorded, and reported.

General Comments

Weather Data, page 45 to 46.

It is recommended that more than one rain gauge be placed at the study site to make sure no problems occur during data collection. The length of time (duration) of each irrigation event should also be reported.

Detection Limits and Justification for Parent and Metabolites:

The registrant will provide information on detection limits and rationale for only analyzing two metabolites when four metabolites were detected in NY as stated in the meeting (USEPA, 1992b,c).

The actual sample volume (water, soil) required to run the analyses for chlorothalonil and chlorothalonil metabolites should be specified.

EFGWB questioned the size of soil, soil-pore water, and ground-water samples collected, and sample size requirements for analysis (For example, 300 grams of soil may be collected, and yet, only 1 gram is required for determination of total nitrogen by Micro-Kjeldahl method). Specifically, EFGWB wanted the sample size specified including soil samples. Sample sizes were indicated in the draft protocol for the well water samples (250 mL), but not for soil-pore water and soil samples. During the meeting, the registrant indicated that rather than 250 mL that 700 mL would be required for analysis. It is assumed that this volume is required for both well-water and soil-pore water samples.

Sample Size and composited samples:

The registrant and EFGWB have agreed to a soil-pore water sampling program with out using composited water samples. The registrant should have no trouble in collecting adequate quantities of soil and well-water samples to conduct the appropriate analyses, whether 250 or 700 mL are required. EFGWB's concern is for the suction lysimeters. EFGWB recognizes the difficulty in predicting the volume of water collected by individual suction lysimeters, and the need for a certain quantity to conduct the necessary analysis. However, it can be assumed that the volumes collected by an individual lysimeter will vary spatially (aerially), with depth, and with time. EFGWB believes that significantly more information can be obtained if samples are collected and analyzed separately for each suction lysimeter.

Hexachlorobenzene

The proposed response to HCB appears to be adequate. The registrant should include in this discussion the range of HCB levels that can occur in products with chlorothalonil as the active ingredient, and provide available environmental fate data (field dissipation half-life, solubility, K_d) (USEPA, 1992b,c).

REFERENCES

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Eichner, E.M. and A.J. Carbonell (eds). 1990. The Cap Cod Golf Course Monitoring Project. Cap Cod Commission, Water Resources Office. Barnstable, MA.

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USEPA. 1991c. Evaluation of Ground-Water Contamination Potential. Dated: 10/31/91 EFGWB # 90-0491. OPP/EFED/EFGWB Washington, DC

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USEPA. 1992c. Note to Andy Ertman from J. Wolf and E. Waldman. Dated 6/25/92. Response to ISK response letter dated June 11, 1992 to Andy Ertman (USEPA-SRRD) from Ralph Burton (ISK

Biotech) concerning the 5/28/92 meeting. OPP/SRRD. Washington, DC

USEPA. 1992d. Memorandum: Chlorothalonil Ground-Water Study. Response to telephone conversations with J.R. French and L. Thompson, Jr. Dated 11/18/92. To A. Ertman form J.K. Wolf. OPP/EFED/EFGWB/GTWS. Washington, DC

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ATTACHMENTS

The EFGWB memorandums concerning the 28 May 1992 meeting between the Registrant and EFGWB staff are included as attachments for easy reference.

ATTACHMENT # 1:

USEPA. 1992b. Chlorothalonil Ground-Water Study Initial-Protocol Preliminary Review Meeting. J. Wolf and E. Waldman to A. Ertman. Dated 6/12/92. OPP/EFED/EFGWB/GTWS. Washington, DC

ATTACHMENT # 2:

USEPA. 1992c. Note to Andy Ertman from J. Wolf and E. Waldman. Dated 6/25/92. Response to ISK response letter dated June 11, 1992 to Andy Ertman (USEPA-SRRD) from Ralph Burton (ISK Biotech) concerning the 5/28/92 meeting. OPP/EFED/EFGWB/GTWS. Washington, DC

ATTACHMENT # 3:

USEPA. 1992d. Memorandum: Chlorothalonil Ground-Water Study. Response to telephone conversations with J.R. French and L. Thompson, Jr. Dated 11/18/92. To A. Ertman form J.K. Wolf. OPP/EFED/EFGWB/GTWS. Washington, DC

ATTACHMENT # 1:

USEPA. 1992b. Memorandum: Chlorothalonil Ground-Water Study Initial- Protocol Preliminary Review Meeting. J. Wolf and E. Waldman to A. Ertman. Dated 6/12/92. OPP/EFED/EFGWB/GTWS. Washington, DC

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

MEMORANDUM Original dated and signed June 12, 1992

SUBJECT: Chlorothalonil Ground-Water Study
Initial Protocol Preliminary Review Meeting
DP Barcode D174771; EFGWB # 92-0545

FROM: James K. Wolf, Soil Scientist

and

Estella Waldman, Hydrologist
Ground Water Section
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

TO: Andy Ertman
Reregistration Branch
Special Review and Reregistration Division (H7508W)

THRU: Elizabeth Behl, Head
Ground Water Technology Section
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

Participants: John R. French, Ph.D, Manager, Technical Development
Jerry R. Lucietta, Manager, Regulatory Affairs
Elizabeth D. Owens, Ph.D., Manager, Product Registration
ISK Biotech Corporation

David L. Ballee, Manager, Residue Analysis
Ricerca, Inc.

Lafayette Thompson, Jr., Ph.D., President
American Agricultural Services, Inc.

Andy Ertman, RB, SRRD
Estella Waldman, James Wolf, EFGWB, EFED

BACKGROUND

A meeting was held on 28 May 1992 to honor ISK Biotech's request to meet with representatives of EFGWB and RB to discuss their recently submitted protocol for a ground-water study chlorothalonil. The Small-Scale Ground Water Study protocol was submitted by ISK Biotech on 4 February 1992 in response to the Data-Call-In for chlorothalonil. Represented in the meeting in addition to ISK Biotech; EFGWB; and RB; were Ricerca, Inc., which will conduct the analytical portion of the study; and American Agricultural Services, Inc., which developed the study protocol and will have the responsibility to implement and conduct the field portion of the study.

CHLOROTHALONIL

Chlorothalonil (Bravo) is a broad-spectrum fungicide used on fruits (including peanuts), vegetables, conifers, and turf. Daconil is another broad-spectrum fungicide product, also containing the active ingredient chlorothalonil, which is used on turf grass, broadleaf trees and shrubs, bulbs and flowering plants, foliage plants and conifers.

Application rates are quite variable and are generally applied at multiple intervals during the growing season. For example, Bravo W-75 (75% active ingredient, or ai) is applied to fruits and vegetables at 1 to 3 lb/acre at intervals ranging from 2 to 3 days to 10 to 14 day intervals. Bravo may be applied to conifers at rates ranging from 1¼ to 5½ lbs/acre at 3 to 4 week intervals. Bravo 720 (54% ai) [6.0 lb/gal, or 0.75 lb/pt] has a maximum application rate of 1.5 lb/acre for peanuts and 2.5 lb/acre for soybeans (a row crop), at 10 to 14 day intervals.

Daconil 2787 Flowable Fungicide (40.4% ai) can be applied to turf at 2.09 to 7.3 lb/acre at 7 to 21 day intervals. Wettable powder formulations of Daconil with 75 and 90% ai can be applied to turf on 7 to 14 day intervals at rates up to 16 and 14 lb/acre, respectively. Other formulations, including Daconil 2787 (75% ai, wettable powder) and Daconil 2787 (90% ai, water dispersible granule) can be applied at rates up to 16 lb/acre depending on crop and formulation.

DISCUSSION

ISK Biotech opened the meeting by stating that it is necessary to obtain site and protocol approval during 1992, and to initiate the field portion of the study in the spring of 1993 to meet deadlines given in the Data-Call-In. The registrant desired to know if any "major" deficiencies were obvious in the protocol which could be identified to help expedite the review and approval.

The following topics were discussed as areas that would require additional information or clarification. **It should be noted that these are preliminary findings, as a complete review of the protocol document had not been completed at the time of the meeting. Also, no final decisions concerning these areas were reached.**

A. Site Selection: The registrant proposes to select a "realistic worst-case" site in North Carolina to conduct a small-scale prospective ground-water

monitoring study. The site-selection process, site-selection criteria, and the historical use of chlorothalonil criteria appear to be adequate. The protocol also specifies the chlorothalonil application rate and frequency. The application rate specified for Bravo 720 will be 2.25 lb/acre, which is 3 pt/acre (2.25 lbs/acre), or almost twice the label rate for peanuts. Bravo will be applied eight (8) times, at 14 day intervals, during the study. However, no chlorothalonil use (state/county/tons/year) information was provided by the registrant.

The registrant indicated in the meeting that the largest single use (40%) of chlorothalonil in the United States is on peanuts, and the areas with greatest use are in the Atlantic Coastal Plain, and Texas and Oklahoma.

Solution: The EFGWB requested that the registrant submit chlorothalonil use information to address this deficiency and to justify conducting the study on peanuts. The registrant agreed to provide the information.

The registrant provided labels for Bravo W-75 and Bravo 90DG.

B. Analytical methods and detection limits:

The analytical methods, and corresponding detection limits to be used to analyze water and soils for chlorothalonil parent and degradates, were not stated in the protocol. Additionally, the protocol indicated that only the parent and principal metabolites would be determined. The principal metabolites were not specified in the protocol. Studies submitted by the registrant identify the formation of at least six (6) metabolites. Ground-water studies have identified the presence of four degradates (SDS-3701, SDS-19221, SDS-46851, SDS-47525) in well water samples. Chlorothalonil has been identified in well water in several states (FL, ME, CA, and possibly MA).

Manufacturing impurities HCB and PCNB were reported to have leached as deep as 9 to 12 inches (USEPA, 1991).

During the meeting, David Ballee of Ricerca, Inc. indicated that the analytes of interest were: the parent and analyte SDS-3701 (4-hydroxy-2,4,5,6-trichloroisophthalonitrile) and SDS-46851 (3-carboxy-2,5,6-trichlorobenzamide). He indicated that SDS-3701 is the primary soil degradate and SDS-46851 is the most mobile.

The registrant indicated that the detection limit for chlorothalonil, SDS-3701, and SDS-46851 in water is 0.1 μg/L. For soils the detection limits were around 10 ng/g.

The registrant also indicated that approximately 700 mL of water is required for the residue analysis, rather than the 250 mL identified in the protocol. The EFGWB was somewhat concerned about the large volume of sample which the registrant indicates is necessary for analysis, since it may be difficult to obtain from the suction lysimeters.

Solution: The registrant will provide information on the analytical methods (including detection limits) and modify the protocol for the change in the volume

of water required for analysis. The weight (or volume and bulk density) of soil required for analysis should be specified.

The registrant must provide documentation and scientific evidence that the two degradates proposed for analysis are sufficient and the other ones are not necessary. The registrant should also address the concentration of HCB (hexachlorobenzene) that is found in the product, and what concentrations may remain in the soil.

C. It was recommended that a conservative tracer (i.e., KBr) be applied at the same time as the first application, and then be monitored for at the same schedule as the residue samples (soil cores, soil-pore water, and ground water).

D. <u>Suction Lysimeters:</u>

The registrant proposes to install three lysimeter clusters each containing three 3-foot, three 6-foot, and three 9-foot suction lysimeters per cluster (i.e., nine lysimeters per cluster), and a total of 27 suction lysimeters. The protocol indicated that the samples from the lysimeters would be composited by cluster rather than by depth. In a telephone conversation (June 11, 1992) between EFGWB and Dr. Fate Thompson, of American Agricultural Services, he clarified that the intent was to composite the samples by depth. This would mean that all of the 3-foot samples would be composited, all of the 6-foot samples would be composited, and all of the 9-foot samples would be composited; resulting in a total of three samples to represent the 3-, 6-, and 9-foot depths.

COMMENTS:

1. The EFGWB thinks additional (deeper) suction lysimeters may be required depending upon the depth to the water (i.e., 15 ft, 22 ft).

2. The EFGWB does not completely agree with the proposal to composite all the suction lysimeters within a lysimeter cluster. We would prefer that samples from each lysimeter be sampled and analyzed individually, but would accept the compositing of samples by depth for each cluster if necessary to obtain an adequate volume for analysis. We recommend, if compositing is required, that samples be composited by depth only within each cluster; resulting in 3 samples from 3 depths from all 3 clusters as shown in the attached table. If sample sizes are not adequate, additional lysimeters could be added to a cluster.

3. The EFGWB recommends that the schedule to sample the soil-pore water and ground water be modified. Soil-pore water and ground-water samples should be collected immediately prior (-1 days) to chlorothalonil applications. Following the last application (8), the schedule will be as proposed by the registrant in the protocol (1-, 3-, 7-, 14- days and 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, and 12-months after the final application).

E. Sampling frequency and intensity

The following soil-pore water sampling is recommended:

Appl. No.	Sampling Interval (After Initial Appl.)	Depth	Composite[1] Samples Per Depth	Total Numbers of Samples
1	-1 day	3	3	9
2	-1 day	3	3	9
3	-1 day	3	3	9
4	-1 day	3	3	9
5	-1 day	3	3	9
6	-1 day	3	3	9
7	-1 day	3	3	9
8	-1 day	3	3	9
8	1 day	3	3	9
8	3 day	3	3	9
8	7 day	3	3	9
8	14 day	3	3	9
8	1 month	3	3	9
8	2 month	3	3	9
8	3 month	3	3	9
8	4 month	3	3	9
8	5 month	3	3	9
8	6 month	3	3	9
8	7 month	3	3	9
8	8 month	3	3	9
8	9 month	3	3	9
8	10 month	3	3	9
8	11 month	3	3	9
8	12 month	3	3	9
Total				216

[1] The number is a composite of 3 soil-pore water lysimeter samples per depth.

CHLOROTHALONIL AND ITS DEGRADATES

Chlorothalonil - 2,4,5,6-tetrachloroisophthalonitrile

Degradates
1. - 3-carboxy-2,5,6-trichlorobenzamide (SDS-46851)
2. - 2-hydroxy-5-cyano-3,4,6-trichlorobenzamide (SDS-47525)
3. - 4-hydroxy-2,5,6,-trichloroisophthalonitrile (SDS-3701)
4. - 3-cyano-2,5,6-trichlorobenzamide (SDS-47524)
5. - 3-cyano-2,4,5-trichlorobenzamide (SDS-47523) isomer of #4
6. - 3-cyano-2,4,5,6-tetrachlorobenzamide (SDS-19221)

REFERENCES

USEPA. 1991. 24(c) Special Local Need in Maine to Support Shorter Rotational Crop Interval on Potatoes. Dated: 05/02/91. EFGWB # 91-0524. OPP/EFED/EFGWB Washington, DC

USEPA. 1992. Review of Small-Scale Prospective Ground-Water Monitoring Protocol for Chlorothalonil. EFGWB # 92-0545. OPP/EFED/EFGWB Washington, DC

ATTACHMENT # 2:

USEPA. 1992c. Note to Andy Ertman from J. Wolf and E. Waldman. Dated 6/25/92. Response to ISK response letter dated June 11, 1992 to Andy Ertman (USEPA-SRRD) from Ralph Burton (ISK Biotech) concerning the 5/28/92 meeting. OPP/EFED/EFGWB/GTWS. Washington, DC

NOTE TO: Andy Ertman, RD Original dated and signed June 25, 1992

FROM: James Wolf, GWTS
Estella Waldman, GWTS

RE: ISK Response letter dated June 11, 1992 to Andy Ertman (SRRD) from Ralph Burton (ISK Biotech) concerning the May 28, 1992 meeting between ISK Biotech and EPA.

Crop Justification

The registrant proposes conducting the study on a peanut crop in North Carolina. Sales information was submitted by the registrant (as part of the June 11, 1992 response letter) to justify the selection of a peanut crop in North Carolina. A portion of the submitted chlorothalonil use data by crop is summarized in Table 1 and geographical use within the United States is summarized in Table 2. It appears that the proposal to conduct the study on peanuts in North Carolina (a portion of the Atlantic Coastal Plain) is justifiable based upon chlorothalonil use information.

TABLE 1. Chlorothalonil Use by Crop.

CROP	% OF TOTAL	CUMULATIVE %
Peanuts	42	42
Vegetables[1]	22	64
Stone Fruits	5	69
Potatoes	4	73
Other Agricultural crops	< 1	73
Turf/Ornamentals	13	86

[1] Includes tomatoes, cucurbits (group), celery, cole crops (group), onions, garlic, and green beans.

TABLE 2. Geographical Distribution of the Agricultural Uses of Chlorothalonil within the United States.

GROWING REGION	% OF TOTAL	CUMULATIVE %
Atlantic Coastal Plain and Gulf Coast	67.3	67.3
Midwest and Lake States	19.1	86.4
Other (West of Rocky Mountains)	13.6	100.0

Current Label for Bravo 720:

The registrant has submitted a current label (with the June 11, 1992 response letter) to aid in the review, and will also address this in the protocol revisions.

Detection Limits and Justification for Parent and Metabolites:

The registrant will provide information on detection limits and rationale for only analyzing two metabolites when four metabolites were detected in NY as stated in the meeting.

The proposed response to HCB appears to be adequate. The registrant should include in this discussion the range of HCB levels that can occur in products with chlorothalonil as the active ingredient, and provide available environmental fate data (field dissipation half-life, solubility, K_d).

Sampling:

After careful consideration, an alternative sampling scheme was recommended in memorandum by J. Wolf and E. Waldman to A. Ertman (dated June 12, 1992). The soil sampling scheme can remain as stated in on page 37 (15.1 Soil Samples). An alternative sampling schedule was suggested for the soil pore-water and ground-water monitoring (pages 39 and 40). EFGWB recommended that soil-pore water and ground-water sampling only be conducted immediately (-1 day) prior to the chlorothalonil applications until the last (8th) application when sampling would be conducted on 1-, 3-, 7-, 14-days and 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, and 12-months after the final application. Soil-pore water and ground-water samples need not be collected or analyzed for immediately after the first seven applications, but after the last (# 8) application as described above.

Sampling Size:

EFGWB questioned the size of soil, soil-pore water, and ground-water samples collected, and sample size requirements for analysis (For example, 300 grams of soil may be collected, and yet, only 1 gram is required for determination of total nitrogen by Micro-Kjeldahl method). Specifically, EFGWB wanted the sample size specified including soil samples. Sample sizes were indicated in the draft protocol for the well water samples (250 mL), but not for soil-pore water and soil samples. During the meeting, the registrant indicated that rather than 250 mL that 700 mL would be required for analysis. It is assumed that this volume is required for both well-water and soil-pore water samples.

Compositing samples: The registrant should have no trouble in collecting adequate quantities soil and well-water samples to conduct the appropriate analyses, whether 250 or 700 mL are required. Our concern is for the suction lysimeters. EFGWB recognizes that it is much more difficult to evaluate and predict the volume of water collected by individual suction lysimeters. However, it can probably be assumed that the volumes collected by an individual lysimeter will vary spatially (aerially), with depth, and with time. EFGWB thinks that much more information can be obtained if samples are collected and analyzed separately for each suction lysimeter. This would result in a total of 27 samples per sampling event; nine for each depth (3-, 6-, and 9-feet). We also understand that sample sizes must be large enough so that analysis can be conducted. Therefore, EFGWB will only accept compositing when required to obtain an adequate sample volume (a previously defined volume). Samples could be collected twice from each lysimeter over a two day period (and these be composited), or additional suction lysimeters per cluster could be installed, so that some information concerning spatial variablity could be ascertained. Records of sample volumes collected from each lysimeter for each sampling date will need to be determined and reported.

TRACERS:

The utilization of a conservative tracer, such as KBr, is often used to get a feeling for the movement of water and solute through the soil/vadose zone. The Br^{-1} anion most likely will travel faster than the chlorothalonil residues. Bromide concentration can be measured with a ion specific electrode. The EFGWB recommends the registrants contact researchers with the USDA-ARS or North Carolina State University that may have more local experience as to what would be a suitable application rate for peanuts and if any analytical interferences could be anticipated.

Site Characterization Information

EFGWB agrees with the points addressed by the registrant dealing with site characterization. These are:

a. Submit site characterization data ahead of time so that EFGWB can review the data and provide any guidance prior to study initiation.

b. Provide an "idealized" site plan map with a general site layout. EFGWB agrees that the modifications will probably be required during actual site development.

c. A study site with a minimum area of 2 acres would appear to adequate.

ATTACHMENT # 3:

USEPA. 1992d. Memorandum: Chlorothalonil Ground-Water Study. Response to telephone conversations with J.R. French and L. Thompson, Jr. Dated 11/18/92. To A. Ertman form J.K. Wolf. OPP/EFED/EFGWB/GTWS. Washington, DC

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

MEMORANDUM: Original signed and dated November 18, 1992

SUBJECT: Chlorothalonil Ground-Water Study
Response to telephone conversation with John R. French (7/24/92) and Lafayette Thompson, Jr. (7/29/92)
PC Code: 081901; EFGWB # 92-0545; DP Barcode D174771

FROM: James K. Wolf, Soil Scientist
Ground Water Section
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

TO: Andy Ertman
Reregistration Branch
Special Review and Reregistration Division (H7508W)

THRU: Elizabeth Behl, Section Head
Ground Water Section
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

Background

A meeting was held on 28 May 1992 to honor ISK Biotech's request to meet with representatives of EFGWB and RB to discuss their recently submitted protocol for a ground-water study chlorothalonil. The Small-Scale Ground Water Study protocol was submitted by ISK Biotech on 4 February 1992 in response to the Data-Call-In for chlorothalonil. Two documents were prepared by the EFGWB's Ground Water Section in response to this meeting. The first, a Memorandum to Andy Ertman from J.K. Wolf and E. Waldman, dated June 12, 1992; and the second a note to Andy Ertman from J.K. Wolf and E. Waldman (in response to ISK Biotech's meeting response), dated June 25, 1992.

These documents have generated several telephone conversations with John R. French of ISK Biotech and Lafayette Thompson of American Agricultural Services, Inc and EFGWB. The registrant desired some additional clarification or wanted to address some concerns about the EFGWB's responses. The following addresses concerns expressed during the telephone conversions, and provides resolutions which will satisfy EFGWB, and hopefully ISK Biotech's concerns. The other items addressed in the two

aforementioned documents appear to have been resolved.

TELEPHONE CONVERSATION:
NAME OF CALLER: John R. French, Ph.D.
ISK Biotech Corporation
Mentor, Ohio 44061-8000
Date of Call: July 24, 1992; 3:40 pm

1. ISK wanted EFGWB to reconsider the soil sampling interval (schedule) stated in the Wolf and Waldman memos in light of their proposal in the June 11 letter from R. Burton. It should be noted that the EFGWB sampling schedule was identical to the one originally submitted by the registrant in the protocol document.

Summary: no final resolution on this is was reached on July 24, 1992. We agreed to discuss these topics further on July 28, 1992. On July 28, we agreed to postpone any discussion until I had completed re-evaluating the protocol in light of the concerns of Dr. French and Dr. Thompson. The resolution of this issue is addressed later in this memorandum.

2. ISK desired to reduce the number of suction lysimeters to three per cluster (3 depths: 3, 6, and 9 feet), rather than 9 per cluster with three for each depth. Three suction lysimeters per depth per cluster were proposed to obtain an adequate sample volume for analysis.

Dr. French (and later Dr. Thompson) indicated that adequate sample volumes can be obtained if a constant suction is applied to the suction lysimeters and by multiple sampling over time. Thus samples would be drawn over a period of several hours, or days, resulting in compositing samples over a short time increment for analysis.

Resolution: I indicated that this would be an acceptable to EFGWB. The sampling scheme will provide 9-samples per sampling interval (three 3-foot samples, three 6-foot samples, and three 9-foot samples) for analysis. This corresponds to current guidelines.

3. ISK expressed concern about the physical ability to obtain water samples with suction lysimeters from depths greater than about 10 feet (physical limitations of the pump to lift water that height). I expressed my concern about the need to address the movement of residues from 10 feet below the surface to the ground water (water table) at 15 to 20 feet (or deeper - as suitable sites could have a water table as deep as 30 feet). No resolution was reached. ISK would evaluate the problem, as they see the merit in the deeper samples. I agreed with ISK, that the method may not allow for sample collection, and that some other

method may need to be considered to sample soil or soil-pore

water below 10 feet.

Summary: no final resolution on this is was reached on July 24, 1992. We agreed to discuss these topics further on July 28, 1992. On July 28, we agreed to postpone any discussion until I had completed re-evaluating the protocol in light of the concerns of Dr. French and Dr. Thompson. The resolution of this issue is addressed later in this memorandum, and in the protocol review (EFGWB # 92-0545).

TELEPHONE CONVERSATION:
NAME OF CALLER: Lafayette Thompson, Ph.D.
American Agricultural Services, Inc.
Cary, NC 27712
Date of Call: July 29, 1992; 10:00 am.

Dr. Thompson expressed concern over the same issues as Dr. French. An additional issue was also raised as to whether ground-water samples could be collected after every other chlorothalonil application (14 days between applications) rather than after every application. This would result in ground-water samples being collected on an approximately monthly basis.

Discussion:
SHALLOW SOIL SAMPLING

The original protocol defined the shallow soil sampling on page 38 [15.1, 15.1.1 Shallow Soil Samples] and is summarized by Table 1. Soil samples are to be collected prior to (-1 days) and immediately after (0 days) the 8 chlorothalonil applications, and at specified intervals after the final application (As stated in the protocol document) as shown in Table 1. Soil cores were to be collected from the three sectors (Sect), with 6 sampling (Depth) increments (0-6, 6-12, 12-18, 18-24, 24-36, and 36-48 inches); resulting in 18 samples per sampling date (# of samples). The protocol indicated that no soil samples were to be collected at 5, 7, 8, 10, and 11-months, but were proposed for 15 and 18 months after the last application. This plan would net 486 samples, excluding the 15 and 18-month samplings.

Resolution: The EFGWB proposes the following modified sampling schedule as summarized in Table 1. Soil samples (3 sectors, 6 depths) should be collected and analyzed prior (-1 days) to the 8 chlorothalonil applications as defined above. Soil samples shall also be collected and analyzed after the each chlorothalonil application from each sector and 1 depth (0 to 6 inches). Soil samples shall also be collected and analyzed monthly after the last chlorothalonil application following the original sampling plan (3 sectors, 6 depths, 18 samples). This results in 384 soil analyses. Sampling beyond 12 months after the last chlorothalonil application will depend upon study results as does the approval to terminate the study.

Table 1. Comparison of Original Shallow Soil Sampling Scheme and Modified (required) Soil Sampling Scheme

APPL. NO.	TIME AFTER APPLICATION	ORIGINAL			MODIFIED		
		SECT	DEPTH	# OF SAMPLES	SECT	DEPTH	# OF SAMPLES
1	-1 days	3	6	18	3	6	18
1	0 days	3	6	18	3	1	3
2	-1 days	3	6	18	3	6	18
2	0 days	3	6	18	3	1	3
3	-1 days	3	6	18	3	6	18
3	0 days	3	6	18	3	1	3
4	-1 days	3	6	18	3	6	18
4	0 days	3	6	18	3	1	3
5	-1 days	3	6	18	3	6	18
5	0 days	3	6	18	3	1	3
6	-1 days	3	6	18	3	6	18
6	0 days	3	6	18	3	1	3
7	-1 days	3	6	18	3	6	18
7	0 days	3	6	18	3	1	3
8	-1 days	3	6	18	3	6	18
8	0 days	3	6	18	3	1	3
8	1 days	3	6	18	-	-	--
8	3 days	3	6	18	-	-	--
8	7 days	3	6	18	-	-	--
8	14 days	3	6	18	-	-	--
8	1 months	3	6	18	3	6	18
8	2 months	3	6	18	3	6	18
8	3 months	3	6	18	3	6	18
8	4 months	3	6	18	3	6	18
8	5 months	-	-	--	3	6	18

APPL NO.	TIME AFTER APPLICATION	ORIGINAL			MODIFIED		
		SECT	DEPTH	# OF SAMPLES	SECT	DEPTH	# OF SAMPLES
8	6 months	3	6	18	3	6	18
8	7 month	-	-	--	3	6	18
8	8 months	-	-	--	3	6	18
8	9 months	3	6	18	3	6	18
8	10 months	-	-	--	3	6	18
8	11 months	-	-	--	3	6	18
8	12 months	3	6	18	3	6	18
	Total			486**			384
8	15 months	3	6	18			
8	18 months	3	6	18			

Original (Protocol) 522 samples
Modified (Burton Letter) 288 samples
** Reflects the original sampling plan for the first 12 months (522 - 36 = 486).

SOIL-PORE WATER

Three issues concerning the collection of soil-pore water were presented by the registrant. The first was the number of suction lysimeters, second was the sampling schedule, and third was the installation of suction lysimeters deeper than 9 feet.

The original protocol called for three suction lysimeter clusters with nine lysimeters in each cluster (three 3-foot, three 6-foot, and three 9-foot depths). The soil pore-water samples were to be composited. (The exact compositing scheme presented in the protocol was confusing, and therefore unclear). EFGWB was concerned that the samples from all cluster were to be composited for analysis (page 31), resulting in three analysis per sampling event. (As stated above, the compositing scheme was not clear. Therefore, it was unclear whether the analysis would represent composites by depth or by cluster (sector)).

Issue #1. The number of lysimeters and the compositing of samples for analysis resulted from the registrants concern that an insufficient volume of sample would be collected for analysis (the required volume went from 250 mL to 700 mL). American Ag. Services is currently conducting a prospective monitor program elsewhere and have been able to collect adequate sample volumes

from a single suction lysimeter at each depth. The registrant and consultant are comfortable that adequate samples for analysis can be collected from one lysimeter per depth (three suction lysimeters per cluster). Therefore, the registrant will modify the study protocol to reflect that each suction lysimeter cluster will contain three lysimeters rather than the nine as originally describe in the protocol.

Resolution: EFGWB will accept the registrants proposal to reduce the number of suction lysimeters to three per cluster (one 3-foot, one 6-foot, and one 9-foot). This also is in agreement with guideline requirements. Samples will be collected individually from each lysimeter; three lysimeter clusters with three depths (3, 6, and 9-foot) per cluster, resulting in a total of nine samples (and analysis) per sampling event.

Issue #2. The EFGWB in a previous memo (7/25/92) recommended that the soil pore-water and ground water wells need only be sampled prior to (-1 days) the 8 application, and at 1-,3-,7-, 14- days, and monthly after the final application for 12 months, but not immediately after (0 days) applications.

Resolution: Soil pore-water samples will be collected prior (-1 days) to the 8 chlorothalonil applications, and 1, 3, 7, 14 days, and 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12-months after the final application (24 samplings). This results in a net of 216 soil pore-water samples for analysis and is summarized in Table 2.

Issue #3. The registrant indicates that the installation of suction lysimeters deeper than about 10 feet is extremely difficult. Additionally, the ability to pump the water out of the suction lysimeters for analysis is difficult to impossible. The EFGWB concurs that these are both realistic limitations of deeper placement of the suction lysimeters.

Resolution: EFGWB agrees that the installation of suction lysimeter deeper than the proposed 9 feet is not realistic and concur with the registrants request. However, a concern still remains as to how to monitor pesticide residues below the depth of suction lysimeters and above the water table (10 to 30 feet).

The protocol calls for collecting soil samples from the surface to the water table six months after the last chlorothalonil application. Deep soil sampling can be used address this concern. This will receive further consideration in the protocol review. The ultimate deep sampling scheme depends upon the specific conditions at the site selected.

GROUND WATER SAMPLING SCHEDULE

A questioned was also raised as to whether ground-water samples could be collected after every other chlorothalonil

application (14 days between applications) rather than after every application. This would result in ground-water samples being collected on an approximately monthly basis. The protocol proposed that ground-water samples be collected prior to the first application, and then monthly after the first application for 12 months (15.2 Water Well Samples, page 41). The number of samples (18) reflects the collection of a primary sample for analysis plus a duplicate sample. Only the primary sample is to be analyzed. Therefore, each sampling event will net 9 samples (three clusters with 3-wells per cluster) for analysis.

Resolution: The EFGWB generally agrees with the registrants request to sample ground-water monitoring wells, during the chlorothalonil application period, at every other application. The EFGWB will accept the following sampling schedule for the ground-water monitor wells. Water samples from the ground-water monitoring wells should be collected for analysis prior to Application number 1, 3, 5, 7, and 8, then monthly after the last application. This sampling schedule will result in the collection of an additional 72 samples (primary and duplicate), and an additional 36 analyses.

Table 2. Soil Pore-Water Sampling Frequency and Intensity.

Appl. No.	Sampling Interval	Sectors	Depths	# of Samples
1	-1 day	3	3	9
2	-1 day	3	3	9
3	-1 day	3	3	9
4	-1 day	3	3	9
5	-1 day	3	3	9
6	-1 day	3	3	9
7	-1 day	3	3	9
8	-1 day	3	3	9
8	1 day	3	3	9
8	3 day	3	3	9
8	7 day	3	3	9
8	14 day	3	3	9
8	1 month	3	3	9
8	2 month	3	3	9
8	3 month	3	3	9
8	4 month	3	3	9
8	5 month	3	3	9
8	6 month	3	3	9
8	7 month	3	3	9
8	8 month	3	3	9
8	9 month	3	3	9
8	10 month	3	3	9
8	11 month	3	3	9
8	12 month	3	3	9
Total				216