unmasked.

DATA EVALUATION RECORD

STUDY 5

CHEM 108401 Thiobencarb 165-5

FORMULATION--12--EMULSIFIABLE CONCENTRATE

STUDY ID (Acc. No. 247109)
Fujie, G.H. 1983. Addendum to a baseline assessment of a brackish water ecosystem, April 1, 1982 through March 31, 1983; Matagorda, Texas. Biospherics Project No. 382. Chevron Test No. S-2132. Residue analysis. Chevron File No. 721.11/S-2132. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA.

STUDY ID 00145834
Fujie, G.H. 1984. Addendum to impact of Bolero runoff on a brackish water ecosystem in Matagorda, Texas, first treatment year (second study year). Protocol No. P-8301-03. Biospherics Project No. 382-1983. Chevron Test No. S-2132. Unpublished study performed by and submitted by Chevron Chemical Company, Richmond, CA.

STUDY ID (Acc. No. 256967)
Fujie, G.H. 1985. Addendum to impact of Bolero runoff on a brackish water ecosystem in Matagorda, Texas. II. Second treatment year (third study year). Biospherics Project No. 382. Chevron Test No. S-2132. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA.

STUDY ID 00133563
Kennedy, J.H. 1983. Baseline assessment of a brackish water ecosystem, April 1, 1982 through March 31, 1983; Matagorda, Texas. Report/Project No. S-2132. Unpublished study performed by Biospherics Incorporated, Rockville, MD, and submitted by Chevron Chemical Company, Richmond, CA.

STUDY ID 00145835
Kennedy, J.H. 1984. The impact of Bolero run-off on a brackish water ecosystem in Matagorda, Texas. III. Second treatment year (third study year.) Biospherics Project No. 382. Chevron Test No. S-2132. Unpublished study performed by Biospherics Incorporated, Rockville, MD and submitted by Chevron Chemical Company, Richmond, CA.

STUDY ID (00145834)
Kennedy, J.H. 1985a. Addendum to final report: Impact of Bolero runoff on a brackish water ecosystem. First treatment year (second study year); Matagorda, Texas. Biospherics Project No. 382-1983. Chevron Project No. S-2132. Protocol No. P-8301-03. Unpublished study performed by Biospherics Incorporated, Rockville, MD, and submitted by Chevron Chemical Company, Richmond, CA.

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(1)

STUDY ID 00145833
Kennedy, J.H. 1985b. Impact of Bolero runoff on a brackish water ecosystem, first treatment year (second study year); Matagorda, Texas. Final report. Biospherics Project No. 382-1983. Chevron Test No. S-2132. Protocol No. P-8301-03. Unpublished study performed by Biospherics Incorporated, Rockville, MD, and submitted by Chevron Chemical Company, Richmond, CA.

STUDY ID 00145835
Kennedy, J.H. 1985c. Impact of Bolero runoff on a brackish water ecosystem, second treatment year (third study year), Matagorda, Texas. Final report. Biospherics Project No. 382-1984. Chevron Project No. S-2132. Unpublished study performed by Biospherics Incorporated, Rockville, MD, and submitted by Chevron Chemical Company, Richmond, CA.

DIRECT REVIEW TIME = 40

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CONCLUSIONS:

Field Accumulation - Aquatic Non-Target Organisms

1. This study cannot be used to fulfill data requirements at this time.

2. Thiobencarb accumulated in fish and shrimp living in drainage water from rice paddies that had been treated with thiobencarb once each year (1983 and 1984) at 2-4 lb ai/A in Texas. The maximum concentrations of thiobencarb in fish and shrimp were 2400 and 970 ppb, respectively, in 1983, and 1600 and 210 ppb, respectively, in 1984. The thiobencarb degradate 4-chlorobenzyl methyl sulfone accumulated only in shrimp, with maximum concentrations of 300 ppb in 1983 and 120 ppb in 1984.

3. This study is scientifically sound, but does not meet Subdivision N guidelines for the following reasons:

storage stability data for water, sediment, and animal tissue substrates were not provided;

water and sediment samples were analyzed only for thiobencarb, and animal tissues were analyzed only for thiobencarb and 4-chlorobenzyl methyl sulfone; and

soils and sediment in the test ares were not characterized.

4. In order for this study to fulfill the field accumulation in aquatic non-target organisms data requirement, the registrant must: provide storage stability data for all substrates; must demonstrate that thiobencarb is the only compound of concern in the water and soil, and that thiobencarb and 4-chlorobenzyl methyl sulfone are the only compounds of concern in animal tissue; and must characterize the soil and sediments in the study area.

METHODOLOGY:

Thiobencarb (Bolero 8EC, 8 lb ai/gal EC, Chevron) was aerially-applied at 2-4 lb ai/A/year to rice grown near Matagorda, Texas. Water from the test site emptied into a tidal drainage ditch on the perimeter of the one treated paddy through two one-way flap gates (Figures 1-3). Water from other nearby (distance not specified) thiobencarb-treated rice paddies that were not adjacent to the ditch drained into the same ditch. A total of 725 acres drained into the study ditch, of which 502.5 acres were treated. An untreated area located approximately 8 miles upstream of the study site served as a control. Four sampling stations were established within the ditch; additional sampling stations were established in the study area (Figures 1-3, Table 1).

Preexisting conditions at the study site were determined between April 1982 and March 1983. On June 1, 1983, thiobencarb was aerially-applied once at 4 lb ai/A to a 100-acre site planted to rice located directly adjacent to the drainage ditch. Other paddies draining into the ditch were treated with thiobencarb at 4 lb ai/A between March 20 and April 20, 1983. The test site was not treated again during the study period; other paddies draining into the ditch were treated with thiobencarb (Bolero 8EC) at approximately 2-4 lb ai/A between April 4 to May 1, 1984. Water from treated areas drained into the study ditch above station I, between stations I and II, and above station IV. The total treated acreage that drained into the study ditch above Stations I-III was 387 acres; an additional 162 acres drained into the study ditch above Station IV (total 549 acres).

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The temperature, dissolved oxygen, pH, conductance, and salinity of the water in the study ditch were measured at the sample stations from 2 to 4 times weekly during the study. Sediment, water, and biological samples were collected from Stations I through IV and IX according to the schedule in Tables 2 and 4; sampling was based on rainfall events (>0.5 inch in 24 hours; Tables 3 and 5). Duplicate water samples were collected in 1-quart glass jars (method of collection not specified); the tops were covered with aluminum foil, capped, and maintained at ambient temperature until analysis (length of storage up to 21 days before extraction for baseline study samples; length not specified for study years 1 and 2). Sediment was collected using a 6-inch Eckman dredge, and duplicate samples were transferred to 1-L polyethylene bottles. Sediment samples were stored frozen at -20 C until analysis (length of storage in baseline study up to 30 days before extraction; length not specified for study years 1 and 2). Fish were collected in a one-half inch mesh seine; grass shrimp (Palaemonetes pugio) were collected in a 6-mm mesh net. Fish and shrimp samples were stored frozen at -20 C until analysis (length of storage not specified).

Aliquots of the water samples were extracted by shaking with hexane for 2 minutes. Sodium chloride was added if needed to break the emulsions and the hexane was then decanted through anhydrous sodium sulfate. The hexane extract was reduced to dryness by vacuum rotary evaporation in a heated waterbath (temperature not specified), and the residues were reconstituted in a small volume of hexane. Aliquots of the solutions were then analyzed by GC with nitrogen-phosphorus flame ionization detection; peaks were quantified by comparison to standard curves. Recoveries of thiobencarb from fortified tap water samples (5 ppb) averaged 101-103%; the method limits of detection were 0.5-3 ppb.

A portion of the sediment sample was extracted three times by mixing with ethyl acetate for 5 minutes; after each extraction, the ethyl acetate was decanted through anhydrous sodium sulfate. The combined ethyl acetate extracts were reduced to dryness by vacuum rotary evaporation in a heated waterbath (temperature not specified). The residue was transferred to the top of a pre-washed alumina column with a small volume of hexane, and the column was washed with ethyl ether:hexane (5:95); thiobencarb was then eluted with ethyl ether:hexane (15:85). The eluate was reduced to dryness by vacuum rotary evaporation in a heated waterbath (temperature not specified); the residues were reconstituted in a small volume of hexane. Aliquots of the solution were then analyzed by GC with nitrogen/phosphorus flame ionization detection; peaks were quantified by comparison to standard curves. Recoveries of thiobencarb from fortified sediment (100 ppb) averaged 86.2-92%; the method limits of detection for thiobencarb were 10-40 ppb. Before analysis, the moisture content of the sediment was determined; results were corrected for moisture content.

Fish and shrimp tissue were analyzed for thiobencarb and 4-chlorobenzyl methyl sulfone by the following method. A portion of macerated tissue was acidified with 5 M phosphoric acid. The acidified tissue was then extracted three times by blending with ethyl acetate for 5 minutes; after each extraction, the solids were allowed to settle and the ethyl acetate was decanted through anhydrous sodium sulfate. The ethyl acetate extracts were combined and reduced to dryness by vacuum rotary evaporation in a heated waterbath (temperature not specified). The residue was transferred to a separatory funnel with hexane:acetonitrile (100:25, v:v), the solution was shaken, and the acetonitrile phase was removed. The hexane phase was extracted twice more with acetonitrile; after each extraction, the acetonitrile phase was removed. The acetonitrile phases were combined and reduced to dryness by vacuum rotary evaporation in a heated waterbath (temperature not specified). The residue was redissolved in methylene chloride:cyclohexane (15:85) and transferred to a gel permeation column (Bio-Beads S-X3) and eluted with methylene chloride:cyclohexane (15:85); the eluate was reduced to dryness by vacuum rotary evaporation in a heated waterbath (temperature not specified). The residue was redissolved in acetone:hexane (20:80) and transferred to a pre-washed alumina column, and the thiobencarb and 4-chlorobenzyl methyl sulfone were eluted with acetone:hexane (20:80). The eluate was reduced to dryness by vacuum rotary evaporation in a heated waterbath (temperature not specified), and the residues were reconstituted in a small volume of hexane or benzene. Aliquots of the solution were then analyzed for thiobencarb by GC with nitrogen/phosphorus flame ionization detection; aliquots of the solution were analyzed for 4-chlorobenzyl methyl sulfone by GC with flame photometric detection for sulfur (394 nm); peaks were quantified by comparison to standard curves. Recoveries from fish tissues fortified with 100 ppb of both thiobencarb and 4-chlorobenzyl methyl sulfone averaged 80.2-100 and 80.2-90.8%, respectively. Recoveries from shrimp tissues fortified with 100 ppb of both thiobencarb and 4-chlorobenzyl methyl sulfone averaged 88.9-100 and 84-94.1%, respectively. The method limits of detection for both thiobencarb and 4-chlorobenzyl methyl sulfone were 10-30 ppb. It was not specified if results were reported on a wet-weight basis.

DATA SUMMARY:

Thiobencarb accumulated in fish and shrimp living in drainage water from rice paddies that had been treated with thiobencarb (Bolero, 8 lb ai/gallon EC) once each year (1983 and 1984) at 2-4 lb ai/A in Texas. The maximum concentrations of thiobencarb in fish and shrimp were 2400 and 970 ppb, respectively, in 1983, and 1600 and 210 ppb, respectively, in 1984 (Tables 6-9). The thiobencarb degradate

4-chlorobenzyl methyl sulfone

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accumulated only in shrimp, with maximum concentrations of 300 ppb in 1983 and 120 ppb in 1984 (Tables 10-13). The maximum concentrations of thiobencarb and 4-chlorobenzyl methyl sulfone in the fish and shrimp occurred 1 day following the 1983 treatment of the paddy adjacent to the drainage ditch, and coincided with the maximum concentrations of thiobencarb in the drainage water.

Thiobencarb and 4-chlorobenzyl methyl sulfone were generally not detected in fish prior to the application of the pesticide to the adjacent paddy in 1983. In 1983, prior to the treatment of the study site but following the treatment of the other paddies in the watershed, thiobencarb in the fish ranged from <40 to 520 ppb (Table 6). One day after the application of thiobencarb to the adjacent paddy, thiobencarb in the fish ranged from 90 to 2400 ppb; thiobencarb ranged from <40 to 620 ppb between 5 and 27 days posttreatment and were below the limits of detection (<10-<30 ppb) at 41 through 212 days. In 1984, when only the nonadjacent rice paddies were treated with thiobencarb, thiobencarb was 60-170 ppb in the fish on April 29, 180-1600 ppb on May 2 (1 day after the last nonadjacent paddy was treated with thiobencarb), 10-410 ppb from May 4 to 15, and was at or below the limits of detection by May 31 (Table 7). At all sampling intervals, the concentration of 4-chlorobenzyl methyl sulfone in fish was at or below the limits of detection (Tables 10 and 11).

Thiobencarb and 4-chlorobenzyl methyl sulfone were generally not detected in shrimp prior to the application of the pesticide to the adjacent paddy in 1983. In 1983, prior to the treatment of the study site but following the treatment of the other paddies in the watershed, thiobencarb in the shrimp was up to 160 ppb (Table 8). One day after the application of thiobencarb to the adjacent paddy, thiobencarb in the shrimp ranged from 90 to 970 ppb; thiobencarb ranged from 10 to 390 ppb between 5 and 7 days posttreatment and <40 ppb at 11 through 270 days. In 1984, when only the nonadjacent rice paddies were treated with thiobencarb, thiobencarb was <60 ppb in the shrimp on April 29, 50-190 ppb on May 2 (1 day after the last nonadjacent paddy was treated with thiobencarb), 10-210 ppb on May 4, 10-70 ppm on May 8, and was at or below the limits of detection by May 15 (Table 9). In 1983, prior to the treatment of the study site but following the treatment of the other paddies in the watershed, 4-chlorobenzyl methyl sulfone in the shrimp was <80 ppb (Table 12). One day after the application of thiobencarb to the adjacent paddy, 4-chlorobenzyl methyl sulfone in the shrimp ranged from 10 to 300 ppb; 4-chlorobenzyl methyl sulfone ranged from 10 to 160 ppb between 5 and 11 days posttreatment and <120 ppb at 11 through 270 days. In 1984, when only the nonadjacent rice paddies were treated with thiobencarb, 4-chlorobenzyl methyl sulfone was $\leq$40 ppb in the shrimp on April 29, 40-120 ppb on May 2 (1 day after the last nonadjacent paddy was treated with thiobencarb), 40-90 ppb on May 4, and was at or below the limits of detection by May 15 (Table 13).

Thiobencarb was not detected in the irrigation water prior to the application of the pesticide to the adjacent paddy in 1983. In 1983, prior to the treatment of the study site but following the treatment of the other paddies in the watershed, thiobencarb was ≤1.2 ppb; thiobencarb was a maximum 21.8 ppb immediately after the treatment of the adjacent paddy, 15.5 ppb at 4-7 days, and <1.8 ppb at all other sampling intervals (Table 14). In 1984, when only the nonadjacent rice paddies were treated with thiobencarb, thiobencarb was a maximum 12.7 ppb during the treatment of the other paddies in the watershed (4/28, 4/30, and 5/1), a maximum 25.1 ppb on May 2, a maximum 5.4 ppb on May 3, and was ≤3.4 ppb at intervals after May 4 (Table 15).

Thiobencarb was not detected in the sediment prior to the application of the pesticide to the adjacent paddy in 1983, and was ≤60 ppb at all other sampling intervals (Tables 16 and 17).

During the study, water temperatures ranged from 1.5 to 39 C; pH ranged from 6.3 to 9.8; dissolved oxygen in the water at the test sites ranged from 1.8 to 15.8 mg/L; salinity ranged from 0.0 to 20.75 o/oo; and conductivity ranged from 181 to 29700 umho/cm. Air temperatures ranged from 7 to 84 F. The rainfall total during the study period was not provided; significant rainfall events (>0.5 inches precipitation) were listed in Tables 3 and 5.

COMMENTS:

General

1. Storage stability data for thiobencarb in water, sediment, and animal tissues, and for 4-chlorobenzyl methyl sulfone in animal tissues were not provided.

2. The water and the sediment were analyzed for thiobencarb residues only. The fish and shrimp samples were analyzed for thiobencarb and 4-chlorobenzyl methyl sulfone only.

3. The soils in the test paddies and sediments at the sample sites were not characterized. The sediment in some of the ditches was described as "soft gumbo clay."

4. No soil samples were collected from the treated fields to confirm the application rates.

5. During the study, the methods for determination of thiobencarb and 4-chlorobenzyl methyl sulfone in water, sediment and animal tissues were modified. The portion size of the subsample extracted was changed for the water samples. The detection method for the GC was changed from FP to flame ionization detection for residues in all substrates. These modifications decreased the limits of detection for all substrates.

6. Detection limits for residues in fish and shrimp tissues were not consistent throughout the experiment. The study author stated that the detection limits were related to insufficient sample sizes.

7. The drainage ditch used for the study flowed into the Colorado River, which "discharges into the intercoastal waterway and the Gulf of Mexico approximately 2 miles south of the test site"; "considerable tidal action is apparent in the drainage ditch". Sample stations were located adjacent to road crossings over the ditch , and "had similar physical characteristics (i.e., depth of water) and habitats."

8. Stations VI and VIII were not discussed since they were in the river, and the locations were significantly different from the test area.

9. Much of the information provided in this study is not pertinent to current Subdivision N guidelines, and so was not reviewed.

Baseline study

1. Data tables for the baseline study were illegible; values were confirmed by consulting the original data sheets.

2. The rice paddies draining into the study area in 1982 were treated with molinate (1 qt/A), propanil (1-2 gal/A), and propanil/butachlor. No thiobencarb was used in the study area the first year. Rice was planted in March; 130 units of nitrogen were applied to a 150 acre site draining into the study area on April 20 and June 1, 1982.

First treatment year

1. In the first year, the test site was seeded with rice (seeding method and population not specified) on May 15, 1983 (approximately 2 weeks prior to the first treatment). The rice paddies draining into the study area were treated with thiobencarb at 4 lb ai/A; other pesticides applied to paddies in the area included molinate, propanil, and bentazon. No pesticides other than thiobencarb were applied to the rice site directly adjacent to the drainage ditch (test site) during 1983.

Second study year

1. A minor fish kill was observed at Station 4 on May 4, 1984. Samples of live and dead fish were taken from the location and analyzed as described previously. The study author reported that thiobencarb residues in the dead fish were approximately 10x higher than levels found in live fish (Table 7). No other fish kills were observed.

2. Pesticides applied to the site included propanil and bentazon. Paddies in the area were seeded with rice (seeding method and rate not specified) between March 22 and April 6, 1983 (9-30 days prior to treatment); plots were also fertilized (quantities not specified).

Page _____ is not included in this copy.

Pages 9 through 41 are not included in this copy.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of quality control procedures.

_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

_____ A draft product label.

_____ The product confidential statement of formula.

_____ Information about a pending registration action.

✓ FIFRA registration data.

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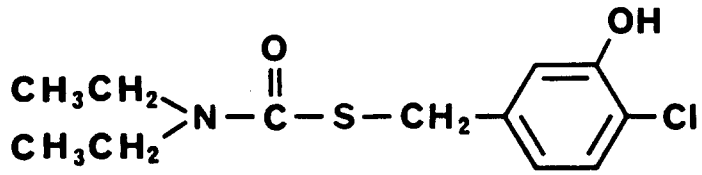
The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

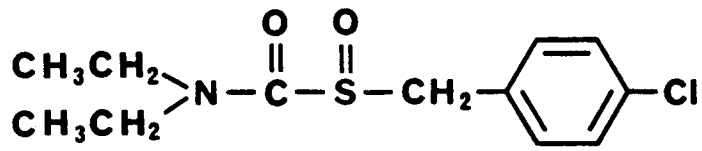
APPENDIX

THIOBENCARB AND ITS DEGRADATES



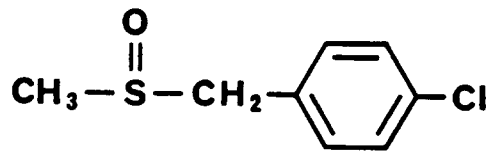
3-hydroxy thiobencarb

(S-[(4-chloro-3-hydroxyphenyl)methyl] diethylcarbamothioate, compound 43)



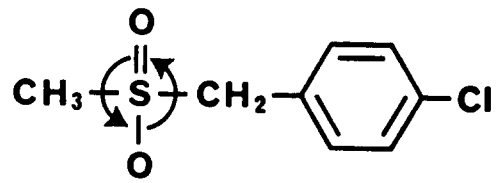
thiobencarb sulfoxide

(S-oxy-S-[(4-chlorophenyl)methyl] diethylcarbamothioate, compound 56)



4-chlorobenzyl methyl sulfoxide

(compound 58)



4-chlorobenzyl methyl sulfone

(compound 59)