6/2/97

MEMORANDUM

SUBJECT: Transmittal of EFED's RED chapter for thiobencarb (Chemical # 108401, Case # 2665, DP Barcode # D214608, D214609, and D214610), associated data reviews (DP Barcodes # D182567, D199775, D200554, D200560, D204352, D205496, and D208936), and EFED's recommendations for thiobencarb

FROM: F. Nicholas Mastrota, Task Team Leader
Environmental Risk Characterization Branch
Environmental Fate and Effects Division (7507C)

THRU: Elizabeth M. Leovey, Chief
Environmental Risk Characterization Branch
Environmental Fate and Effects Division (7507C)

TO: Jay Ellenberger, Chief
Accelerated Reregistration Branch
Special Review and Reregistration Division (7508W)

Attached to this memo is the EFED chapter for the Thiobencarb RED (Case # 2665). The attached product contains drop-in chapters for both the environmental fate assessment and the ecological risk assessment, as well as an integrated risk characterization. Also attached are Data Evaluation Reports for eight environmental fate studies and two ecological effects studies. The sponsor of these data is Valent USA Corporation.

Data Requirements

Environmental Fate DERs

DERs are attached for the following new environmental fate studies:

GLN	Study Type	MRID	Fulfills Guideline?
160-1	Hydrolysis	41609012	Yes
161-2	Photodegredation--water	42257801	Yes
162-1	Aerobic soil metabolism	43300401	Yes
162-3	Aerobic aquatic metabolism	43252001	Yes
163-1	Mobility	43150601	Yes
164-2	Aquatic field dissipation	42003404	Partial
165-3	Accumulation in crops	43148201	Yes
165-4	Bioaccumulation in fish	42460401	Yes

The study submitted for the aquatic field dissipation in California (GLN 164-2, MRID 41722504 only partially fulfills the guideline requirement because the study report lacked some vital information. The study report did not provide enough details on the water management practices used and did not provide information on the storage stability of thiobencarb. This study could be repaired to fulfill the guideline if this information is submitted and is judged to be acceptable by EFED.

All of the other environmental fate studies were acceptable and fulfill their respective guideline requirements. DERs for these studies are attached. Since thiobencarb is used primarily on rice, with only minor uses on terrestrial crops, a terrestrial field dissipation study is not required. No additional environmental fate studies are required for thiobencarb.

Ecological Effects DERs

DERs are attached for the following new ecological effects studies:

GLN	Study Type	MRID	Fulfills Guideline?
72-3(c)	Acute shrimp	00079117	No, supplemental
72-4(b)	Shrimp life-cycle	00079117 & 43031701	No, supplemental
72-4(b)	Shrimp life-cycle	43976801	No, supplemental

MRID 00079117, a study submitted by the registrant, included both an acute and chronic tests with the mysid. The acute test was classified supplemental because primarily because the test organisms were too old. However, this guideline has already been fulfilled by other studies. The chronic test was classified as supplemental because the experiment design lacked proper replication, measured concentrations were highly variable, and dry weights of mysids were not measured at the end of the test. This study is not repairable. The cover memo for these DERs (D197655) provide additional information on these tests.

MRID 43976801 was a paper from the open literature that was reviewed in attempt to fulfill the data gap. Although this paper provided useful information on the

chronic toxicity of thiobencarb to shrimp, the study design was inappropriate for fulfilling the guideline requirement. A new chronic toxicity test with a shrimp or mysid [GLN 72-4(b)] is thus required.

Requirements for Additional Studies

Four additional toxicity studies are required to complete EFED's data base. The risk assessment has been performed without these studies. This risk assessment is adequate for completing the RED; the additional studies are confirmatory.

Avian Acute Toxicity

The guideline requirement for avian single-dose oral testing [GLN 71-1(a)] has been fulfilled, but the requirement for avian dietary testing [GLN 71-2(a) and 71-2(b)] have not been fulfilled. The guidelines specify that both an upland game species and a waterfowl species be tests. Only one supplemental study has been submitted with the bobwhite quail, an upland game species. Based on the low acute toxicity determined in this supplemental study as well as the core acute oral study, EFED has sufficient information to conclude that thiobencarb is not an acute risk to avian species. The guideline requirement for avian dietary testing with an upland game species [GLN 71-2(a)] is waived. However, no acute toxicity data are available for a waterfowl species. Therefore, an additional study must be submitted testing the avian dietary toxicity of technical thiobencarb to a waterfowl species, preferable the mallard [GLN 71-2(b)].

The value added of these data is moderate. There is a chance that the mallard may be more sensitive to thiobencarb than the bobwhite, and this could change the conclusion of the risk assessment. In general, however, the acute toxicity of thiobencarb is not a major concern.

Avian Chronic Toxicity

A core avian reproduction study has been submitted for an upland game species (the bobwhite), but only a supplemental study is available for a waterfowl species (the mallard). This supplemental data for the mallard indicates that it is the more sensitive species and was thus used in the risk assessment. The data requirement for an avian reproduction study with a waterfowl is still outstanding. The value added of this information is low since the results of a new study likely would not be very different from those of the supplemental study. Also, the conclusion of the risk assessment is not dependent on these data since high risk could be concluded based on the results of the core study with the bobwhite.

Chronic Fish Toxicity

Guideline requirements have not been fulfilled for a fish early life-stage test [GLN 72-4(a)]. EFED does not require a new study for this guideline, but instead requires that the registrant submit a fish life-cycle test (GLN 72-5) with technical thiobencarb. ***The Agency is justified in requiring a fish life-cycle test because the end-use product is intended to be applied directly to water or is expected to***

transport to water from the intended use site (rice), and because the EEC is greater than one-tenth of the NOEC in the invertebrate life-cycle test. This test should be conducted with a freshwater fish, preferably the fathead minnow or rainbow trout. The value added of this information is high because thiobencarb appears to have high chronic toxicity in aquatic organisms, yet just how toxic it is to fish cannot be known until an NOEC is determined. ***The Agency reserves the right to require a second fish life-cycle study using a saltwater species at a later time.***

Chronic Marine/Estuarine Shrimp Toxicity

The guideline requirement for a life-cycle toxicity study with a marine/estuarine shrimp or mysid [72-4(b)] has not been fulfilled. A new life-cycle study is required. The value added by this study would be low to moderate since a high chronic risk has already been established based on the supplemental information. The benefits of a new study would be for establishing a definitive toxicity value that would improve the quality of the risk assessment and enable comparative analysis with other chemicals.

Seedling Emergence

The guideline requirement for seedling emergence testing [123-1(a)] is only partially fulfilled. The test was classified supplemental for the two most sensitive species, lettuce and ryegrass, because there was significant mortality of plants at the lowest test concentration. The EFED requests that additional testing be done for these two sensitive species using lower test concentrations that do not result in mortality of plants. The value added of this information is moderate. It would increase the confidence of the risk assessment on terrestrial plants. Also, this information would be required for comparative analysis of thiobencarb with other herbicides.

Thiobencarb Use Patterns Addressed in Risk Assessment

Thiobencarb is an herbicide used to control grasses and broadleaved weeds. It is applied to soil or water (in rice fields) to kill weeds before they emerge. Being a carbamothioate, its mode of action is inhibition of cell growth.

The primary use of thiobencarb is to control terrestrial and aquatic weeds in rice production. Over 95% of the use of thiobencarb is on rice. The maximum label use rate on rice is 4 lb/A, and the average rate is approximately 3 lb/A. Application may be by aircraft or ground equipment. For rice grown in the Gulf Coast and Mississippi River Valley, thiobencarb is usually applied as a liquid (EC formulation) to nonflooded fields. "Dry-seeded" rice is frequently grown in this area, in which seeds are sowed and grown in dry seed beds for several weeks before flooding. If there is no rainfall, fields are irrigated with a small volume of water (i.e. flushed) to promote seed germination. Some rice in this area is "water-seeded", meaning that seeds are applied to water in flooded fields. In this part of the country, thiobencarb is usually applied to fields before they

are flooded. Fields are then flooded for seeding with rice. These floods are normally dropped temporarily after seeding to allow rice seedlings to grow, resulting in a discharge of water. In California, the majority of rice grown is water-seeded with a continuous flood. Unlike the southern region, thiobencarb in California is almost always applied as a granule to water in flooded fields. A small percentage of rice farmers in California use "pin-
point flood" culture, in which case thiobencarb may be applied as a liquid to dry-ground before fields are flooded. California state regulations prevent rice farmers from discharging tailwater from rice fields for 4 to 30 days after application.

Relatively minor uses of thiobencarb are on lettuce, endive, and celery. These registrations are restricted to Florida. The maximum label rate is 6 lb ai/A for lettuce and endive and 8 lb ai/A for celery. Application is by boom sprayers.

Summary of Risks

Thiobencarb is exceptional as an herbicide in that it poses a risk not only to nontarget plants (as do most herbicides) but also substantial risk to virtually all aquatic and terrestrial wildlife. The ecological risks of the various uses are summarized below.

Summary of Risk Conclusions and RQ Values

Use Site	Birds	Mammals	Honey Bees	Freshwat-er Fish1	*Aquatic Inverts.*	*Estuarine Fish*	*Estuarine Inverts.*	*Terrestrial Plants*	*Aquatic* Plants
Rice in CA (granules)	High (chronic)	High (chronic)	Minimal	Moderate3 (chronic)	Moderate3 (chronic)	Minimal	Minimal	Minimal	Moderate
Rice in CA (liquid)2	High (chronic: 0.6-9.6)	*High (chronic: 3-48, acute: <0.1-0.6)*	*Minimal*	*Moderate3 (chronic)*	*Moderate3 (chronic)*	*Minimal*	*Minimal*	*High (aerial appl. only)*	*Moderate*
Rice in SE US	*High (chronic: 0.6-9.6)*	*High (chronic: 3-48, acute: <0.1-0.6)*	*Minimal*	*Moderate3 (acute)/ High (chronic)*	*High (chronic)*	*High (chronic)*	*High (acute and chronic)*	*High (aerial appl. only)*	*High*
Lettuce and endive	*High (chronic: 0.9-14.4)*	*High (chronic: 19-53, acute: <0.1-0.8)*	*Minimal*	*High (chronic)*	*High (chronic: 76, acute: 1.4)*	*High (chronic: >0.8)*	*High (chronic: 4-29, acute: 0.9)*	*High*	*High (6)*
Celery	*High (chronic: 1.2-19.2)*	*High (chronic: 22-57, acute: 0.02-1.1)*	*Minimal*	*High (chronic)*	High (chronic: 102, acute: 1.9)	High (chronic: >1)	High (chronic: 5-38, acute: 1.2)	High	High (11)

1 The chronic risk assessment for freshwater fish is tentatively based on chronic effects observed in a supplemental study with an estuarine fish (MRID 00079117). These risk conclusions will need to be reevaluated if additional data on chronic effects to fish are submitted.
2 Liquid formulations account for a small percentage of thiobencarb use in California.
3 In this table, "moderate risk" indicates that some risk exists, but it is likely limited to small areas and/or infrequent events that are associated with unusually high exposures.

O All uses of thiobencarb pose a high chronic risk to birds and mammals.

O Use of liquid formulations also pose some acute risk to mammals. The acute

risk to birds is minimal.

- Use of thiobencarb on celery, lettuce, and endive in Florida poses a very high risk of causing chronic effects to fish and freshwater invertebrates. It likely contributes to the degradation of water quality in the northern sections of the Everglades, including Loxahatchee National Wildlife Refuge. Additionally, this use poses a high risk of causing acute effects to freshwater and estuarine invertebrates.

- Use of thiobencarb on celery, lettuce, and endive in Florida poses a high risk to terrestrial plants, semiaquatic plants, and algae. It may also pose a risk to seeds and emerging seedlings of vascular aquatic plants.

- Use of thiobencarb on rice in the southeast US poses a high risk of chronic effects to freshwater and estuarine invertebrates, including shrimp and mollusks. The risk characterization concluded that thiobencarb could cause significant harm to populations of juvenile shrimp. The risk of chronic effects to fish is assumed to be high as well, but additional data are needed to confirm this. This use of thiobencarb may also poses a high risk of acute effects to fish and aquatic invertebrates in certain high-exposure situations.

- Use of thiobencarb on rice in California poses a risk of causing chronic effects to fish and aquatic invertebrates in the smaller drains and waterways, but not in the larger rivers. The EFED does not consider this to be a serious threat to the environment. This use poses minimal risk of acute effects to fish and aquatic invertebrates.

- Minimal risk of both acute and chronic effects is expected for all estuarine organisms in California due to minimal exposure.

- All uses of thiobencarb on rice may pose a risk of killing emerging seedlings of aquatic plants, especially aquatic grasses.

- Use of thiobencarb on rice may harm aquatic algae in the southeast US and in smaller drains and waterways in California.

- Spray drift from aerial application of liquid thiobencarb on rice poses a high risk to nontarget terrestrial and semiaquatic plants. Drift from applying granular thiobencarb (primarily in California) and spraying liquid thiobencarb with ground equipment pose minimal risk to these plants.

Recommendations for Risk Mitigation

The EFED is not able to propose specific recommendations for risk mitigation at this time. Possible actions that would likely reduce ecological risks are discussed

below. These are meant to be options for consideration. The EFED recognizes that some of these actions may not be feasible. Also, other measures not discussed may be effective in mitigating risk. The EFED recommends that risk mitigation actions be negotiated with the registrant and other interested parties.

Risk Mitigation for Use Granular Thiobencarb on Rice in California

Almost all granular thiobencarb is used on rice in California. Granular thiobencarb poses a high risk of causing chronic effects to all types of terrestrial vertebrates, as well as possible acute effects to mammals. The following measures are options that could be used reduce these risks:

1. Allow application only by ground equipment and require that granules be applied only to areas of the field that will be flooded (excluding levees). Require flooding of fields with at least 4 inches of water immediately after application.

2. Require the use of global positioning system (GPS) technology when applying granules by air to make the placement of the granules more precise. Also, the applicator could be required to use a set-back from the edge of flooded areas when applying granules. This set-back would account for the swath width of granular application to minimize the number of granules falling on dry ground on levees and field edges.

3. Granules possibly could be made aversive or less attractive to wildlife by altering the size, shape, or carrier, or by adding a taste repellent. To be acceptable, the effectiveness of any such modification of granules at deterring consumption by wildlife would have to be well established by published literature studies or new field or pen studies approved by the EFED.

The EFED believes that the water-holding requirements already required by the state government of California are adequate for minimizing risk to aquatic habitats from granular thiobencarb in that state. Any strengthening of these measures, such as lengthening water holding periods, would further mitigate this risk. Requiring that mixing/loading/handling be carried out some distance from surface water habitats would also be beneficial in reducing risks.

For any granular thiobencarb sold for use in the southeastern US, the mitigation measures for reducing aquatic risks from liquid formulations, discussed below, should be applied.

Risk Mitigation for Use of Thiobencarb on Rice in the Southeast

1. Reduction of the maximum label use rate would reduce risk.

2. Risk to shrimp and estuarine ecosystems could be mitigated by allowing use of

thiobencarb within 1 mile of tidal waters only on farms that have a pond or other facility that temporarily retains tailwater discharged from the field before it is released in the environment. This would reduce the amount of thiobencarb entering estuaries by allowing time for dissolved residues to dissipate and for suspended sediment with absorbed thiobencarb residues to settle out before the water is released.

3. Movement of the chemical in runoff is significantly reduced if thiobencarb is allowed time to bind to the soil before it is flooded or flush. Therefore, risk could be reduced by prohibiting flooding or flushing with irrigation water for several days following application.
4. The highest levels of contamination to aquatic habitats probably occurs when there is heavy rain immediately following application. A statement such as the following may reduce this risk:

> *Avoid application when heavy rainfall (>0.5 inch) is expected to occur within 48 hours.*

5. Restrict discharging of water from the field for several days after application. Flood gates on the outer levees would have to remain closed during this period, releasing only enough rain or irrigation water from the field needed to prevent the levees from rupturing.

6. Require a set-back of mixing/loading/handling areas from surface water habitats (streams rivers, lakes, wetlands, etc.).

Risk Mitigation for Uses in Florida

Over ten years ago, the EFED concluded that the use of thiobencarb in Florida on lettuce and endive would result in high acute and chronic risks to aquatic organisms (Section 18 review, Registration No. 83-FL-05) or on celery (Section 18 review, Registration No. 83-FL-26). The 1983 Section 18 review for celery also stated that the adverse effects of thiobencarb "could materialize on the Loxahatchee National Wildlife Refuge". The EFED still agrees with this conclusion. Most of the use of thiobencarb in Florida on vegetables is concentrated in the Palm Beach County, as well as some additional use on rice in this county. Since the agricultural areas in this county flow directly into the Loxahatchee National Wildlife Refuge, adverse effects from thiobencarb may be occurring. Also, the current risk assessment indicate that these uses pose additional chronic risks to birds and mammals, and a high risk of harming nontarget terrestrial and aquatic plants. The EFED therefore concludes that the reregistration of the use of thiobencarb on lettuce, endive, and celery in Florida result in continued high risks to many types of organisms in nearby habitats.

With chronic aquatic risk quotients of 102 for celery and 76 for lettuce and endive, the EFED doubts that practical risk mitigation could be imposed that would remove the characterization of "high risk". Actions that could reduce the risk somewhat

include reducing the use rate, requiring soil incorporation, and establishing buffer zones or vegetative filter strips between fields and bodies of water. However, the EFED recommends eliminating this use as the best way to mitigate risk.

cc (by cc:Mail): Denise Keehner
Kathleen Knox
Anthony Maciorowski
Henry Jacoby
Kathy Monk
Daniel Rieder
Mary (Betsy) Grim
James Breithaupt
Robert Hitch
David Wells
William Effland
Ronald Kendall
Renee Costello
Stephanie Syslo

C. ENVIRONMENTAL ASSESSMENT

The environmental assessment consists of four sections: Ecological Toxicity Data; Environmental Fate and Transport; Ecological Exposure and Risk Assessment; and Environmental Risk Characterization. The first section reports ecological toxicity data from laboratory studies. The second section describes the environmental fate and transport data from field and laboratory studies, assesses the impact to water resources, and details the environmental fate assessment. The third section estimates ecological exposure and assesses the effects to non-target terrestrial and aquatic organisms. The fourth section, the Environmental Risk Characterization Section, integrates the exposure and effects assessment to determine the extent and potential for risk to the environment.

1. Ecological Toxicity Data

a. Toxicity to Terrestrial Animals

(1) Birds, Acute and Subacute

An oral (LD_{50}) study (preferably mallard or bobwhite quail) and two subacute dietary (LC_{50}) studies (one species of waterfowl, preferably the mallard duck and one species of upland game bird, preferably bobwhite quail) are required to establish the toxicity of a pesticide to birds. Results of these tests are tabulated below.

Table : Avian Acute Oral Toxicity Findings (LD_{50})

Species	% A.I.	LD_{50} (mg a.i./kg)	MRID No. Author/Year	Toxicity Category	Fulfills Guideline Requirement?
Northern bobwhite	96.9	> 1938[a]	MRID 42600201 S.M. Campbell and M. Jaber. 1992.	Practically nontoxic	Yes
Northern bobwhite	Technical IMC 3950	--	Acc. No. 095106	--	No, invalid[b]
Mallard duck	Technical IMC 3950	--	Acc. No. 095106	--	No, invalid[b]

[a] There were no mortalities in birds receiving a dose of 1938 mg ai/kg thiobencarb.
[b] This study was performed by Industrial Bio-Test Laboratories, Inc. Data from all studies performed by this laboratory are considered invalid and cannot provide any information for ecological risk assessments.

Table : Avian Subacute Dietary Toxicity Findings (LC_{50})

Species	% A.I.	LC_{50} (ppm ai)	MRID No. Author/Year	Toxicity Category	Fulfills Guideline Requirement?
Northern bobwhite	"Technical"	>5620[a]	Acc. No. 241483. 1979.	Practically nontoxic	No, supplemental
Northern bobwhite	"Technical"	--	MRID 00057224 Acc. No. 095086	--	No, invalid[b]
Mallard duck	"Technical"	--	MRID 00057225	--	No, invalid[b]

[a] In this range-finding test for reproductive effects, there were no treatment-related mortalities in eight birds that were fed a diet containing 5620 ppm for eight weeks.
[b] This study was performed by Industrial Bio-Test Laboratories, Inc. Data from all studies performed by this laboratory are considered invalid and cannot provide any information for ecological risk assessments.

These results indicate that thiobencarb is practically nontoxic to avian species on an acute oral basis. A supplemental study (Acc. No. 241483), which was designed to be a range-finding study for determining dose levels for a reproductive study, suggests that thiobencarb is probably also practically nontoxic to the bobwhite on a subacute dietary basis. This conclusion is uncertain, though, since the study was not designed to test subacute dietary toxicity and because only eight birds were used in the control and each test level rather than the recommended ten. The guideline requirements for the acute oral testing [GLN 71-1(a)] are fulfilled. The guideline requirements for subacute dietary testing [GLN 71-2(a and b)] are not fulfilled. The Agency requires that additional data be submitted on the subacute dietary toxicity to a waterfowl species, preferable the mallard duck [GLN 71-2(b)]. The Agency is not requesting additional testing with an upland game species [GLN 71-2(a)]. (MRID 42600601)

(2) Birds, Chronic

Avian reproduction studies using the technical grade of the active ingredient (TGIA) are required when birds may be exposed to a pesticide repeatedly or continuously through its persistence, bioaccumulation, or from multiple applications, or if mammalian reproduction tests indicate possible adverse reproductive effects. The preferred test species are the mallard duck and bobwhite quail. Avian reproduction studies are required for thiobencarb because it is persistent in the terrestrial environment and may bioaccumulate. Results of these tests are tabulated below.

Table : Avian Reproduction Findings

Species	% A.I.	NOEC (ppm ai)	LOEC (ppm ai)	Endpoints Affected	MRID No. Author/Year	Fulfills Guideline Requirement?
Northern bobwhite	97.5	267	930	Hatchling weight, number of hatchlings per live embryos	MRID 43075401 J. Beavers, K. Chafey, L. Mitchell, and M. Jarber. 1993.	Yes
Northern bobwhite	Technical	--	--	--	MRIDs 00025776, 00025774, 00025775	No, invalid
Mallard duck	95.5	100	300	Number of eggs laid, number of normal hatchlings	Acc. No. 241483	No, supplemental
Mallard duck	--	--	--	--	Acc. No. 095106	No, invalid[a]
Japanese Quail	50.0 (Saturn EC)	750	350	fertility and hachability	Acc. No. 095106	No, supplemental

[a] This study was performed by Industrial Bio-Test Laboratories, Inc. Data from all studies performed by this laboratory are considered invalid and cannot provide any information for ecological risk assessments.

The results indicate that dietary concentrations greater than 100 ppm can impair reproduction in birds. The guideline requirement for testing with an upland gamebird species [71-2(a)] is fulfilled , but the guideline requirement for testing with a waterfowl species [71-2(b)] is not fulfilled. Additional avian reproduction testing with the mallard is requested. (MRID 43544902)

(3) Mammals

Wild mammal testing may be required on a case-by-case basis, depending on the results of the lower tier studies such as acute and subacute testing, intended use pattern and pertinent environmental fate characteristics. This testing has not been required for thiobencarb. Acute oral LD_{50} data for laboratory rats submitted to the Health Effects Division (HED) for evaluation of human toxicity were used to assess the mammalian acute toxicity of thiobencarb. The LD_{50} for male and female rats are 1033 and 1130 mg ai/kg, respectively (MRID 42130701). The risk assessment for wild mammals is based on the geometric mean of these values, 1080 mg ai/kg. These results classify thiobencarb as slightly toxic to mammals on an acute basis.

Smith (1993) reports that the LD_{50} of technical grade thiobencarb is 920-1903 mg/kg in the rat, which supports the definitive findings reported above. Smith (1993) also reports the LD_{50} of technical grade thiobencarb for the mouse to be 2745 mg/kg, indicating that the mouse is less sensitive than the rat.

Results from chronic mammalian studies were discussed in section **[cite appropriate section of HED section on mammalian toxicity studies]**. In a chronic feeding study, rats receiving thiobencarb at a dietary concentration of 100 ppm (5 mg/kg/d) had decreased body weight gains, food consumption, food efficiency, and increased blood urea nitrogen (MRID 00154506). The NOEL for this study was 20 ppm (1 mg/kg/d). In a reproductive study, parental rats receiving a dietary concentration of 40 ppm (2 mg/kg/d) had histopathological effects on the liver (MRIDs 40446201, 40985701). As this was the lowest concentration tested, the NOEL was < 40 ppm. Changes in body weights and increased kidney weights were observed at 2000 ppm (100 mg/kg/d). No reproductive effects were observed at any test concentration, yielding a NOEL of >2000 ppm. Based on these results, 20 ppm is considered to be a conservative NOEL for effects of thiobencarb on wild mammals. (MRIDs 42130701, 00154506, 40446201, 40985701)

(4) Insects

A honey bee acute contact LD_{50} study using the technical grade of the active ingredient is required when the proposed use will result in honey bee exposure. A honey bee acute contact study is not required for this pesticide because its use sites are

not expected to result in significant exposure to bees.

b. Toxicity to Aquatic Animals

(1) Freshwater Fish, Acute

Two freshwater fish toxicity studies using the technical grade of the active ingredient are required to establish the toxicity of a pesticide to freshwater fish. One study should use a coldwater species (preferably the rainbow trout), and the other should use a warmwater species (preferably the bluegill sunfish). Results of these tests are given below.

Table : Freshwater Fish Acute Toxicity Findings

Species	% A.I.	LC_{50} (mg ai/L)	MRID No. Author/Year	Toxicity Category	Fulfills Guideline Requirement?
Bluegill sunfish	10[a]	0.56	MRID 00050665, 1980	Highly toxic	Yes, for TEP only
Rainbow trout	10[a]	1.5	MRID 00050664, 1980	Moderately toxic	Yes, for TEP only
Rainbow trout	95.5	1.2	U.S.D.I., Access. No. 095106, 1973.	Moderately toxic	No, supplemental
Bluegill sunfish	95.5	2.5	U.S.D.I., Access. No. 095106, 1973.	Moderately toxic	No, supplemental
Channel catfish	95.5	2.3	U.S.D.I., Access. No. 095106, 1973.	Moderately toxic	No, supplemental
Bluegill sunfish	Technical	2.6	Acc. No. 095106, 1974	Moderately toxic	No, supplemental
Carp	Technical	2.8	Acc. No. 095106, 1974	Moderately toxic	No, supplemental
Bluegill sunfish	84.0[b]	1.7	U.S.D.I., Access. No. 095106, 1973.	Moderately toxic	No, supplemental
Rainbow trout	84.0[b]	1.1	U.S.D.I., Access. No. 095106, 1973.	Moderately toxic	No, supplemental
Channel catfish	84.0[b]	2.3	U.S.D.I., Access. No. 095106, 1973.	Moderately toxic	No, supplemental

[a] Bolero 10 G
[b] Bolero 8 EC

The majority of the results indicate that thiobencarb is moderately toxic to fish on an acute basis. The sole exception was an acute test of bluegill sunfish exposed to Bolero 10 G (10% ai) that determined the LC_{50} to be 0.56 ppm ai. This result is inconsistent with the results of two other acute tests which both determined that the LC_{50} for the bluegill sunfish was greater, in the range of 2.5 to 2.6 ppm ai. Results of tests with rainbow trout found that LC_{50}'s for this species are slightly greater than 1, putting it in the the moderately toxic range (>1-10 ppm) but close to the highly toxic range (0.1-1 ppm). The EFED therefore concludes that thiobencarb is moderately to

highly toxic to freshwater fish.

The only fully acceptable studies on the acute toxicity of thiobencarb to fish were conducted with Bolero 10 G. These studies fulfill only the guideline requirements for testing with a TEP [GLN 72-1(b) and 72-1(d)]. The guideline requirements for testing with the technical grade [GLN 72-1(a) and 72-1(c)] are not fulfilled by any particular studies, but the group of ten acute freshwater fish studies, when considered in its entirety, is sufficient for fulfilling these guidelines. (MRID 00050664 and 00050665, Acc. No. 095106).

(2) Freshwater Fish, Chronic

A freshwater fish early life-stage test using the TGAI is required for thiobencarb because the end-use product may be applied directly to water or expected to be transported to water from the intended use site (rice) and because the following conditions are met: (1) some aquatic acute LC_{50} and EC_{50} are less than 1 mg/l, (2) EECs in water (based on measured concentrations) were greater than 1% of acute LC_{50} and EC_{50} values, and (3) the half-life in water is greater than 4 days. No study with a freshwater fish species has been submitted. A study with a marine/estuarine species (sheepshead minnow) was submitted (MRID 00079112), but this study does not fulfill the guideline because it failed to determine the NOEC. The guideline for an early life-stage toxicity study with a fish species [GLN 72-4(a)] has not been fulfilled. However, the EFED does not request that the registrant submit a study for this guideline. Instead, the EFED requests that the registrant submit a core study that tests the effects of technical thiobencarb over the life-cycle of a fish (GLN 72-5). The Agency is justified in requiring a fish life-cycle test for thiobencarb because the end-use product is intended to be applied directly to water or is expected to transport to water from the intended use site (rice), and because the EEC is greater than one-tenth of the NOEC in the invertebrate life-cycle test. This test should be conducted with a freshwater fish, preferably the fathead minnow or rainbow trout.

(3) Freshwater Invertebrates, Acute

A freshwater aquatic invertebrate toxicity test using the TGAI is required to assess the toxicity of a pesticide to freshwater invertebrates. The preferred test organism is *Daphnia magna*, but early instar amphipods, stoneflies, mayflies, or midges may also be used. Results of this test are tabulated below.

Table : Freshwater Invertebrate Toxicity Findings

Species	% A.I.	LC_{50} or EC_{50} (ppm ai)	MRID No. Author/Year	Toxicity Category	Fulfills Guideline Requirement?
Daphnid *Daphnia magna*	94.4	EC_{50} = 0.10	MRID 00025788 Acc. No. 25788, 1978.	Highly toxic	Yes
Daphnid *Daphnia magna*	82.25[a]	EC_{50} = 0.17	MRID 00079118 1980.	Highly toxic	Yes, for TEP
Daphnid *Daphnia magna*	10[b]	EC_{50} = 0.46[c] LC_{50} = 1.2	MRID 00050666 1980.	Highly toxic	No, supplemental
Scud *Gammarus pseudolimimaeus*	95.5	LC_{50} = 0.72	U.S.D.I., Acc. 095106, 1973.	Highly toxic	No, supplemental
Scud *Gammarus pseudolimimaeus*	85[a]	LC_{50} = 1.0	U.S.D.I., Acc. 095106, 1973.	Moderately toxic	No, supplemental
Crayfish *Procambarus clarkii*	95.5	LC_{50} = 2.0	Acc. No. 095106	Moderately toxic	No, supplemental
Apple snail *Pomacea aludosa*	85[a]	LC_{50} = 1.85	MRID 40031001	Moderately toxic	No, supplemental

[a]Bolero 8 EC
[b]Bolero 10G
[c]The effect used to determine the EC_{50} was clumping of organisms.

The results indicate that thiobencarb is highly toxic to aquatic invertebrates on an acute basis. The guideline requirements for testing the TGAI [72-2(a)] and the TEP [72-2(b)] are fulfilled. (Acc. No. 25788 and MRID 00079118).

(4) Freshwater Invertebrate, Chronic

An aquatic invertebrate life-cycle test using *Daphnia magna* using the TGAI is required for thiobencarb because the end-use product may be applied directly to water or expected to be transported to water from the primary use site (rice) and because the following conditions are met: (1) some aquatic acute LC_{50}'s and EC_{50}'s are less than 1 mg/l, (2) EECs in water (based on measured concentrations) were greater than 1% of acute LC_{50} and EC_{50} values, and (3) the half-life in water is greater than 4 days. *Daphnia magna* is the preferred test species.

A life-cycle toxicity study measured the toxicity of thiobencarb (95.2-95.9 percent pure) to the daphnid, *Daphnia magna*. The NOEC and LOEC were 1.0 ppb and 3.0 ppb, respectively. The MATC was 1.7 ppb. Chronic effects observed were reduced number of young produced and adult mortality. These results indicate that concentrations of thiobencarb greater than 1 ppb can be detrimental to the survival and reproduction of freshwater invertebrates. The guideline requirement for life-cycle testing with a freshwater invertebrate [72-4(b)] is fulfilled. (Acc. No. 241483).

(5) Estuarine and Marine Animals, Acute

Acute toxicity testing with estuarine and marine organisms (fish, shrimp, and oysters) using the technical grade of the active ingredient is required when an end-use product is intended for direct application to the marine/estuarine environment or is expected to reach this environment in significant concentrations. The preferred test organisms are the sheepshead minnow, mysid shrimp and eastern oyster. Estuarine/marine acute toxicity testing is required for this pesticide because its use on rice is expected to result in significant exposure to marine and estuarine environments. Application of thiobencarb on rice fields will contaminate tailwater (i.e., water discharged from the water management system) which may flow into estuaries. The tables below show the results of these tests for fish and aquatic invertebrates.

Table : Acute Toxicity Findings for Marine/Estuarine Fish

Species	% A.I.	LC_{50} (ppm)	MRID No. Author/Year	Toxicity Category	Fulfills Guideline Requirement?
Sheepshead minnow	95.1	0.66	MRID 00079112, 1979.	Highly toxic	Yes
Sheepshead minnow	95.1	0.9	MRID 00079110, 1979.	Highly toxic	Yes
Sheepshead minnow	85.5[a]	1.4	MRID 00079111, 1979.	Moderately toxic	Yes, for TEP only
Sheepshead minnow	90	> 0.9	Borthwick and Walsh, 1981.	Not more than "highly toxic"	Open literature, supplemental
California grunion *Leuresthes tenuis* (Static tests)	90	0.31 (0 d old) 0.48 (7 d old) 0.59 (14 d old) 0.50 (28 d old)	Borthwick et al., 1985.	Highly toxic	Open literature, supplemental
California grunion *Leuresthes tenuis* (Flow-through tests)	90	0.27 (0 d old) 0.24 (7 d old) 0.38 (14 d old) 0.33 (28 d old)		Highly toxic	
Atlantic silverside *Menidia menidia* (Static tests)	90	0.46 (0 d old) 0.45 (7 d old) 0.63 (14 d old) 0.75 (28 d old)		Highly toxic	
Atlantic silverside *Menidia menidia* (Flow-through tests)	90	0.39 (0 d old) 0.20 (7 d old) 0.41 (14 d old) 0.68 (28 d old)		Highly toxic	
Tidewater silverside *Media peninsulae* (Static tests)	90	0.53 (0 d old) 0.40 (7 d old) 0.51 (14 d old) 1.2 (28 d old)		Moderately to highly toxic	
Tidewater silverside *Media peninsulae* (Flow-through)	90	0.30 (0 d old) 0.46 (7 d old) 0.39 (14 d old) 0.82 (28 d old)		Highly toxic	

[a]Bolero 8 EC

The results indicate that thiobencarb is highly toxic to marine/estuarine fish on an acute basis. The guideline requirements for fish are fulfilled for the TGAI [GLN 72-3(a)] and for a TEP, Bolero 8 EC [GLN 72-3(d), MRID]. (MRID 00079110, 00079111, and 00079112).

Table : Acute Toxicity Findings for Marine/Estuarine Invertebrates

Species	% A.I.	EC_{50} (ppm)	MRID No. Author/Year	Toxicity Category	Fulfills Guideline Requirement?
Eastern oyster (embryo-larvae)	95.1	0.56	MRID 00079114, 1979.	Highly toxic	Yes
Eastern oyster (embryo-larvae)	85.5[a]	0.32	MRID 00079115, 1979.	Highly toxic	Yes, for TEP
Eastern oyster (embryo-larvae)	90	0.9 - 9.0	EPA-600/4-81-076, Office of Research and Development, 1981.	Moderately to highly toxic	Open literature, supplemental
Mysid shrimp (<1 day old)	94.6	0.15	MRID 00050667, 1980	Highly toxic	Yes
Mysid shrimp (6-8 days old)	95.1	0.29	MRID 00079117, 1979.	Highly toxic	No, supplemental
Mysid shrimp (<1 day old)	90	0.33	Borthwick and Walsh, 1981.	Highly toxic	Open literature, supplemental
Grass shrimp *Palaemonetes pugio*	85.5[a]	1.0 (adults), 0.38-0.57 (juveniles)	Acc. No. 095106, 1975	Highly toxic	No, supplemental
Pink Shrimp *Penaeus duorarum*		0.57		Highly toxic	
White Shrimp *Penaeus setiferus*		0.31		Highly toxic	
Brown shrimp *Penaeus azetecus*		0.47		Highly toxic	
Ghost shrimp		1.1		Moderately toxic	
Fiddler crab	85.5[a]	4.4	MRID 00079113	Moderately toxic	No, supplemental
Shore crab	"Tech."	3.6	Acc. No. 095106	Moderately toxic	No, supplemental

[a]Bolero 8 EC

The results indicate that thiobencarb is highly toxic to marine/estuarine mollusks on an acute basis. The guideline requirements for mollusks are fulfilled for the TGAI [GLN 72-3(b)] and for a TEP, Bolero 8 EC [GLN 72-3(e)]. The results indicate that thiobencarb is also highly toxic for marine/estuarine shrimp. The guideline requirements for shrimp are fulfilled for the TGAI [GLN 72-3(c)]. (MRID 00079114, 00079115, and 00050667).

(6) Estuarine and Marine Animals, Chronic

Data from estuarine/marine fish early life-stage and aquatic invertebrate life-

cycle toxicity tests are required if the product is applied directly to the estuarine/marine environment or expected to be transported to this environment from the intended use site, and when any **one** of the following conditions exist: (1) the pesticide is intended for use such that its presence in water is likely to be continuous or recurrent regardless of toxicity; (2) any acute LC_{50} or EC_{50} is less than 1 mg/L; (3) the EEC in water is equal to or greater than 1% of any acute EC_{50} or LC_{50} value; or (4) the actual or estimated environmental concentration in water resulting from use is less than 0.01 of any acute EC_{50} or LC_{50} value *and* any of the following conditions exist: studies of other organisms indicate the reproductive physiology of fish and/or invertebrates may be affected, physicochemical properties indicate cumulative effects, or the pesticide has a half-life in water greater than 4 days. The preferred test organisms are the sheepshead minnow and mysid shrimp.

Chronic testing with thiobencarb is required because it has a primary use (rice) for which it is applied directly to water or is applied to land which is subsequently flooded with water. In addition, concentrations of thiobencarb measured in aquatic field studies are as great as 0.085 ppm, which is greater than 0.01 of the LC_{50} for marine/estuarine fish and aquatic invertebrates. Results of this test are given below.

Table : Estuarine/Marine Chronic Toxicity Findings[a]

Species	% A.I.	NOEC (ppb)	LOEC (ppb)	MATC (ppb)	MRID No. Author/Year	Endpoints Affected	Fulfills Guideline Requirement?
Mysid	95.1	ND, EC_{05}= 9.8[b]	ND	ND	MRID 00079117	Reproduction, survival of offspring	No, supplemental
Grass shrimp	84.7	<21[c]	21[c]	<21[c]	Acc. No. 241484, 1977.	Adult mortality	No, supplemental
Opossum Shrimp	"Technical"	3.2	6.2	4.5	MRID 43976801 Bailey, 1993	Survival of offspring	No, supplemental
Mysid	Not reported	22	35	28	McKenney, 1985	Number of young produced	Open literature, supplemental
Sheepshead Minnow	95.1	ND	150	<150	MRID 00079112, 1979.	Wet weight	No, supplemental

[a] ND designates that the value was not determined.
[b] The NOEC could not determined because the control had no replication. A nonlinear regression analysis (Bruce and Versteeg, 1992) was used to calculate the EC_{05} which can be used in lieu of the NOEC.
[c] Levels are highly uncertain because measured concentrations were highly variable.

The results indicate that a concentration of 150 ppb can adversely affect the growth of juvenile fish. Concentrations less than 150 ppb may also have had adverse effects if they had been tested. Because the study failed to determine NOECs, the guideline requirement for a fish early life-stage study [72-4(a)] has not been fulfilled. (MRID 00079112)

The EFED does not request that the registrant repeat the fish early life-stage study [GLN 72-4(a)]. Instead, the EFED requires that the registrant submit a core

study that tests the effects of technical thiobencarb on the life-cycle of a fish (GLN 72-5). The Agency is justified in requiring a fish life-cycle test because the end-use product is intended to be applied directly to water or is expected to transport to water from the intended use site (rice), and because the EEC is greater than one-tenth of the NOEC in the invertebrate life-cycle test. This test should be conducted with a freshwater fish, preferable the fathead minnow or rainbow trout. The Agency reserves the right to require a second fish life-cycle study using a saltwater species at a later time.

Chronic toxicity of thiobencarb to crustaceans is uncertain because none of the studies submitted to the Agency was conducted in accordance to the guidelines for this study. Based on supplemental data, the MATCs for crustaceans range from 4.5 to 35 ppb. Because the use of thiobencarb on rice in the Gulf Coast region may affect estuarine crustaceans, including economically important shrimp, core data on the chronic effects of thiobencarb on shrimp is essential for the risk assessment. The EFED therefore request that the registrant submit a study that tests the effects of thiobencarb over the life-cycle of a shrimp or mysid [GLN 72-4(b)]. (MRID 00079117)

(7) Aquatic Field Studies

The conclusion of high risk to aquatic organisms, based on results from laboratory toxicity tests, triggered the requirement for aquatic field testing with thiobencarb (GLN 72-7). The following aquatic field studies have been conducted on the use of thiobencarb on rice.

Title	Location and Date	Reference	Performed By	Sponsor	Fulfills Guideline Requirements?
Studies in Halls Bayou to Test the Effects of a Pre-Emergent Herbicide, Bolero, on Aquatic Organisms	Halls Bayou/ Chocolate Bay, Brazonia County, Texas 1979	Acc. No. 241484	Harper Environmental Consulting Company	Chevron Chemical Company	No, supplemental
Impact of Bolero Runoff on a Brackish Water Ecosystem	Matagorda, Texas 1982 - 1984	MRIDs 92182086 & 92182089	Biospheric, Inc.	Chevron Chemical Company	Yes[1]
Thiobencarb: Studies on Residue Level and Behavior in Selected Irrigation Creeks in Agricultural Areas in Saga Prefecture, Southwestern Japan	Saga Prefecture, Kyushu, Japan 1975	Acc. No. 241476	Life Science Research Institute	Unknown	No, supplemental

[1] Following the review of this study, an additional aquatic field study was requested to monitor aquatic residues in other localities where rice is grown. This additional study, however, was waived in December 1993. No further field studies are requested for thiobencarb at this time.

Hall's Bayou Study: The first field study conducted in the U.S, was in rice fields

bordering Halls Bayou, a tidally influenced, narrow stream that empties into West Bay near Galveston, Texas. This study is also referred to as the Chocolate Bay study. This estuarine area is a complex and highly important ecosystem that supports many commercial species. . Contaminated water was released into the bayou when rice fields were irrigated with a small amount of water (i.e. flushed) to moisten the soil. Also, heavy rainfall occurring during the experiment resulted in two additional releases of contaminated water. Sampling sites were established 500 ft downstream and 500 ft upstream of the point of discharge from the rice fields. Water samples collected at the field outlets and in Halls Bayou were analyzed for residues of thiobencarb. Fish, nektonic macroinvertebrates, benthic organisms, and phytoplankton were also sampled in these areas before, during, and after discharge from the rice fields. Fish and macroinvertebrates were also held in cages in Halls Bayou to monitor their response to the discharge of thiobencarb.

Due to poor experimental design and experimental conditions that caused excessive stress to the caged organisms, the EFED concluded that the results of the caged tests with fish and shrimp were invalid. They thus yield no information which can be used for risk assessment. Other parts of the field study provided some information and were thus classified as supplemental

The highest concentrations of thiobencarb were measured on a day when heavy rainfall (3.23 inches) occurred on the same day that thiobencarb was applied, resulting in an unscheduled flush overflow. Peak thiobencarb concentrations were 8.9 ppm (8900 ppb) where the tailwater exited the rice field and 690 ppb at the point where the drainage water entered Halls Bayou. The highest concentrations measured in the Halls Bayou on days that were not associated with heavy rainfall were 83 ppb at the upstream station (E) and 64 ppb at the downstream station (F). The abundance of fish, invertebrates, and plankton sampled at the downstream station were similar to or greater than those sampled at the upstream station. Gillnet catches declined in only one of the two areas sampled after discharges from the rice fields. Seine and trawl sampling indicated a decline in abundance of fish and invertebrates occurred near the end of the study. All declines were observed at both the upstream and downstream stations. Some differences in species composition of fish and invertebrates were observed between the upstream and downstream stations, and some changes in the species composition of benthic organisms were observed over time. None of these differences, however, could be conclusively linked to the discharge of thiobencarb.

The biological findings of the Halls Bayou study were inconclusive since there were no significant differences in species abundance or clear trends in the changes in species composition between stations upstream and downstream of the point of discharge. The upstream stations, being only 500 feet upstream of the site of discharge, were likely close enough to be affected by contamination moving upstream as the result of tidal mixing. Also, the abundance and composition of species were

probably influenced by other factors, including tidal cycles, salinity changes, and release of other pesticides from neighboring areas. Small samples sizes further limited the usefulness of this study. This study does not provide much useful information on the effects of thiobencarb on the estuarine environment.

Matagorda Study: A larger aquatic field study was conducted in 1982-1984 near Matagorda, Texas. The site consisted of a rice field that drained through a ditch into the tidal waters of the lower Colorado River of eastern Texas. As with Hall's Bayou, this estuarine area is a complex and highly important ecosystem that supports many commercial species. No thiobencarb applications were made in 1982; this year provided baseline data for the site. Baseline thiobencarb concentrations were as high as 9 ppb. In 1983 and 1984, approximately 500 acres of the field were treated with thiobencarb at a rate of 4 lbs ai per acre. Fields were flushed with water within 3 to 12 days after application. Data collected from 1982 through 1984 included (1) residues of thiobencarb in water, sediment, fish and shrimp; (2) catch per unit effort measurements of fish and aquatic invertebrates; and (3) percentages of grass shrimp (*Palaemonetes pugio*) that were gravid. While samples were collected during all three years of the study, the sampling effort on the third year was very poor.

A control station was also planned on the Colorado River upstream of the confluence with the drainage ditch. However, during the course of the study, the Agency and the registrants agreed that this station could not serve as a control for the field study because it contained preexisting residues of thiobencarb. It was therefore only possible to compare residues and biological samples collected during 1983 and 1984 to those collected during 1982, before the initial treatment. This represents a shortcoming of this study since the results could have been influenced by yearly fluctuations in environmental conditions that are unrelated to the applications of thiobencarb. Another shortcoming is that other pesticides (ordram, basegran, machette, and propanil) were applied to fields that drain into the test ditch during the period of this study. The toxicity of these pesticides could have contributed to the observed effects.

The results of the study were:

1. Residues of thiobencarb were transported into the estuary via runoff and drift. Residues in water exceeded the aquatic invertebrate MATC (1.7 ppb). Maximum residues measured in water, sediment, fish, and shrimp were 25.1 ppb, 50 ppb, 2400 ppb, and 970 ppb, respectively.

2. Although the overall population of fish was apparently not affected, marked declines were observed during the treatment years in three species, *Gambusia affinis*, *Dormitator maculatus*, and *Poecilia latipenna*.

3. Several taxa of aquatic invertebrates showed substantial decline in numbers caught per unit effort. Species richness and diversity also declined significantly during treatment years.

4. The percentage of gravid shrimp decreased significantly in 1983 compared to 1982. The decline was about 50% at stations 1 and 2, and averaged 23% for all four stations. (Sampling was inadequate to assess the effect on the percentage of gravid shrimp in 1984.)

5. A kill of the fish menhaden (*Brevoortia patronus*) was observed in the area where the field runoff entered the drainage ditch. It occurred at the point of discharge from the drainage canal, one to two days after a post-application flush of the rice fields. Although other pesticides that were applied that year (ordram, basegran, and propanil) may have been present in the tailwater, this kill was attributed to thiobencarb contamination because the dead fish contained high residues of thiobencarb (mean of 3.56 ppm).

6. Field BCF for thiobencarb were estimated to be 109X for fish and 44X for shrimp.

Declines in fish, aquatic invertebrates, and gravid shrimp cannot conclusively be attributed to the use of thiobencarb. Nevertheless, the findings in the field were consistent with effects demonstrated in laboratory studies. They suggest that the application of thiobencarb to rice fields may result in significant environmental damage to the adjacent estuarine habitat. Possible effects include chronic effects to sensitive fish, acute and chronic effects to ecologically important aquatic invertebrates, chronic effects to grass shrimp and possibly to commercial shrimp, and indirect detrimental effects to organisms at higher trophic levels that depend on these organisms for food.

Japan Study: The EFED reviewed a study that measured residues of thiobencarb in creek water after application to rice paddies in Japan. Thiobencarb was applied in the form of 7% granules at a rate of 30 kg/ha, which is equivalent to 1.9 lb ai/A. Water samples were taken from ten stations along creeks that flow through the rice fields and drain into the Hayatsue River. Water sampling was conducted from March through November, with thiobencarb treatments being made from June 28 through July 2. The creeks served as storage for irrigation water until May, when the water is pumped onto the fields. The creeks resembled large ponds during the storage period.

Very low thiobencarb concentrations (0.2 ppb or less) were reported at all stations in March and April before applications were made. Concentrations peaked at the sampling period of July 1, when concentrations at most stations were between 20 and 40 ppb. The greatest concentration was measured was 40.5 ppb. Concentrations declined fairly rapidly thereafter; the half-life of thiobencarb in creek water was

estimated to be 8.8 days. This rate of decline represents dilution as well as biological and physical degradation processes. EFED cannot interpret the significance of these results or extrapolate conclusions to other areas because of the lack of important information on the test conditions, such as flow rates within the creeks and rainfall during the study.

A difficulty with all three of the field studies was that water flow measurements were not made, making it impossible to discern effects of dissipation versus dilution. While water residues were generally short-lived, it is not clear whether thiobencarb residues were broken down by chemical or biological forces, or they were swept away and diluted by tidal flow. Because it is possible that dilution was the primary mode of dissipation in all three studies, the rate at which thiobencarb degrades by chemical or biological means in estuaries remains unknown. Thiobencarb residues thus may persist longer in other areas where dilution is of less importance in the dissipation of residues.

The three biological field studies demonstrate that application of thiobencarb on rice can cause significant contamination to water, sediments, and aquatic organisms in off-site aquatic habitats. Harm to estuarine and freshwater ecosystems is possible when thiobencarb is used in southeastern United States. Although shortcomings of these studies make it impossible to identify thiobencarb as the sole cause of observed adverse effects, the studies fail to refute the Agency's presumption that the use of thiobencarb on rice results in severe effects on aquatic ecosystems.

c. Toxicity to Plants

(1) Terrestrial

Terrestrial plant testing (seedling emergence and vegetative vigor) is required for herbicides which have terrestrial non-residential outdoor use patterns and which may move off the application site through volatilization (vapor pressure $\geq 1.0 \times 10^{-5}$ mm Hg at 25°C) or drift (aerial or irrigation), and/or which may have endangered or threatened plant species associated with the application site. Terrestrial plant testing is required for thiobencarb because it is an herbicide with a terrestrial nonresidential use pattern (rice) and because aerial applications may result in drift.

For the seedling emergence and vegetative vigor testing the following plant species and groups should be tested: (1) six species of at least four dicotyledonous families, one species of which is soybean (*Glycine max*), and another of which is a root crop, and (2) four species of at least two monocotyledonous families, one species of which is corn (*Zea mays*).

Results of Tier II seedling emergence toxicity testing on technical thiobencarb are given below.

Table : Nontarget Terrestrial Plant Seedling Emergence Toxicity Findings (Tier II)

Species	% AI	Parameter Affected	EC_{25} (lb ai/A)	NOEC (lb ai/A)	MRID No. Author/Year	Fulfills Guideline Requirement?
Monocot--Corn	96.6	Shoot length	>1.7	1.7	MRID 41690902 Hoberg, J.R. 1990	Yes
Monocot--Oat		Shoot length	0.086	0.055		Yes
Monocot--Onion		Shoot length	2.0	0.94		Yes
Monocot--Ryegrass		Mortality	0.019	0.0051[1]		Yes[2]
Dicot/Root Crop--Carrot		Shoot length	>3.1	2.1		Yes
Dicot--Cabbage		Shoot length	0.082	0.071		Yes
Dicot-Cucumber		Shoot length	>1.7	0.16		Yes
Dicot--Lettuce		Mortality	0.27	--		No, supplemental
Dicot--Soybean		Shoot length	>1.7	0.94		Yes
Dicot--Tomato		Shoot length	1.1	0.94		Yes

1 This NOEL is based on 17% mortality of plants occurring at the next higher test level, 0.011 lb ai/A.
2 Seedling emergence data for ryegrass is upgraded from supplemental to core.

In the tier II seedling emergence test, mortality of test plants occurred in the tests with ryegrass, cabbage, and lettuce. Mortality was the most sensitive toxic endpoint for these species (plants tended to die shortly after emerging). Grasses appear to be exceptionally sensitive to thiobencarb. The most sensitive species was ryegrass, a monocot, for which the EC_{25} based on mortality (i.e. LC_{25}) was 0.019 lb ai/A. The most sensitive dicot was lettuce. The lettuce EC_{25} based on mortality was estimated to be 0.27 lb ai/A, but this is not a definitive result since it was calculated from supplemental data.

The guideline requirement for seedling emergence testing [123-1(a)] is only partially fulfilled. Core seedling emergence data is outstanding for lettuce. Lower dosages may need to be tested to determine the NOEC for this species. (MRID 41690902)

Results of Tier II seedling vegetative vigor toxicity testing on the technical thiobencarb are given below.

Table : Nontarget Terrestrial Plant Vegetative Vigor Toxicity Findings (Tier II)

Species	% A.I.	Parameter Affected	EC_{25} (lb ai/A)	NOEC (lb ai/A)	MRID No. Author/Year	Fulfills Guideline Requirement?
Monocot- Corn	96.6	Shoot length, shoot weight, and root weight	>2.2	2.2	MRID 41690902 Hoberg, J.R. 1990	Yes
Monocot--Oat		Shoot weight	0.17	0.12		Yes
Monocot--Onion		Shoot length	1.2	0.80		Yes
Monocot--Ryegrass		Shoot length	0.073	0.020		Yes
Dicot/ Root Crop--Carrot		Shoot length, shoot weight, and root weight	>2.2	2.2		Yes
Dicot--Cabbage		Root weight	1.2	1.4		Yes
Dicot--Cucumber		Shoot weight and root weight	--[a]	<0.12		Yes
Dicot--Lettuce		Root weight	1.3	0.80		Yes
Dicot--Soybean		Shoot weight	1.2	0.80		Yes
Dicot--Tomato		Root weight	1.8	2.2		Yes

[a]Greater than a 25% reduction was recorded at some or all exposure levels, but the EC_{25} could not be determined because no dose-response relationship was apparent.

In the Tier II vegetative vigor tests, soybean was the most sensitive dicot and ryegrass was the most sensitive monocot. The guideline requirement for vegetative testing [123-1(b)] is fulfilled. (MRID 41690902)

(2) Aquatic

Aquatic plant testing is required for any herbicide which has outdoor non-residential terrestrial uses in which it may move off-site by runoff (solubility >10 ppm in water), by drift (aerial or irrigation), or which is applied directly to aquatic use sites (except residential). The following species should be tested: *Kirchneria subcapitata*, *Lemna gibba*, *Skeletonema costatum*, *Anabaena flos-aquae*, and a freshwater diatom. Aquatic plant testing is required for thiobencarb because it may be applied directly to water, it may be applied aerially, and it is applied to rice paddies where it is expected to contaminate the tailwater that leaves the field.

Results of Tier II toxicity testing on technical thiobencarb are given below.

Table : Nontarget Aquatic Plant Toxicity Findings (Tier II)

Species	% A.I.	EC_{50} (ppb)	NOEC (ppb)	MRID No. Author/Year	Fulfills Guideline Requirement?
Freshwater diatom *Navicula pelliculosa*	96.6	380	65	MRID 41690901 Giddings, J.M. 1990.	Yes
Duckweed *Lemna gibba*		770	140		Yes
Green algae *Selenastrum capricornutum*		17	13		Yes
Marine diatom *Skeletonema costatum*		73	18		Yes
Blue-green algae *Anabaena flos-aquae*		>3100	3100		Yes
Marine diatom *Skeletonema costatum*	95.5	327-459[a]	--	EPA-600/4-81-076, Office of Research and Development, 1981.	Open literature, supplemental

[a]96-hour EC_{50}

The Tier II results indicate that green algae is the most sensitive aquatic plant species. A thiobencarb concentration of 17 ppb ai is predicted to cause a 50% reduction in the growth and reproduction of this species. The guideline requirement (123-2) is fulfilled (MRID 41690901).

2. Environmental Fate

a. Environmental Fate Assessment

Thiobencarb is generally nonpersistent in the water column but moderately persistent in soils and sediments. Thiobencarb dissipates in the environment by binding to soil, by aerobic soil metabolism at the soil/H_2O interface, and by aqueous photolysis in the presence of photosensitizers. Ground water contamination is not likely from use on the primary crop, rice, and surface water is not likely to receive significant amounts of thiobencarb unless there is excess rainfall soon after application, leading to uncontrolled runoff. When used on the rice, thiobencarb is more likely to be found in the soil than in the paddy water. Furthermore, greater quantities of thiobencarb are associated with soil when applied preflood to soil rather than in standing water. The parition of thiobencarb associated with soil was approximately 10 times more when applied preflood to soil than when applied to standing water, primarily since thiobencarb has time to bind to soil prior to flooding. As a result, sensitized aqueous photolysis is expected to be more significant as a dissipation route when thiobencarb is applied to water than when it is applied to dry soil, due to a greater amount of thiobencarb remaining in paddy water containing natural photosensitizers.

Thiobencarb has a water solubility of 27.5 ppm, a vapor pressure of 2.2×10^{-5} Torr, and a Henry's Law Constant of 2.71×10^{-7} atm m^3/mol. It is stable to hydrolysis, **non-sensitized** aqueous photolysis, soil photolysis, anaerobic aquatic metabolism, and aerobic aquatic metabolism. In an aqueous photolysis study with and without the use of **photosensitizers**, the half-lives were 12 and 190 days, respectively. Since photolysis humic substances in natural waters have been shown to act as photosensitizers (Chou and Eto, 1980; Zepp et al, 1985; Mudambi and Hassett, 1988, attached), the 12-day half-life was used in the risk assessment. Thiobencarb also degraded moderately slowly under aerobic conditions with calculated half-lives of 27-58 days in soils that typically support rice production (58 days was used for risk assessment).

Thiobencarb slowly mineralizes in soil without forming significant quantities of non-volatile degradates. The major degradate in both the aqueous photolysis and soil metabolism studies was 4-chlorobenzoic acid, reaching 56 and 5 % respectively. CO_2 and bound residues are the primary products from soil metabolism studies, occurring in proportions of 42-77 and 23-42 %, respectively. Aqueous residues did not exceed 4.5 % in soil metabolism studies.

Parent thiobencarb was moderately mobile to immobile in the tested soils with Freundlich K_{ads} values of 5.42-20. The K_{oc} values ranged from 384-6750. 4-Chlorobenzoic acid, a degradate of thiobencarb, was very mobile to moderately mobile in the tested soils with Freundlich K_{ads} values of 0.74-3.26. The corresponding K_{oc} values ranged from 84-416. Mobility generally decreased with increasing clay content, increasing organic matter content, and increasing cation exchange capacity.

Results from an aquatic field dissipation study in Louisiana, where thiobencarb was applied as a spray directly to soil and flooded 7 days later, show half-lives of 5.8 days in flood water and 36 days in hydrosol. The median ratio of soil:water thiobencarb residues was 63.5:1.

In two field studies in California where granules were applied into standing water, the half-lives in flood water were 8.7 days (guideline study) and 4.5 days (literature review, Ross and Sava, 1986). The half-lives in hydrosol were 153 and 56 days, respectively. The median ratios of soil:water thiobencarb residues were 5.6:1 and 6.6:1.

Thiobencarb moderately accumulated in bluegill sunfish with maximum bioconcentration factors of 128x, 639x, and 411x for edible (muscle) tissue, nonedible tissue, and whole fish, respectively. Depuration is rapid, with 93-95% of the accumulated [^{14}C]residues being eliminated from the tissues in three days. The degradates 4-chlorobenzylmethylsulfoxide, thiobencarb sulfoxide, desethylthiobencarb, and 2-hydroxythiobencarb were identified in edible and nonedible tissue. Based on

results of crop accumulation studies, thiobencarb does not appear to accumulate in plants.

b. Environmental Fate and Transport

(1) Degradation

(a) Hydrolysis

Thiobencarb is stable to degradation by hydrolysis. Thiobencarb did not degrade in sterile aqueous buffer solutions (pH 5, 7, and 9) that were incubated in darkness at 25 °C for 30 days. The guideline requirement (GLN 161-1) is fulfilled. (MRID 41609012)

(b) Photodegradation

In Water

Thiobencarb photodegraded with a calculated half-life of 190 days in a nonsensitized sterile pH 7 aqueous buffer solution at 25 °C. Photodegradation was more rapid in a solution photosensitized with acetone with a half-life of 12 days. Thiobencarb did not degrade in the dark control (non-sensitized). The photoproducts identified in the nonsensitized and sensitized irradiated solutions were 4-chlorobenzoic acid, 4-chlorobenzaldehyde, 4-chlorobenzyl alcohol, and N,N-diethyl-4-(chlorobenzylthio)carbamate S-oxide (thiobencarb sulfoxide). In the non-sensitized, irradiated solution, no photoproduct exceeded 3.9 % of the applied. The major photoproducts in the sensitized solutions were 4-chlorobenzoic acid and 4-chlorobenzaldehyde, reaching maximum amounts of 56 and 29.4 % of applied, respectively. 4-Chlorobenzyl alcohol reached 6.1-6.7 % of applied by 14-30 days and thiobencarb sulfoxide reached a maximum amount of 5 % by 14 days, and declined to 1.1 % by 30 days. One additional degradate, O-[(4-chlorophenyl)methyl]diethyl carbamate (bencarb), was isolated in the irradiated sensitized solution and reached 8.3 ~~17.7~~ % by 21 days, and declined to ~~12.4~~ % by 30 days. The guideline requirement (GLN 161-2) is fulfilled. (MRID 422257801)

See Table VII of study w/ DER

8.1

On Soil

Based on 30-day studies, thiobencarb slowly photodegraded on sandy loam soil irradiated under natural sunlight at Richmond, California with an extrapolated half-life of 168 days, and degraded in the dark controls with a calculated half-life of 280 days. In the study, no volatile or non-volatile degradates exceeded 1.3 % of applied. Non-extractable residues did not exceed 8.7 % in the irradiated samples and 5.7 % in the

dark control samples by 26 days. The guideline requirement (161-3) is fulfilled. (MRID 41215312)

Photodegradation in Air

No data were reviewed. This study was waived (4/29/91) because volatility is not a significant dissipation route in the environment for thiobencarb.

(c) Aerobic Soil Metabolism

Thiobencarb is moderately persistent in soils in California and Louisiana that support rice production. The calculated half-lives in three soils were 27-58 days in two acceptable studies (MRID's 43300401, 00040925). One supplemental study (MRID 43121201) provided additional information that supported the results of the two acceptable studies.

Thiobencarb appeared to degrade in a biphasic pattern with half-lives of 58 days for 0-56 days after treatment and 137 days for 56-366 days in a Stockton Clay Adobe soil from California (24 % sand, 30 % silt, 46 % clay, 2.2 % OC, pH 6.1). The biphasic pattern may be a result from thiobencarb binding to soils. After the 56-day sampling interval, the rate of degradation was significantly slower. There were six non-volatile degradates detected in the study, but none of the degradates exceeded 5.4 % of the applied dose (3.1 ppm). The primary degradates were carbon dioxide, reaching 42.5 % of the applied by the end of the study (366 days), and bound residues, reaching 23.2 % by the end of the study. Nonvolatile residues were becoming more tightly bound to soil with time. All of the non-volatile degradates were ring rearrangements of parent thiobencarb. The guideline requirement (162-1) is fulfilled. (MRID 43300401)

The reviewer-calculated half-lives in a clay soil from Biggs, California and a silty clay loam from Crowley, Louisiana were 37 and 27 days, respectively. The clay soil (18 % sand, 26 % silt, 56 % clay, 1.13 % OC, pH 4.6, CEC 32.5 meq/100g) and the silty clay loam from Crowley, LA (3 % sand, 69 % silt, 28 % clay, 0.79 % OC, pH 5.8, CEC 14.5 meq/100g) were representative soils from major rice growing regions of the U.S. Evolved CO_2 increased to 54-77 % by 1 year. The extractable, non-volatile degradates did not exceed 5 % of applied, and bound residues increased to a maximum of 42 % of applied by 1 year. (GLN 162-1, MRID 00040925)

In a supplemental guideline study using a California soil, CO_2 increased to 8.6 % of applied by 132 days, and bound residues increased to 23.3 % of applied. The soil was a Stockton Clay Adobe (18 % sand, 27 % silt, 55 % clay, 2.0 % OC, pH 6.0). This was intended to be an aged soil mobility study, but determination of meaningful Freundlich coefficients was not possible due to the stability of thiobencarb.

Thiobencarb decreased from 87.1 % at time zero to 57.2 % by 132 days of incubation. The calculated half-life was 250 days. Thiobencarb slowly mineralized in soil without forming significant quantities of non-volatile degradates. (GLN 163-1, MRID 43121201)

(d) Anaerobic Soil Metabolism

Anaerobic soil metabolism studies were not required because the registrant submitted an anaerobic aquatic metabolism (GLN 162-3, MRID 00040925) instead. (GLN 162-2, waived)

(e) Anaerobic Aquatic Metabolism

Thiobencarb is stable under anaerobic aquatic conditions. The registrant-calculated half-life in sediment was 1962 days (5.4 years) (MRID 43252001). In supplemental guideline studies, the registrant-calculated half-lives were 243 days in a sediment from Louisiana and >181 days in a sediment from California (Walker et al., 1988). Supplemental information from open literature reported half-lives of 9-517 days in sediment, and 31 and 82 days in non-sterile and sterile water, respectively. The 9-day half-life in sterile sediment reported in the literature study is not consistent with the other data that show thiobencarb to be more persistent in sterile test conditions than in non-sterile conditions. The guideline (GLN 162-3) is fulfilled. (MRID 43252001)

Anaerobic metabolism of thiobencarb was measured in clay sediment from the Sacramento Valley (Stockton Clay Adobe, 16 % sand, 32 % silt, 52 % clay, 2.0 % OC, pH 6.1) and water from the Sacramento River (pH 7.1, 44 mg/L alkalinity, total hardness of 50.4 mg/L $CaCO_3$). The extrapolated half-life was 5.4 years (1962 days). The percentages of total thiobencarb residues in the sediment were 66.2 % at time zero, 76.6-86.8 % from 7-272 days, and 65 % by 363 days. Residues in water decreased from 20 % at time zero to 3.1-7.5 % from 7-272 days, and then increased to 23.3 % by 363 days. Volatile residues did not exceed 0.9 % of applied. The degradate 4-chloro-benzoic acid reached 14.2 % of the radioactivity in water at 70 days, which was only 0.3 % of the applied. It then decreased to 1.3-12.1 % of the radiocarbon in water (<0.3 % of the applied). No other degradate reached 10 % of the radiocarbon in water. The guideline requirement is fulfilled. (GLN 162-3, MRID 43252001)

In a study that was considered supplemental because of deficient material balance, the registrant-calculated half-lives were >181 and 243 days in clay soil (Biggs, California, 18 % sand, 26 % silt, 56 % clay, 1.13 % OC, pH 4.6, CEC 32.5 meq/100g) and silty clay loam (Crowley, Louisiana, 3 % sand, 69 % silt, 28 % clay, 0.79 % OC, pH 5.8, CEC 14.5 meq/100g)/water systems, respectively. Aqueous residues did not exceed 4.5 % of applied in the study. Non-volatile degradates and

CO_2 did not exceed 3.8 %, indicating thiobencarb partitioned primarily into the sediment. Unextracted residues increased to 42.8 % in the clay soil and 27.8 % in the silty clay loam by 364 days. (GLN 162-3, MRID 00040925)

Walker et al. (1988) determined the first order biotic and abiotic degradation rate constants for 14 pesticides (including thiobencarb) in estuarine water and sediment/water slurry systems (sterile and non-sterile) . The half-lives in non-sterile and sterile sediment ranged from 9-517 days. The half-lives in sterile water and non-sterile water were 31.5 and 82 days, respectively. (Walker et al., 1988)

Chen et al. (1982) created a model aquatic ecosystem and applied ^{14}C-thiobencarb to determine its partitioning in the laboratory environment. It was not possible to calculate a half-life because of limited sampling. By the end of the experiment (23 days), thiobencarb partitioned mostly into sand (23.2 % of applied) and to a lesser ectent into water and biota (2.7 and 0.31 % of applied, respectively) . The authors attributed the low recovery of radioactivity to volatility, photodecomposition, and microbial decomposition. (Chen et al., 1982)

(f) Aerobic Aquatic Metabolism

Thiobencarb was stable to aerobic aquatic metabolism in a clay soil/water system from the rice-growing area of California. The guideline requirement (162-4) is fulfilled. (MRID 42015301)

(2) Mobility

Unaged Mobility (Batch Equilibrium)

Thiobencarb was moderately mobile to immobile in five soils. Freundlich K_{ads} values ranged from 5.4 to 20.1 in the tested soils, and Koc's ranged from 384 to 1435 (see below Table). The unaged portion of the guideline requirement (GLN 163-1) is fulfilled. (MRID 41215313)

Table : Results of aged mobility studies with thiobencarb

Soil Texture (% OC)	Freundlich K_{ads}	Freundlich Koc_{ads}	Freundlich K_{des}	Freundlich Koc_{des}	N (slope values) for adsorption and desorption
Sandy Loam (0.5)	5.4	1084	14.3	2860	0.8, 1.0
Loam (1.9)	7.3	384	21.7	1142	1.1, 1.1
Silty Clay (1.5)	9.3	618	28.8	1920	1.1, 1.1
Clay Loam (1.1)	11.3	1027	46.7	4245	1.2, 1.2
Silt Loam (1.4)	20.1	1435	94.5	6750	1.0, 1.1

Aged Mobility

Based on batch equilibrium experiments, the degradate 4-chlorobenzoic acid was very mobile to moderately mobile in the tested soils with Freundlich K_{ads} of 0.7-3.3 (See below Table). Mobility generally decreased with increasing clay content, increasing organic matter content, and increasing cation exchange capacity. The aged portion of the guideline requirement (GLN 163-1) is fulfilled. (MRID 43150601)

Table : Results of aged mobility studies with thiobencarb

Soil Texture (% OC)	Freundlich K_{ads}	Freundlich Koc_{ads}	Freundlich K_{des}	Freundlich Koc_{des}	N (slope values) for adsorption and desorption
Sandy Loam (0.88)	0.74	84	2.2	250	1.6, 1.6
Loam (0.76)	1.0	130	1.9	250	1.6, 1.5
Silt Loam (0.88)	1.2	140	2.4	280	1.6, 1.6
Clay (2.0)	3.3	160	8.3	420	1.3, 1.2

Laboratory and Field Volatility

Volatility testing was waived (4/29/91) since volatility is not a significant means of dissipation of thiobencarb. (GLNs 163-2 and 163-3, waived, see also GLN 161-4))

(3) Accumulation

Accumulation in Irrigated Crops

Thiobencarb was detected (detection limit of 0.07 ppm) in the tops of table beets grown in plots of clay soil in California that were sprinkler-irrigated five times at 8- to 13-day intervals with water containing thiobencarb (Bolero 8 EC, 85% emulsifiable concentrate) at approximately 200 ppb. Thiobencarb was not detected (detection limit of 0.01 ppm) in either the beet root or in tomato fruits grown under similar conditions. In addition, the potential degradate 4-chlorobenzylmethyl sulfone was not detected in

beet tops or roots, or in tomato fruits. In the 0- to 6-inch depth of the treated soil, parent thiobencarb and the degradate thiobencarb sulfoxide were 0.04-0.13 and $\leq$0.02 ppm, respectively, at all sampling intervals. There was no apparent pattern of accumulation or decline of either parent thiobencarb or the degradate. (GLN 165-3, MRID 43148201)

Bioaccumulation in fish

Thiobencarb residues accumulated in juvenile bluegill sunfish exposed to [^{14}C]thiobencarb at 0.05 mg/L, with maximum bioconcentration factors of 128x, 639x, and 411x for edible (muscle) tissue, nonedible tissue, and whole fish, respectively. The degradates 4-chlorobenzylmethylsulfoxide, thiobencarb sulfoxide, desethylthiobencarb, and 2-hydroxythiobencarb were identified in edible and nonedible tissue. By day 3 of the depuration period, 93-95% of the accumulated [^{14}C]residues were eliminated from the tissues. The guideline requirement (GLN 165-4) is fulfilled. (MRID 42460401)

(4) Field Dissipation

(a) Terrestrial Field Dissipation

The registrant has submitted sufficient information on terrestrial field dissipation (164-1) to do an environmental fate assessment for the 40,000 acres of vegetables in Florida. Considering the small acreage of this use, the aquatic field dissipation study for rice in Louisiana provided adequate information on the fate of thiobencarb under terrestrial conditions, in addition to aquatic conditions. Therefore, terrestrial field dissipation data are reserved for any future terrestrial uses of thiobencarb.

(b) Aquatic Field Dissipation

In two field studies in California where granules were applied into standing water, the half-lives in water were 8.7 days in the guideline study (MRID 43404005) and 4.5 days in the literature study (Ross and Sava, 1986). The soil half-lives determined in the two studies were 153 and 56 days, respectively. The median amounts of thiobencarb in soil were 5.6 and 6.6 times higher than in water, respectively. No leaching was observed below 6 inches of depth. GLN. 164-1, MRID 42003404. The guideline is only partially satisfied since the registrant did not provide storage stability of samples and since the movement of water in the CA guideline study (MRID 43404005) was not described in detail.

Thiobencarb dissipated with an observed half-life of approximately 6 days in silty clay loam soil in Louisiana that had been planted to rice. The plot was flooded at

7 days posttreatment; thiobencarb dissipated from the floodwater with a registrant-calculated half-life of 5.8 days. Thiobencarb was not detected in the soil below 10 centimeters. The degradates 1-(((4-chlorophenyl)methyl)sulfonyl)-N,N-diethylformamide (thiobencarb sulfoxide) and 4-chlorobenzyl-methylsulfone were detected primarily in the upper 5 cm of the soil and in the floodwater. (MRID 42003404)

Thiobencarb (10 G) was applied in one application by air at 4 lbs ai/A to flooded plots of Anita clay loam (28 % sand, 26 % silt, 46 % clay, 2.47 % OC, pH 6.1, CEC of 46). Soil cores were taken to 30 cm (1 foot) of depth throughout the study at 0-551 days after treatment. There was one 8-foot core taken at 153 days, which was divided into segments ranging from 5 cm at the surface to 30 cm at lower depths. Water samples were taken at 0-92 days after treatment. Water samples were also collected from the fallow field replicates from days 15-21 and day 27.

The half-life in soil was 20 days for the 0-92 day (flooded) sampling periods, and was 153 days when all sampling intervals (0-551 days) were considered. The half-life in water was 4.8 days when the 0-33 day sampling intervals were considered. (MRID 43404005)

Ross and Sava (1986) studied two commercial rice fields in the Sacramento Valley of CA. Thiobencarb was applied at 4 lbs ai/A using fixed-wing aircraft into standing water when rice plants had not yet emerged (1-3 leaf growth stage). Water was held at 10.4 inches of depth for 6 days with no inflow or outflow (stagnant water). After 6 days, the field was rapidly drained to 6.8 inches of depth with intermittent inflow and outflow. Water temperatures averaged 28 °C (82 °F) for 30 days. Water, soil, and vegetation samples were collected from four pads within each rice field. The pads were located at the field inlet and outlet and two randomly-chosen points in between. Samples were taken at -1, 0, 2, 4, 8, 16, and 32 days after application near the pads and where the water flow was slower. The dynamics of herbicide dissipation were examined using a split plot analysis or variance (ANOVA). Air, water, soil, and vegetation were analyzed using GC.

Thiobencarb was predominantly distributed between water (34.5 %) and soil (43 %), with less than 1 % associated with air and vegetation. Thiobencarb water concentrations at 0, 2, 4, 6, 8, 16, and 32 days after treatment were 79. 567, 576, 515, 367, 56, and 8 µg/L, respectively. Soil concentrations of thiobencarb were 3250, 2880, 3350, 3860, 2020, 2260, and 2330 µg/kg (ppb), respectively. Thiobencarb air concentrations at 0, 1, 2, and 3 days after treatment were 1.4, 0.9, 0.8 and 0.43 $\mu g/m^3$, respectively. The calculated half-life in air was 2.2 days. The evaporative flux rates were 37, 8, 16, and 6 $ng/cm^2\ h^{-1}$ at 0, 1, 2, and 3 days after treatment, respectively. Thiobencarb vegetative concentrations were 78, 691, 1750, 1360, 1280, 796 and 169 µg/kg (ppb), respectively, leading to a calculated half-life of 8.5 days using natural

logarithm data. Concentrations in water, soil, and vegetation were significantly higher in the holding period than in the postholding period. Water and vegetation concentrations were stable in the holding period and only declined with time during the postholding period. In contrast, soil concentrations did not change during either period. The mass balance (including air, water, soil, and vegetation) increased from 41 % at 0 days after treatment to 67-70 % by 2-6 days after treatment and then decreased to 26-27 % by 16-32 days after treatment.

The guideline requirement (GLN 164-2) is only partially fulfilled. This guideline can fulfilled if the field dissipation study conducted in Louisiana (MRID 42003404) is upgraded by the submittal of more detailed information on the water management used at the study site and the storage stability of the test samples. (GLN 164-2, MRID 41722504, 42003404, 43404005).

(5) Spray Drift (Droplet Size Spectrum/Drift Field Evaluation)

No thiobencarb specific studies were reviewed. Droplet size spectrum (GLN 201-1) and drift field evaluation (GLN 202-1) studies are required for thiobencarb, since the different formulations may be applied by aircraft and it is estimated that there will be detrimental effects to non-target terrestrial and semi-aquatic plants due to drift. However, to satisfy these requirements the registrant, in conjunction with other registrants of other pesticide active ingredients, formed the Spray Drift Task Force (SDTF). The SDTF has completed and submitted to the Agency its series of studies which are intended to characterize spray droplet drift potential due to various factors, including application methods, application equipment, meteorological conditions, crop geometry, and droplet characteristics. During 1996 the Agency plans to evaluate these studies. In the interim, and for this assessment of thiobencarb, the Agency is relying on previously submitted spray drift data and the open literature for off-target drift rates. The estimated drift rates at 100 feet downwind of the treated sites are 1% at the applied spray volume from ground applications and 5% from aerial applications. After review of the new studies the Agency will determine whether a reassessment is warranted of the potential risks of the application of thiobencarb products.

c. Water Resources

(1) Ground Water

The Office of Pesticide Programs (OPP) evaluates the persistence and mobility of each pesticide for ground water concerns. If the data indicate that the parent and/or degradates are persistent and mobile, then a small-scale prospective ground water study may be requested. The basic triggering criteria include: weight of the evidence from laboratory and field dissipation studies indicating that the pesticide has properties and characteristics similar to pesticides that are known to leach or have been detected in

ground water; movement of the parent or degradates 75-90 cm through the soil profile or plow layer in a field dissipation study; reports of detections in ground water from other monitoring studies and information about toxicity. In addition, use patterns, application rates, timing of application, potential acreage treated, depth to ground water, soil types, hydraulic gradient, and climate are also evaluated as part of the triggering criteria.

Persistence, mobility, and detections in ground water are also used to evaluate a chemical to determine whether its use should be restricted for ground water concerns. A pesticide may be recommended as a candidate for restriction if it exceeds one or more criteria for *each* of the three factors (persistence, mobility, and detections).

(a) Persistence and Mobility

Thiobencarb was evaluated for persistence and mobility in relation to its potential to leach to ground water. Below is a summary of that evaluation.

Table : Mobility and Persistence of Thiobencarb Relative to Restricted Use Criteria

Factor		Characteristic	Restricted Use Criteria	Reported Values[a]
Persistence	1	Field dissipation half-life	> 3 weeks	8, 21.9 weeks (56, 153 days)[b]
	2	Lab-derived aerobic soil metabolism half-life	> 3 weeks	3.9 - 8.3 weeks (27 - 58 days)
	3	Hydrolysis half-life	< 10% in 30 days	Stable
	4	Photolysis half-life (Soil)	< 10% in 30 days	50% in 168 days (calculated)
Mobility	5	Soil adsorption: K_d	< or = 5 ml/g	5.4 - 20.1 ml/g
	6	Soil adsorption: K_{oc}	< or = 500 ml/g	384, 618, 1024 - 1435 ml/g
	7	Depth of leaching in field dissipation study	75 cm	15 cm[b]

[a] Shaded area indicates that parameter exceeds trigger.

[b] Because thiobencarb is used almost exclusively on rice, no terrestrial field dissipation studies were submitted by the registrant. Aquatic field dissipation studies were conducted to address this use. The half-lives reported are aquatic field dissipation for soil. Refer to Section C.2.b. of the EFED RED chapter for additional data.

(b) Degradates and Binding

The aerobic metabolism studies found that, after one year, the degradation to carbon dioxide and binding of residues to soil were significant pathways for dissipation of thiobencarb (see Section C.2.b.). Carbon dioxide accounted for 42-77% of the applied and bound residues accounted for 23-42% of the applied. Literature data reported that the thiobencarb in the soil slowly mineralized without forming significant

quantities of non-volatile degradates. This will significantly reduce the amount of thiobencarb available to leach through the soil profile.

(c) Ground Water Detections

EFED has limited monitoring information for thiobencarb in ground water in the United States. The "Pesticides in Ground Water Database" (Hoheisel et al., 1992) reports sampling for thiobencarb in 270 wells in California and 65 wells in Missouri. Two detections of thiobencarb in ground water were reported in Missouri, these were very low (0.2 - 0.3 ppb). A summary of this is presented below.

Table : Mobility and Persistence of Thiobencarb Relative to Restricted Use Criteria

Criterion	Characteristic	Restricted Use Criteria	Reported Detections
Detections	Number of wells per state with detections	25 wells in 4 or more states or	2 wells in 1 state
	Number of counties with detections > 10% of reference point	3 counties at >10% of MCL or HAL	No MCL or HA Established

(d) Restricted Use

Thiobencarb met the persistence and mobility triggers for classification as a restricted use chemical for ground-water concerns, but not the detections triggers. EFED believes that ground water concerns do not warrant use restrictions.

(e) Ground Water Reference Points

There is no MCL established for thiobencarb residues in drinking water. The lifetime Health Advisory for thiobencarb also has not yet been established, but an estimated Health Advisory can be calculated from the Reference Dose. HED has established the RfD of thiobencarb at 0.01 mg/kg/day.

EFED estimated the lifetime HA for thiobencarb to be 70 ppb. This was calculated from the Reference Dose as follows:

Assumed: Adult with body weight of 70 kg consuming 2 L water/day
RfD for thiobencarb = 0.01 mg/kg/day (HED)
RSC = Relative source contribution, assumed to be 20%

$$\text{DWEL} = \frac{(\text{RfD})\,(70\text{ kg})}{(2\text{ L/d})} = \frac{(0.01\text{ mg/kg/day})\times 70\text{ kg}}{(2\text{ L/d})} = 0.35\text{ mg/L}$$

Lifetime HA = DWEL x RSC = 0.35 mg/L x 0.20 = 0.07 mg/L = 70 ug/L (ppb)

(e) Ground Water Concerns

Thiobencarb is slightly persistent in water, generally not very mobile, tends to bind to soil organic matter, and doesn't desorb. EFED has estimated the Lifetime Health Advisory for thiobencarb residues in drinking water to be 70 ppb. Thiobencarb also has low acute mammalian toxicity. Based on the limited data available and very low concentrations found in ground water, there is no indication that thiobencarb concentrations in ground water would exceed the estimated HA of 70 ppb.

The principle use of thiobencarb is rice in the lower Mississippi Valley and the Central Valley of California. Rice fields are usually underlain by a clay layer to restrict water movement through the soil and help contain the water in the flooded field. This clay layer will significantly limit the amount of leaching that occurs in the rice fields.

Although thiobencarb does exceed several of the criteria for restricted use, EFED does *not* consider thiobencarb to be a candidate for restricted use due to ground water concerns. EFED does not consider thiobencarb to be a concern in ground water, nor a human health concern from residues in drinking water that are derived from ground water.

(2) Surface Water

Environmental fate information indicates thiobencarb is non-persistent[1] in the water column (aquatic field dissipation half-lives ranging from approximately 6 to 9 days). It is stable to degradation from abiotic hydrolysis; however, degradation via aqueous photolysis with photosensitizes was shown in the laboratory studies. The vapor pressure and Henry's Law constant indicate thiobencarb will not volatilize readily from surface water environments. Based on the Freundlich adsorption coefficients (K_{ads} range: 5.42-20 ml/g), thiobencarb adsorbs to soil and sediment particles and may be transported on entrained sediment in surface runoff. Partitioning of thiobencarb onto soil or sediment was demonstrated in three aquatic field dissipation studies where thiobencarb concentrations on soil were approximately 5 to 64 times greater than water concentrations. However, the results of field monitoring studies indicate thiobencarb can be transported primarily via dissolution in runoff water if sufficient rainfall occurs immediately following field application. In surface waters, thiobencarb dissipates principally by binding to sediment, and degrading by sensitized aqueous photolysis. There is also some mineralization under aerobic conditions which

[1] Based on the criteria established by McEwen and Stephenson (1979).

occur at the soil-water interface in rice fields. Thiobencarb has the potential to contaminate surface water from releases of rice paddy water which closely follow field application, or from spray drift associated with aerial or ground spray application.

Thiobencarb is not currently regulated under the Safe Drinking Water Act (SDWA); therefore, a Maximum Contaminant Level (MCL) is not established. It is classified as category III for oral acute toxicity. The estimated lifetime Health Advisory level (HA) is 70 μg/L using the Reference Dose of 0.01 mg/kg/day. Public water supply systems are not required to sample and analyze for thiobencarb.

In the EPA Office of Water's STORET database, thiobencarb detections in surface waters were reported for filtered water samples only (detections limits varied from 0.002-0.008 μg/L). Detections of thiobencarb were listed for 8 states: California, Georgia, Maryland, North Carolina, Oregon, Oklahoma, Texas, and Washington.[2] Thirty-nine positive detections were reported for 3,130 samples (approximately 1%) with a maximum concentration of 0.24 μg/L (7/22/92 and 8/26/92; Klamath Falls, OR) and a mean concentration of 0.10 μg/L. Whole (i.e., unfiltered) water samples did not find detectable levels of thiobencarb. Surface water concentrations for the field monitoring studies are several orders of magnitude greater (approximately 100 to 3000 times larger) than the detections reported in the STORET database. The sources of this variation are not known; however, the filtered sample results (0.7 μm filters) in the STORET data suggest very low concentrations of thiobencarb in the aqueous phase of surface water samples. This finding is consistent with the partitioning of thiobencarb onto sediment which would lower the concentrations in the aqueous phase. It is not clear whether the results from the field monitoring studies were determined from filtered or unfiltered water samples. Additional surface water monitoring data are described in Section 3a(2)(b).

Aquatic EEC modeling for rice uses was not conducted because the EFED currently does not have a computer simulation model which will estimate these concentrations. For the lettuce, endive and celery uses, the GENEEC model was used to complete a Tier 1 exposure assessment (Table I). The range of aquatic EECs was 140 μg/L for the 6 lb a.i. application rate and 180 μg/L for the 8 lb a.i. application rate. The initial (peak) EEC varied by a factor of 23 μg/L for each pound increase in thiobencarb. Comparison of the initial EECs with the 21-day and 56-day EECs indicates thiobencarb dissipates in the pond water at an approximate rate of 0.4-0.6 μg/L/day.

---

[2] EFED does not know why thiobencarb was detected in these states since, with the exception of California, registered uses of thiobencarb should not occur within these states.

3. Exposure and Risk Characterization

a. Ecological Exposure and Risk Characterization

(1) Background Information

Risk Quotients and the Levels of Concern

Levels of Concern (LOCs) are criteria used to indicate potential risk to nontarget organisms. Exceeding the criteria indicate that a pesticide, when used as directed, has the potential to cause undesirable effects to nontarget organisms. Two general categories of LOC (acute and chronic) exist for each of the four nontarget faunal groups, and one category (acute) exists for each of two nontarget floral groups. To determine if an LOC has been exceeded, a risk quotient is derived and compared to the LOC. A risk quotient is calculated by dividing an appropriate exposure estimate, e.g. the estimated environmental concentration (EEC), by the appropriate toxicity test effect level. The acute effect levels are:

-- EC_{25} (terrestrial plants)
-- EC_{50} (aquatic plants and invertebrates)
-- LC_{50} (fish and birds)
-- LD_{50} (birds and mammals)
-- EC_{05} or NOEC (endangered plants)

The chronic effect levels are the:

-- NOEC (avian and mammal reproduction studies)
-- NOEC or MATC for aquatic species.

When the RQ exceeds the LOC for a particular category, risk is presumed. Risk presumptions, along with the corresponding LOCs, are tabulated below.

Table A: Risk Quotients and LOCs for Animals

ENDPOINT	RISK QUOTIENT (RQ)	LOC
Birds		
Acute High Risk	EEC/LC_{50} or LD_{50}/sq. ft or LD_{50}/day	0.5
Acute Restricted Use	EEC/LC_{50} or LD_{50}/sq. ft or LD_{50}/day (or LD_{50} < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC_{50} or LD50/sq. ft LD_{50}/day	0.1
Chronic High Risk	EEC/NOEC	1
Chronic Endangered Species	EEC/NOEC	1
Wild Mammals		
Acute High Risk	EEC/LC_{50} or LD50/sq. ft or LD_{50}/day	0.5
Acute Restricted Use	EEC/LC_{50} or LD_{50}/sq. ft or LD_{50}/day (or LD_{50} < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC_{50} or LD50/sq. ft or LD_{50}/day	0.1
Aquatic Animals		
Acute High Risk	EEC/LC_{50} or EC_{50}	0.5
Acute Restricted Use	EEC/LC_{50} or EC_{50}	0.1
Acute Endangered Species	EEC/LC_{50} or EC_{50}	0.05
Chronic High Risk	EEC/MATC or NOEC	1
Chronic Endangered Species	EEC/MATC or NOEC	1

Table B: Risk Quotients and LOCs for Plants

ENDPOINT	RISK QUOTIENT (RQ)	LOC
Terrestrial and Semi-Aquatic Plants		
Acute Plants	EEC/EC_{25}	1
Acute Endangered Species	EEC/EC_{05} or NOEC	1
Aquatic Plants		
Acute Plants	EEC/EC_{50}	1
Acute Endangered Species	EEC/EC_{05} or NOEC	1

At this time, EFED has no procedures for assessing chronic risk to plants, acute or chronic risks to nontarget insects, or chronic risk from granular/bait formulations to mammalian or avian species.

Thiobencarb Use Patterns Addressed in Risk Assessment

Thiobencarb is an herbicide used to control grasses and broadleaved weeds. It is applied to soil or water in rice paddies to kill weeds before they emerge. Being a carbamothioate, its mode of action is inhibition of cell growth.

The majority of thiobencarb use (95%) is to control terrestrial and aquatic weeds in rice production. The maximum label use rate on rice is 4 lb ai/A, and the average rate is approximately 3 lb ai/A. Application may be by aircraft or ground equipment. For rice grown in the Gulf Coast and Mississippi River Valley, thiobencarb is usually applied as a liquid (EC formulation) to nonflooded fields. "Dry-seeded" rice is frequently grown in this area, in which seeds are sowed and grown in dry seed beds for several weeks before flooding. If there is no rainfall, fields are irrigated with a small volume of water (i.e. flushed) to promote seed germination. Some rice in this area is "water-seeded", meaning that seeds are applied to water in flooded fields. In this part of the country, thiobencarb is usually applied to fields before they are flooded. Fields are then flooded for seeding with rice. These floods are normally dropped temporarily after seeding to allow rice seedlings to grow, resulting in a discharge of water. In California, the majority of rice grown is water-seeded with a continuous flood. Unlike the southern region, thiobencarb in California is almost always applied as a granule to water in flooded fields. A small percentage of rice farmers in California use "pin-point flood" culture, in which case thiobencarb may be applied as a liquid to dry-ground before fields are flooded. California state regulations prevent rice farmers from discharging tailwater from rice fields for 4 to 30 days after application.

Additionally, a relatively small amount of thiobencarb is used on lettuce, endive, and celery. Registrations for these uses are restricted to Florida. The maximum label rate is 6 lb ai/A for lettuce and endive and 8 lb ai/A for celery. Application is by boom sprayers.

(2) Exposure and Risk to Nontarget Terrestrial Animals

(a) Birds

Liquid Applications- Acute and Chronic Risk

For thiobencarb products applied as a liquid to soil, risk is assessed by comparing LC_{50} values to estimated residues (i.e. EECs) on dietary food items immediately following application. The table below gives the predicted 0-day maximum and mean residues of thiobencarb that are expected to occur on selected avian or mammalian dietary food items.

Table D: Maximum EECs on Avian and Mammalian Food Items for Uses of Thiobencarb

Use Site	Maximum Application Rate (lbs a.i./A)	Maximum EEC (ppm)			
		Short grass	Long grass	Broadleaf plants and insects	Fruit
Rice	4	960	440	540	60
Lettuce and Endive	6	1440	660	810	90
Celery	8	1920	880	1080	120

In an avian dietary LC_{50} test with the northern bobwhite (Acc. No. 241483), no mortality occurred at the maximum test level, 5620 ppm. Environmental concentrations are predicted to be much less than 5620 ppb. **The acute risk to birds from all uses of thiobencarb is minimal. No acute effects to threatened and endangered species are expected.**

The chronic risk quotients for liquid applications are given below.

Table E: Avian Chronic Risk Quotients (RQs) for Liquid Applications Based on a Mallard Duck NOEC and Maximum EECs

Crop	Maximum Application Rate (lbs a.i./A)	Food Items	Maximum EEC (ppm)	NOEC (ppm)	Chronic RQ (EEC/NOEC)	Number of Days EEC > NOEC
Rice	4	Short grass	960	100	9.6	29
		Long grass	440	100	4.4	19
		Broadleaf plants and insects	540	100	5.4	21
		Fruit	60	100	0.6	0
Lettuce and Endive	6	Short grass	1440	100	14.4	34
		Long grass	660	100	6.6	24
		Broadleaf plants and insects	810	100	8.1	26
		Fruit	90	100	0.9	0
Celery	8	Short grass	1920	100	19.2	37
		Long grass	880	100	8.8	27
		Broadleaf plants and insects	1080	100	10.8	30
		Fruit	120	100	1.2	3

In addition to the magnitude of the RQs, chronic risk can be assessed by estimating the duration when EECs are expected to be high enough to possibly cause

effects in birds. This duration is based on the magnitude of the initial EEC and the rate of dissipation. The dissipation of thiobencarb from foliage was estimated from data collected in a biological field study conducted at Halls Bayou, Texas (Acc. No. 241484). Thiobencarb residues were measured from broadleaf weeds and sedges collected 12 m downwind of the edge of the field on 0, 7, 14, and 21 days after application. The calculated foliage half-lives for broadleaf weeds and sedges were 5.4 and 8.6 days, respectively. These values are consistent with those estimated for other pesticides (Willis and McDowell, 1987). The more protective value of 8.6 days was used in the risk assessment. Assuming a first-order rate of dissipation, EECs are predicted to exceed the mallard NOEC for up to 37 days, depending on the use rate and type of plant (Table E).

Most of the chronic risk quotients exceed the LOC of 1 for use on rice, lettuce, endive, and celery. The use rate would have to be reduced to 0.4 lb/A, one-tenth the current maximum label rate for rice, to reduce all of the chronic RQs to below the LOC. Furthermore, the maximum EECs for all food types except fruit exceed the mallard NOEC for relatively long durations, generally three weeks or more. **These results indicate that all uses of thiobencarb pose a risk of causing chronic effects to birds and may cause chronic adverse effects to threatened and endangered bird species.**

Granular Applications--Acute Risk

A granular formulation is used only when thiobencarb is applied to flooded rice fields. Most of the granules will fall onto the water surface and sink to the bottom. These granules would not be accessible to many birds, although they possibly could be ingested by waterfowl and sandpipers which feed off the bottoms of the flooded fields. A small portion of the granules may fall on levees built around and within rice fields or get caught in emerging rice plants. These granules could be available for birds to consume. Some exposure of granular pesticides to birds is therefore expected, but the overall degree of exposure is probably less than when thiobencarb is applied on dry fields.

Thiobencarb has very low acute toxicity to birds. In an acute single-dose test with the northern bobwhite, a dose of 1938 mg ai/kg Bwt resulted in no mortality or overt signs of toxicity (MRID 42600201). **The EFED expects that the risk of acute effects to birds from exposure to granular thiobencarb is minimal.**

Granular Applications--Chronic Risks

The Agency currently does not have a procedure for assessing the chronic risk posed by granular applications.

(b) Mammals

Acute hazard to small mammals was addressed using the acute oral LD_{50} value for the rat converted to an estimated LC_{50} value for dietary exposure. The estimated LC_{50} was derived using the following formula:

$LC_{50} = LD_{50}$ x body weight (g) / food consumed per day (g)

Acute risk to mammals was assessed by calculating RQs for three representative species: the meadow vole, the field mouse, and the least shrew. Estimated mammalian LC_{50} values for these three species of small mammals are presented below:

Table F: Estimated Small Mammal Dietary Exposure (Based on an LD_{50} = 1080 mg/kg)

Small Mammal	Body Weight (g)	Percent of Weight Eaten Per Day	Food Consumed Per Day (g)	Estimated LC_{50} (ppm)
Meadow vole	46	61 %	28.1	1770
Adult field mouse	13	16 %	2.1	6690
Least shrew	5	110 %	5.5	982

The above table is based on information contained in Principles of Mammalogy by D. E. Davis and F. Golly, published by Reinhold Corporation, 1963.

The risk quotients are calculated by dividing the EECs (i.e. residues) by the estimated LC_{50}'s. The table below shows the risk quotients for peak exposures of thiobencarb.

Table G: Mammalian Acute Risk Quotients

Species and Diet	Use Site	Application Rate (lb ai/A)	Maximum EEC[1] in Food Item (ppm)	Risk Quotient
Meadow vole consuming short grasses	Rice	4	960	0.54
	Lettuce and Endive	6	1440	0.64
	Celery	8	1920	1.09
Adult field mouse consuming seeds	Rice	4	60	<0.1
	Lettuce and Endive	6	90	<0.1
	Celery	8	120	0.02
Least shrew consuming insects	Rice	4	540	0.55
	Lettuce and Endive	6	810	0.82
	Celery	8	1080	1.10

[1]Based on Hoeger and Kenaga (1972) with modifications by Fletcher et al. (1994).

For all use sites, RQs for the meadow vole and the least shrew are greater than 0.5, the LOC for presumption of risk. **This indicates that use of thiobencarb in a liquid formulation on rice, lettuce, endive, and celery poses an acute risk to mammals.**

Liquid Applications--Chronic Risk

RQs were calculated for chronic effects of thiobencarb to mammals. The number of days that the EEC will exceed the chronic mammalian NOEC was also estimated using the method described earlier for chronic effects to birds.

Table H: Mammalian Chronic Risk Quotients (RQs) for Liquid Applications Based on a Rat NOEC and Maximum EECs

Crop	Maximum Application Rate (lbs a.i./A)	Food Items	Maximum EEC (ppm)	NOEC (ppm)	Chronic RQ (EEC/NOEC)	Number of Days EEC > NOEC
Rice	4	Short grass	960	20	48	48
		Long grass	440	20	22	38
		Broadleaf plants and insects	540	20	27	41
		Fruit	60	20	3	14
Lettuce and Endive	6	Short grass	1440	20	72	53
		Long grass	660	20	33	43
		Broadleaf plants and insects	810	20	41	46
		Fruit	90	20	5	19
Celery	8	Short grass	1920	20	96	57
		Long grass	880	20	44	47
		Broadleaf plants and insects	1080	20	54	50
		Fruit	120	20	6	22

All of the chronic RQ for mammals exceed the LOC of 1 for use on rice, lettuce, endive, and celery. Except for exposure on fruit, all RQs are very high (22 or greater). Also, EECs on wildlife foods are expected to persist at levels greater than the mammalian NOEC for many days. **These results clearly indicate that all uses of thiobencarb pose a risk of causing chronic effects to mammals and may cause chronic adverse effects to threatened and endangered species of mammals.**

The specific responses of the tested organisms in the study yielding the 20 ppm NOEL were reduced weight gain and food consumption, food efficiency, and increased blood urea nitrogen at 100 ppm, the next highest test level above 20 ppm. In another study, no reproductive effects were observed at dietary concentrations as high as 2000 ppm. Thus the chronic risk to mammals relate to growth and physiology. Available data do not suggest high risk of reproductive impairment to mammals at any application level.

Granular--Acute Risks

A granular formulation is used only when thiobencarb is applied to flooded rice fields. Most of the granules will fall onto the water surface and sink to the bottom. These granules probably would not be accessible to most mammals. The active ingredient of these granules would disperse into the water, and mammals could then be

exposed by drinking this water. But, considering the large degree of dilution that would take place and the low mammalian toxicity of thiobencarb, this would pose minimal risk to mammals. The primary route of exposure to mammals from granular thiobencarb probably would be from ingestion of granules that fall on the levees within and around the edges of rice fields. Mammals do not intentionally ingest grit, but may inadvertently ingest granules that adhere to food items.

Thiobencarb has low acute toxicity to mammals. In an acute single-dose test with the rat, the LD_{50} was 1080 mg ai/kg BWt (MRID 42130701). **The EFED expects that the risk of acute effects to mammals from exposure to granular thiobencarb is minimal.**

Granular Applications--Chronic

The Agency currently does not have a procedure for assessing the chronic risk posed by granular applications.

(b) Insects

Use of thiobencarb on rice, lettuce, endive, and celery is not expected to cause significant exposure to honey bees. **The risk to honey bees is therefore minimal.**

(2) Exposure and Risk to Nontarget Aquatic Animals

(a) Expected Aquatic Concentrations

The EFED calculated EEC's using the Generic Expected Environmental Concentration Program (GENEEC) to estimate exposure for use of thiobencarb on celery, lettuce, and endive. The resultant EEC's, termed GEEC's, were used for assessing acute and chronic risks to aquatic organisms. Acute risk assessments were performed using 0-day GEEC values for a single application. Chronic risk assessments were performed using the 21-day average GEECs for invertebrates and 56-day average GEECs for fish.

The GENEEC program uses a few basic chemical parameters and pesticide label application information to provide a rough estimate of the expected environmental concentrations. The model calculates the concentration of pesticide in a hypothetical 1-ha, 2-m deep pond taking into account adsorption to soil and sediment, soil incorporation, degradation in soil before runoff to a water body, and degradation within the water body. The model also accounts for direct deposition of spray drift into the water body. The rate of spray drift deposition is assumed to be 1% and 5% of the application rate for ground and aerial applications, respectively.

The following values were selected for input into the GEEC Program:

Soil Organic Carbon Partitioning Coefficient:	384
Soil Aerobic Metabolic Half-life:	58 days
Aquatic Aerobic Metabolic Half-life:	stable
Hydrolysis Half-life:	stable
Photolysis Half-life (at pH 7):	12 days
Water Solubility	27.5 ppm

To be protective, the values were selected to maximize calculated exposure estimates.

GEECs based on runoff from a single application on a 10-hectare field to a 1-hectare x 2-meter deep water body are given below.

Table I: Generic Estimated Environmental Concentrations (GEECs) for Aquatic Exposure

Use Site	Application Method	Maximum Application Rate (lbs a.i./A)	Number of Applications	Initial (Peak) EEC (ppb)	21-day EEC (ppb)	56-day EEC (ppb)
Celery (FL)	Ground, unincorporated	8	1	186	173	157
Lettuce and Endive (FL)	Ground, unincorporated	6	1	140	130	118

(b) Measured Aquatic Concentrations

The Agency used aquatic concentrations measured in field studies and monitoring projects to estimate the exposure of aquatic organisms from use of thiobencarb on rice. Measured water concentrations were available from two biological field studies performed in Texas (MRID 92182086 and 92182089, Acc. No. 241484), two environmental fate field studies performed in Louisiana and California (MRID 42003404 and 43404005), monitoring data from California (MacCoy et al., 1995, MRID 43359700), and studies reported in the open literature (Ross and Sava, 1986; Watanabe et al., 1982). While data from all of these sources were reviewed, the risk assessment for dry-seeded rice in the Southeast was based primarily on data from the two biological field studies and the risk assessment for water-seeded rice in California was based on data from the monitoring programs. These sources were most relevant because they provided measured concentrations of thiobencarb residues in off-site bodies of water, rather than in the rice fields themselves.

Dry-Seeded Rice in the Southeast

The two biological field studies provide examples of residues that can result in slow-moving bodies of water that receive drainage from surrounding dry-seeded rice

fields where thiobencarb is applied. The Agency considers both Halls Bayou and the canal studied near Matagorda, Texas to be representative of small brackish waterways that occur in the rice-growing region of the Gulf Coast. These field studies will also be used in the risk assessment to represent freshwater habitats of the Mississippi Valley since no study specific to this region is available. The 1978 Stream Evaluation Map for the state of Texas categorizes the section of Hall's Bayou where the field study was located as Category I, a "highest-valued fishery resource". The drainage ditch in the Matagorda study was a 120-130 ft wide permanently flooded canal that is also considered to be a biologically significant habitat. Biological sampling in both studies found these waterways are abundant and diverse in fish and invertebrate life.

The greatest exposure from dry-seeded rice culture probably results from the first flush or heavy rainfall that occurs after thiobencarb has been applied. Pesticide residues in the soil are dissolved in this water as it passes over the field and then discharged into an aquatic habitat. As demonstrated in the Hall's Bayou field study, unplanned flushes resulting from rainfall usually result in greater residues in off-site aquatic habitats than do planned flushes. Planned flushes usually occur one to two weeks after application, allowing much of the pesticide to bind to the soil. Furthermore, since rice farmers normally try to use the minimal amount of water required to adequately wet the soil, little water is normally discharged in a planned flush. On the other hand, rainfall may occur soon after the pesticide is applied, and if it is intense, may result in a large volume of water being discharged from the field.

The biological field study that collected water samples from Halls Bayou, Texas [see section C.1.b(7)], provides an example of a near worst-case scenario. Halls Bayou is a long narrow waterway that meanders through rice-growing areas in the Texas coastal plane. During the field study, a very heavy rainfall event (3.23 inches in 24 hours) happened to occurred on the same day that thiobencarb was applied, resulting in unplanned release of water from rice fields. The measured concentrations of thiobencarb in samples taken this day were as great as 8900 ppb in the field outflow and 690 ppb at the point where a ditch draining from the fields discharged into Hall's Bayou. Heavy rainfall of this magnitude is common in the Gulf Coast region, often occurring several times in the same location during the spring. However, the Agency believes that these thiobencarb concentrations represent near the upper bound of concentrations that are likely to occur in aquatic habitats for the following reasons: 1) rainfall occurred on the same day that pesticide is applied; 2) in the area of the field study, Halls Bayou was surrounded by rice fields; and 3) Halls Bayou is a relatively small waterway with little flow or tidal flushing, resulting in little dilution of water draining from rice fields.

The aquatic residues measured at other times during the Halls Bayou study, as well as those measured in a drainage ditch in the biological field study conducted near Matagorda, Texas [see section C.1.b(7)], provide examples of situations that would

result in exposures that are moderately high, but more typical. Other than the concentrations measured after the intense rainfall event of the 19th of April, the greatest thiobencarb concentrations were measured in samples taken on 7 April following several planned flushes in the region during the previous week. Samples taken that day at two sites in the Bayou near the point of discharge of water draining from the rice fields were 83 and 64 ppb. Measured residues were 40 and 48 ppb in two samples taken on 6 April, and 33 ppb in a sample taken on 8 April. Residues remained at a concentration of 10 ppb or greater through April 12, when sampling was ceased.

Aquatic residues measured in the study near Matagorda study were less than those measured at Halls Bayou. The greatest measured residues (average of two replicate samples) was 20 ppb in 1983 and 21 ppb in 1984. Residues were commonly between 1 and 15 ppb for a few days following applications of thiobencarb and/or flushing of fields.

Figure 1 provides an example of the change in aquatic residues over time. This data is from the 1983 sampling in the drainage ditch at the Matagorda study site. Thiobencarb was applied at a rate of 4 lb/A to a 100-A field that bordered the ditch. Prior to this application, thiobencarb had not been applied to fields in the region for 33 days. A peak concentration of 20 ppb was recorded on the day of application at station 2. Unfortunately, no water samples were taken 1, 2, and 3 days after treatment (DAT). By 5 DAT, residues at station 2 had dramatically decreased, but peaks in residues were occurring at the downstream stations 3 and 4. Residues at the point of discharge into the Colorado River peaked on the following day. This data shows that the highest residues measured tend to occur in peaks that last for only a day or two at any particular location, after which the high residues move further downstream.

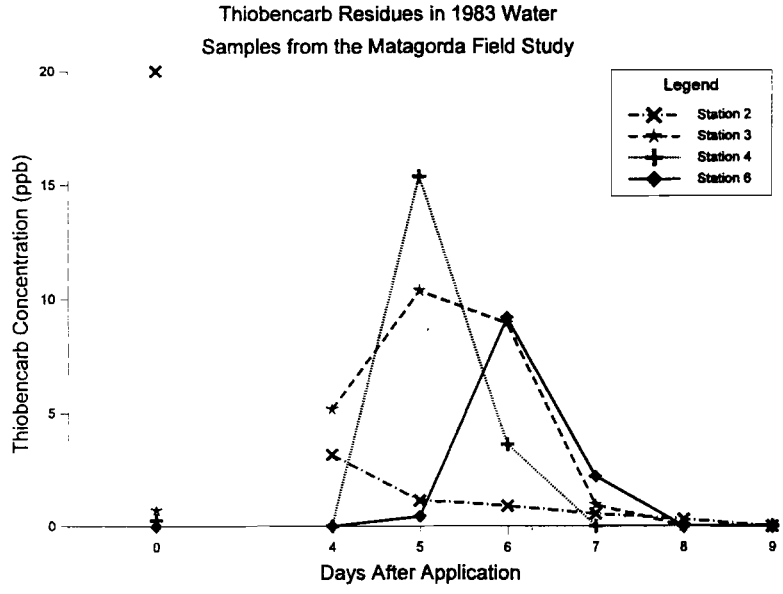


Figure 1. Thiobencarb concentrations in water sampled from a drainage canal (stations2-4) and in the Colorado River at a point downstream of the confluence with the drainage canal (station 6). Thiobencarb was applied on day 0 at a rate of 4 lb/A on 100 A of a field adjacent to the drainage canal. No residues were reported on 1, 2, and 3 days after treatment.

Water-seeded rice in the Southeast

The monitoring data discussed does not represent aquatic EECs resulting from water-seeded rice grown in the Mississippi Valley and Gulf Coast. Also, no monitoring data were available for aquatic concentrations resulting from water-seeded rice in these regions. Unlike in California, thiobencarb is primarily applied to water-seeded rice in these regions by applying a liquid to soil before the fields are flooded. This use is similar to dry-seeded rice in terms of expected environmental exposure. Therefore, the concentrations measured for dry-seeded rice in the biological field studies was also used to represent exposures from water-seeded rice in the southeastern regions.

57

Water-seeded Rice in California

The Agency used surface water monitoring data to approximate the concentration of thiobencarb likely to be found in water in areas of California where water-seeded rice is grown. Two recent sources of data on thiobencarb were available. One was a US Geological Survey Open-file Report on the monitoring of dissolved pesticide concentrations in the San Joaquin River and Sacramento River in 1991 through 1993 (MacCoy et al., 1995). The other source of data was monitoring of thiobencarb concentrations in waterways that drain rice growing areas in the Sacramento River Valley. This data was submitted to the EPA by Valent U.S.A. Corporation under the 6(a)(2) provisions of FIFRA.

Approximately three years of routine water monitoring of the San Joaquin River at Vernalis, California and of the Sacramento River at Sacramento, California (MacCoy et al., 1995) found that thiobencarb concentrations were always low, below 0.05 ppb. For most of the sampling period, thiobencarb residues were not detected or were below 0.025 ppb. The only exception was a 10-12 period during May and June of 1993 when measured residues generally were greater than 0.1 ppb. Peak residues were 0.53 ppb in the San Juaquin River and 0.70 ppb in the Sacramento River.

Monitoring conducted by the California Environmental Protection Agency and submitted by the Valent U.S.A. Company found that levels of thiobencarb in some of the waterways draining into the Sacramento River were occasionally greater than in the river itself. Concentrations were always below 1 ppb in the Butte Slough, but frequently greater than 1 ppb in the Colusa Basin Drain (Table J). A peak concentration of 37 ppb was recorded in the Colusa Basin Drain.

Table J. Thiobencarb concentrations measured in waterways flowing into the Sacramento River, California (nd = not detected)

Date Sampled	Water Sampling Locations			
	CBD1	CBD5	SS1	BS1
5-3-94	--	not detected	--	0.10
5-5-94	--	0.18	--	0.09
5-9-94	--	0.49	--	0.06
5-12-94	--	0.42	--	0.07
5-16-94	0.212	37.4	0.34	0.11
5-19-94	0.103	0.768	0.40	0.09
5-22-94	3.34	1.04	0.26	0.08
5-26-94	0.8	0.992	0.19	0.11
5-30-94	0.46	0.66	0.12	0.18
6-2-94	0.28	4	nd	0.12

Date Sampled	Water Sampling Locations			
	CBD1	CBD5	SS1	BS1
6-6-94	0.58	0.5	0.10	nd
6-9-94	15.8	0.38	0.08	0.10
6-13-94	6.2	0.34	0.08	nd
6-16-94	4.74	0.284	0.10	0.08
6-20-94	--	0.42	--	nd
6-23-94	--	0.11	--	0.53
6-27-94	--	0.51	--	nd
6-30-94	--	0.63	--	nd
7-4-94	--	0.28	--	0.12
7-7-94	--	0.21	--	0.18

(a) Freshwater Fish

The risk of acute effects to freshwater fish from the use of thiobencarb on rice is uncertain. The maximum residue measured in Halls Bayou when heavy rainfall occurred on the day of application was 690 ppb. This exceeded the lowest LC_{50} determined for freshwater fish, 560 ppb for the bluegill sunfish, indicating a high risk to freshwater fish. This conclusion is supported by a fish killed observed in the Matagorda study which was attributable to thiobencarb exposure. Several other supplemental studies, however, found that the LC_{50} for various freshwater fish is greater, in the range of 1.1 to 2.8 ppm (Table **[# for table titled "Freshwater Fish Toxicity Findings"]**). Based on these supplemental data, the acute risk of thiobencarb would be minimum to low. Furthermore, other aquatic residues measured in the Halls Bayou, as well as all of those measured in the Matagorda study, were well below even the lowest LC_{50} of 560 ppb. Therefore, **the acute risk of thiobencarb to fish is uncertain. If there is an acute risk, it apparently would be limited to high exposure situations in which heavy rainfall occurs soon after application discharges contaminated water into a small water body where it would not be greatly diluted.**

Measured aquatic residues from monitoring in California were no greater than 37 ppb. As this is well below levels that are expected to cause acute effects, **use of thiobencarb on rice in California is expected to pose minimal acute risk to freshwater fish. No acute effects on threatened and endangered species are expected.**

For other uses of thiobencarb, acute risk quotients for freshwater fish are given below.

Table K: Risk Quotients (RQs) for Freshwater Fish Based on a Bluegill Sunfish LC_{50}

Use Site	Use Rate (LB/A)	LC_{50} (ppb)	EEC Initial (ppb)	Acute RQ (EEC/LC_{50})
Celery (FL)	8	560	186	0.33
Lettuce and endive (FL)	6	560	140	0.25

These results indicate that use of thiobencarb on vegetables in Florida, at the maximum label rate, does not pose a high acute risk to freshwater fish. They do not exceed the high-risk LOC of 0.5. The risk quotients are greater than 0.1, however, indicating that restricted use may be necessary to mitigate this risk. Also, these uses of thiobencarb may harm endangered species of freshwater fish.

Chronic risk quotients could not be calculated because data is lacking on the chronic toxicity of thiobencarb to freshwater fish. The best approximation of the chronic risk to freshwater fish is given by the chronic risk assessment for marine and estuarine fish [Section 3a(2)(c)].

(b) Freshwater Invertebrates

The maximum residue measured in Halls Bayou after a heavy rainfall was 690 ppb, which was 6.9 times greater than the acute EC_{50} for *Daphnia magna*, 100 ppb. Residues measured in Halls Bayou on another day that was not associated with a heavy rainfall event were 83 and 64 ppb. Risk quotients calculated based on these values are 0.83 and 0.64, respectively, which are greater than the LOC for presumption of high risk, 0.5. Aquatic residues measured in the Matagorda study were less and do not indicate a high risk to acute aquatic invertebrates. **These results indicate that the risk to freshwater invertebrates posed by use of thiobencarb on rice in the southeastern regions range from low to high, depending on the weather and local conditions. High risk probably is limited to aquatic habitats near the discharge of tailwater and during times when heavy rainfall occurs soon after thiobencarb is applied.**

Measured aquatic residues from monitoring in California were no greater than 37 ppb. An acute risk quotient based on this value is 0.37, which is less than the LOC of 0.5. **Therefore, use of thiobencarb on rice in California is expected to pose minimal acute risk to freshwater invertebrates. Possible acute effects on threatened and endangered species, however, cannot be ruled out.**

Based on a chronic toxicity study with the *Daphnia magna*, thiobencarb is predicted to cause chronic effects in freshwater invertebrates when concentrations remain near or above 1 to 2 ppb for an extended period of days. Aquatic residues measured during the two biological field studies indicate that this condition will

commonly occur in areas where thiobencarb is applied. For example, of the 24 samples analyzed from Area II of Halls Bayou between 24 March and 30 April, all but two had thiobencarb concentrations greater than 2 ppb. Even in the Matagorda study, where residues were generally lower, measured residues equal or exceeded 1 ppb for 9 consecutive days in 1983 and 7 consecutive days in 1984. During periods of peak exposure, residues were 12 to 406 times greater than the MATC for *Daphnia magna*. **These findings indicate that use of thiobencarb on rice in the southeast regions poses a definite high risk of causing chronic effects to freshwater invertebrates. Adverse effects to freshwater invertebrates are expected to occur frequently.**

Use of thiobencarb on water-seeded rice in California is predicted to pose less of a chronic risk to aquatic invertebrates than in the southern rice-growing regions. Water sampling from the Sacramento River and San Juaquin River show that thiobencarb concentrations never exceeded 1 ppb, the NOEC for *Daphnia magna*. The majority of readings were less than 0.05 ppb. In contrast, concentrations in smaller waterways occasionally approached or exceeded the NOEC of 1 ppb, as well as the MATC of 1.7 ppb (Table J). The data indicates that the exposure is very pulsed, but several pulses may occur successively to create a chronic exposure. **The risk assessment indicates that the use of thiobencarb in California poses a chronic risk to freshwater invertebrates living in the smaller waterways, but minimal risk to those in the larger rivers.**

For uses other than rice, acute and chronic risk quotients for freshwater invertebrates are given below.

Table L: Risk Quotients (RQs) for Freshwater Invertebrates Based on a Daphnid EC_{50} and a Daphnid MATC

Use Site	LC_{50} (ppb)	MATC (ppb)	EEC Initial (ppb)	EEC 21-Day (ppb)	Acute RQ (EEC/LC_{50})	Chronic RQ (EEC/MATC)
Celery (FL)	100	1.7	186	173	1.86	101.76
Lettuce and endive (FL)	100	1.7	140	130	1.40	76.47

Acute and chronic risk quotients exceed the LOC for high risk. **These results indicate that use of thiobencarb on vegetables in Florida, at the maximum label rate, poses an risk to freshwater invertebrates due to both acute and chronic effects. Because the chronic risk quotients are extremely high, chronic effects on invertebrates are expected to be severe.**

(c) Estuarine and Marine Animals

Based on aquatic residues measured in the biological field study at Halls Bayou, use of thiobencarb on dry-seeded rice can result in concentrations of thiobencarb of 690

ppb. This represents a near worst-case scenario when heavy rainfall occurs immediately after thiobencarb is applied. Concentrations this great would exceed the acute LC_{50} for the mysid (150 ppb) and eastern oyster (320 ppb), and would be close to the LC_{50} for the sheepshead minnow (660 ppb). They would also approach or exceed the LC_{50} values that Borthwick *et al.* (1985) reported for the Atlantic silverside, tidewater silverside, and California grunion. **These findings indicate that the use of thiobencarb on rice in the southeast regions poses a high acute risk to estuarine fish, crustaceans (including shrimp), and mollusks at times of high exposure resulting from heavy rainfall occurring soon after application.**

Other than the one measurement of 690 ppb, however, concentrations in Halls Bayou were not greater than 83 ppb. Furthermore, two years of sampling in the biological field study near Matagorda found that residues reached a maximum of 21 ppb. Using the exposure value of 83 ppb, the risk quotients for fish, mollusks, and shrimp are 0.13, 0.26, and 0.55, respectively. **This indicates that, under conditions other than those described above, the acute risk is minimal to fish and mollusks. The RQ still exceeds the LOC, however, for high risk for shrimp and other crustaceans.**

The measured concentration of 690 ppb, representing a high exposure associated with heavy rainfall, indicates a high chronic risk to fish and crustaceans. In addition, a high chronic risk to crustaceans exists even for exposures measured not associated with heavy rainfall. The MATC from chronic studies with crustaceans found MATCs that ranged from 4.5 to 35 ppb. Water concentrations measured near Matagorda exceed the lower bound of this range, and those measured at Halls Bayou exceed even the upper bound of this range. The lower end of the range was sometimes exceeded for several consecutive days in both of the biological field studies (for example, 8 days in Area II of Halls Bayou, 4 days at Station 1 on the canal in the Matagorda study in 1984). **It is therefore clear that use of thiobencarb on rice in the southeastern regions poses a high chronic risk to shrimp and other aquatic crustaceans.**

Chronic risk to fish is less certain. A test concentration of 150 ppb caused reduced growth in the sheepshead minnow. High exposures of thiobencarb, such as the 690 ppb measured at Halls Bayou, will exceed this level, but probably for only short periods of time. Monitoring data show that peaks in aquatic residues usually last for only a day or two (Fig. 1). Under typical conditions, maximum exposures would be considerably less than 150 ppb. For water-seeded rice, thiobencarb concentrations are expected to exceed 150 ppb in the field, but it is not known if they would exceed 150 ppb in off-site aquatic habitats. **The available data thus indicate that thiobencarb has the potential to cause chronic effects on estuarine fish in the southern growing region. However, the level of this risk is highly uncertain because a chronic NOEC has not been determined.**

In California, the only estuarine habitats that are likely to be exposed to significant residues of thiobencarb are bays near San Francisco that receive water from the Sacramento River and San Juaquin River. All of the rice-growing region in California is drained by these two rivers. Stringent regulation requiring the retainment of floodwater from rice fields have greatly reduced concentrations of thiobencarb occurring in the Sacramento-San Joaquin Delta since 1985 (Bailey, 1993). Monitoring data show that between 1991 and 1993 thiobencarb concentrations in these rivers are always less than 1 ppb, and are usually below 0.1 ppb (MacCoy et al., 1995). This level of exposure would not be expected to cause any significant acute or chronic effects to any estuarine fish or invertebrate. Because concentrations in the bays would be no greater than concentrations in the rivers that feed them, **the risk assessment indicates that use of thiobencarb on rice in California poses minimal acute and chronic risk to marine/estuarine fish and invertebrates (including shrimp and mollusks).**

For uses other than rice, the acute and chronic risk quotients for three estuarine and marine organisms are given below.

Table M: Risk Quotients (RQs) for Freshwater Fish Based on a Daphnid EC_{50} and a Daphnid MATC

Use Site	Test organism	LC_{50} (ppb)	MATC (ppb)	EEC Initial (ppb)	21- or 56-Day [1] (ppb)	Acute RQ (EEC/LC_{50})	Chronic RQ (EEC/MATC)
Celery (FL)	Sheepshead minnow	660	<150	186	157	0.28	>1.04
	Eastern oyster	320	ND	186	173	0.58	--
	Mysid	150	4.5 - 35	186	173	1.24	4.9 - 38
Lettuce and endive (FL)	Sheepshead minnow	660	<150	140	118	0.21	>0.79
	Eastern oyster	320	ND	140	130	0.44	--
	Mysid	150	4.5 - 35	140	130	0.93	3.7 - 29

[1] The 21-day EEC is used for assessing risk to aquatic invertebrates whereas the 56-day EEC is used for assessing risk to fish.

These results indicate that use of thiobencarb on vegetables in Florida, at the maximum label rate, poses a high acute risk to marine/estuarine oysters, shrimp, and other aquatic invertebrates. The RQ for chronic effects to shrimp and other marine/estuarine invertebrates is imprecise because only supplemental data are available. Nevertheless, based on the range of findings from the four available supplemental studies, it is clear that the RQ for these organisms is well above the LOC of 1, signifying a high chronic risk.

The acute RQ for marine estuarine fish in Florida is less than the LOC of 0.5, indicating the acute risk is not high, but it is greater than the LOC of 0.1, indicating that restricted use may be applied. This risk quotient also indicated that threatened and endangered species of fish may be adversely affected.

Definitive chronic RQs could not be determined for marine/estuarine fish because the only available chronic fish study failed to determine an NOEC. However, since adverse effects were observed at a test concentration of 150 ppb, it is certain that both the NOEC and MATC would have been less than this value if lower concentrations were tested. The chronic fish RQ may therefore be expressed as a "greater than" value. At the rate of 8 lb/A, the maximum use rate for celery, the RQ is greater than 1.0, signifying a high chronic risk. At the rate of 6 lb/A, the maximum use rate for lettuce and endive, the RQ is greater than 0.79. Since this value is not much less than the LOC of 1, use at this rate may also pose a high chronic risk to fish. **These findings thus indicate that the use of thiobencarb on vegetables in Florida may pose a high chronic risk to fish. An additional fish life-cycle study (GLN 72-5) is needed to confirm this risk.**

(3) **Exposure and Risk to Nontarget Plants**

(a) **Terrestrial and Semi-aquatic**

The EFED does separate risk assessments for two categories of nontarget plants, terrestrial and semi-aquatic. Non-target terrestrial plants inhabit non-aquatic areas which are generally well drained. Non-target semi-aquatic plants inhabit low-lying areas that are usually wet, although they may be dry during certain times of the year. Both the terrestrial and semi-aquatic plants are exposed to pesticides from runoff, drift, and volatilization. They differ, however, in that terrestrial plants are assumed to be subjected to sheet runoff, whereas semi-aquatic plants are assumed to be subjected to channelized runoff.

The EFED assumes that runoff will expose nontarget plants to a fixed percentage of the application rate. This percentage is estimated based on the water solubility of the active ingredient:

Water Solubility	% Runoff Assumed
< 10 ppm	1%
10 - 100 ppm	2%
> 100 ppm	5%

Since the water solubility of thiobencarb at 20°C is 27.5 ppm, the percent runoff is assumed to be 2%. For non-target terrestrial plants, EFED assumes a scenario in which plants are exposed from sheet runoff. A treated site of 1 acre is assumed to

drain into an adjacent area of 1 acre where terrestrial plants may be impacted. In the scenario used for non-target semi-aquatic plants, exposure from runoff is assumed to be from channelized runoff. A treated site of 10 acres is assumed to drain into a distant low-lying area of 1 acre where semi-aquatic plants may be impacted.

Exposure from spray drift was also assumed to be a fixed percentage of the application rate. Spray drift exposure is assumed to be 1% and 5% of the application rate for ground and aerial applications, respectively.

Formulae for Calculating EECs

Terrestrial plants inhabiting areas adjacent to treatment sites

Unincorporated ground application:

Runoff Loading = maximum application rate (lbs ai/acre) x runoff value
Drift Loading = maximum application rate x 0.01
Total Loading = runoff (lb ai/acre) + drift (lb ai/acre)

Aerial applications:

Runoff Loading = maximum application rate (lbs ai/acre) x 0.6 (assumed application efficiency) x runoff value
Drift = maximum application rate (lbs ai/acre) x 0.05
Total Loading = runoff (lb ai/acre) + drift (lb ai/acre)

Semi-aquatic plants inhabiting wet, low-lying areas

Unincorporated ground application:

Runoff Loading = maximum application rate (lbs ai/acre) x runoff value x 10 acres
Drift Loading = maximum application rate x 0.01
Total Loading = runoff (lb ai/acre) + drift (lb ai/acre)

Aerial applications:

Runoff = maximum application rate (lbs ai/acre) x 0.6 (60% application efficiency assumed) x runoff value x 10 acres
Drift = maximum application rate (lbs ai/acre) x 0.05
Total Loading = runoff (lb ai/acre) + drift (lb ai/acre)

Use of thiobencarb on rice is not expected to result in significant exposure to nontarget terrestrial and semiaquatic plants from runoff. Rice fields are always bordered by a dike or temporary berm which would prevent runoff from leaving the field. These structures do have a gate or opening for the release of water from the field, but this water is normally channeled into a stream or river. Outflow from rice fields will therefore not normally enter dry-land and wetland habitats where terrestrial and semiaquatic plants occur, respectively.

Nontarget plants also may be exposed from spray drift. The EFED calculated risk quotients by dividing the EECs by the vegetative vigor EC_{25} for the most sensitive

of the test species. Spray drift, and thus exposure to nontarget plants, will be negligible when thiobencarb is applied as a granule. The Agency assumes that spray drift from liquid (EC) formulations of thiobencarb results in EECs that are 5% and 1% of the application rate for aerial and ground applications, respectively. When applied at the maximum label rate of 4 lb/A, the EECs for nontarget plants are thus 0.2 lb/A for aerial applications and 0.04 lb/A for ground applications. The EC_{25} for vegetative vigor of the most sensitive test species, ryegrass, is 0.073 lb/A. The risk quotients are 2.7 for drift from aerial applications and 0.55 for drift from ground applications. **These results indicate that spray drift from aerial liquid application of thiobencarb to rice poses a high risk to nontarget plants. Risk to nontarget plants is minimal from all ground applications and aerial applications of granules to rice.**

For uses other than rice, exposure to nontarget terrestrial and semiaquatic plants has a runoff component as well as a spray drift component. Only ground applications are permitted for these uses. Estimated environmental concentrations for terrestrial and semi-aquatic plants are given below.

Table N: Estimated Environmental Concentrations (EECs) For Terrestrial and Semi-Aquatic Plants

Use Site	Use Rate (lb ai/A)	Runoff Value	Runoff Loading		Spray Drift Loading (lb ai/A)	Total Loading	
			Sheet Runoff (lb ai/A)	Channelized Runoff (lb ai/A)		Adjacent Area (Sheet Runoff +Drift)	Semi-aquatic Area (Channel Run-off + Drift)
Celery (FL)	8	0.02	0.16	1.60	0.08	0.24	1.68
Lettuce and endive (FL)	6	0.02	0.12	1.20	0.06	0.18	1.26

Risk to emerging seedlings was assessed by comparing the EECs listed above with levels in the seedling emergence study that caused 25% mortality most sensitive test species. (The toxicity level for plants is normally referred to as the EC_{25}, but since in this case the effect being considered is mortality, it is also the LC_{25}). The EC_{25} for the most sensitive species, ryegrass, was 0.019 lb ai/A, respectively. RQs for nonrice uses are given below.

Table O: Exposure and Risk Quotients for Emerging Seedlings of Terrestrial and Semi-aquatic Plants

Use site	Use Rate (Lb/A)	Type of Plants	Exposure Scenario	EEC (lb ai/A)	Risk Quotients
Celery (FL)	8	Terrestrial	Sheet runoff +spray drift (1%)	0.24	13
		Semi-aquatic	Channelized runoff + spray drift (1%)	1.7	88
Lettuce and endive (FL)	6	Terrestrial	Sheet runoff +spray drift (1%)	0.18	9.5
		Semi-aquatic	Channelized runoff + spray drift (1%)	1.3	66

The RQs are between 9.5 and 88. These are very high, especially when considering that the effect being considered is mortality to 25% of the population rather than just a 25% decrease in growth. **Clearly, the use of thiobencarb on celery, lettuce, and endive will likely kill emerging seedlings of sensitive species of terrestrial and semiaquatic plants.**

Use of thiobencarb on nonrice crops may also expose mature plants by way of spray drift. The EFED calculated risk quotients by dividing the EECs by the vegetative vigor EC_{25} for the most sensitive of the test species. The vegetative vigor EC_{25} for the most sensitive species, ryegrass, is 0.073 lb ai/A. Only ground application is permitted for these uses, for which the Agency assumes that the EEC for offsite areas is 1% of the application rate. For application on celery at the maximum label rate of 8 lb/A, the EECs is 0.08 lb ai/A and the RQ is 1.1. For application on lettuce and endive at the maximum label rate of 6 lb/A, the EEC is 0.06 lb ai/A and the RQ is 0.82. The RQs for lettuce and endive does not exceed the LOC of 1 for presuming risk. Although the RQ for use on celery slightly exceeds the LOC, the magnitude of the RQ is low compared to those calculated previously for emerging seedlings. **The risk assessment indicates that use of thiobencarb on celery, lettuce, and endive in Florida poses a high risk to nontarget terrestrial and semiaquatic plants, primarily through exposure from runoff and drift to emerging seedlings. The risk posed by exposure to vegetation by spray drift is comparatively low.**

(b) Aquatic Plants

Exposure to nontarget aquatic plants may occur through runoff and spray drift from adjacent treated sites. A risk assessment for aquatic vascular plants was performed using duckweed (*Lemna gibba*) as a surrogate species. A risk assessment for nonvascular aquatic plants was performed using green algae (*Kirchneria subcapitata*), which was the most sensitive nonvascular test species. Runoff and drift exposure to aquatic plants was based on actual measurements form water samples for rice uses and GEECs estimated by the GENEEC program [see section 3.a(2)] for

64

Florida vegetable uses. For the latter, risk quotients were determined by dividing the day-0 GEEC in water by the plant EC_{50}.

The concentrations of thiobencarb measured in aquatic habitats in the two biological field studies were many times greater than the EC_{50} for green algae (17 ppb). The maximum residue measured in Halls Bayou after a heavy rainfall was 690 ppb, and residues measured in Halls Bayou at other times that were not associated with a heavy rainfall event were as high as 83 ppb. This suggests that the risk quotient for green algae is in the range of 5 to 41. The field study done near Matagorda found thiobencarb concentrations as high as 21 ppb, which yields a risk quotient of 1.2. **All of these results lead to the conclusion that use of thiobencarb on rice in the southeast regions poses a high risk of harming algae in aquatic habitats.**

Use of thiobencarb on water-seeded rice in California is predicted to pose less of a chronic risk to aquatic plants than in the southern rice-growing regions. Water sampling from the Sacramento River and San Juaquin River show that thiobencarb concentrations never exceeded 1 ppb. Thiobencarb concentrations in these rivers are not expected to approach levels toxic to algae. In contrast, concentrations measured in smaller waterways that feed into the Sacramento River occasionally approached or exceeded the algae EEC of 17 ppb (Table B). **These results indicate that the use of thiobencarb in California poses some risk of affecting algae in the smaller waterways, but minimal risk to algae in the larger rivers.**

The EC_{50} for duckweed is 770 ppb. This indicates that the toxicity of thiobencarb to vascular aquatic plants is low relative to the aquatic EECs for rice. However, the Agency believes that the phytotoxicity test with duckweed poorly represents the toxicity of thiobencarb to many aquatic vascular plants. The seedling emergence studies indicate that grasses are highly sensitive to thiobencarb. Duckweed is not a good surrogate for aquatic grasses and sedges. Duckweed is a dicot with primitive vascular structure, whereas aquatic grasses and sedges are monocots with advanced vascular structure. Furthermore, the primary phytotoxic effect of thiobencarb is inhibiting shoot growth of immature plants. The aquatic plant test with duckweed does not address toxicity through this mode of action. The Agency was unable to perform a reliable risk assessment for the effects on emerging vascular aquatic plants. However, **since thiobencarb is used to control the growth of aquatic weeds in rice fields, the Agency assumes that thiobencarb residues discharged into aquatic habitats poses a risk of killing emerging seedlings of vascular aquatic plants that are sensitive to thiobencarb. The risk appears to be greatest to aquatic grasses. Risk to mature aquatic vascular plants is predicted to be minimal.**

For other uses of thiobencarb, risk quotients for aquatic plants are given below.

Table P: Risk Quotients (RQs) for Aquatic Plants Based on a the EC_{50} of Green Algae (*Selenastrum capricornutum*).

Use Site	Use Rate (LB/A)	Test Species	EC_{50} (ppb)	EEC (ppb)	RQ (EEC/EC50)
Celery (FL)	8	Green algae	17	186	10.9
Lettuce and endive (FL)	6	Green algae	17	140	8.2

These results indicate that use of thiobencarb on vegetables in Florida at the maximum label rate poses a high risk to nonvascular aquatic plants. As with use on rice, the Agency assumes that thiobencarb residues that may reach aquatic habitats by drift and runoff pose a risk of killing emerging seedlings of vascular aquatic plants that are sensitive to thiobencarb.

(4) Endangered Species

The above risk assessment indicates that use of thiobencarb on rice may harm threatened and endangered species (TES) of birds, mammals, fish, and aquatic invertebrates (including crustaceans and mollusks). The greatest risk is from chronic effects, although some risk of acute effects exists for all of these animals except birds. Use of thiobencarb on rice also may harm TES of plants. All types of applications may harm aquatic plants, whereas only aerial applications of liquid formulations are expected to harm terrestrial and semiaquatic plants when thiobencarb is used according to label directions.

Use of thiobencarb on lettuce, endive, and celery in Florida may harm all types of threatened or endangered species (birds, mammals, fish, aquatic invertebrates, and all types of plants).

In 1988, the USFWS determined that use of thiobencarb on rice in Arkansas may jeopardize the fat pocket pearly mussel (*Potamilus capax*). The current label for Bolero 8EC contains use prohibitions to protect this species. These use prohibitions apply to the Arkansas counties of Mississippi, Poinsett, Cross, St. Francis and Lee. In 1987, the USFWS determined that, because thiobencarb is not as toxic to the apple snail as to other aquatic invertebrates, it is not expected to jeopardize the Everglades kite.

The Endangered Species Protection Program is expected to become final in the future. Limitations in the use of thiobencarb will be required to protect endangered and threatened species, but these limitations have not been defined and may be formulation specific. EPA anticipates that a consultation with the Fish and Wildlife Service will be conducted in accordance with the species-based priority approach described in the Program. After completion of consultation, registrants will be informed if any required label modifications are necessary. Such modifications would

most likely consist of the generic label statement referring pesticide users to use limitations contained in county Bulletins.

4. Risk Characterization

a. Extent of Use

Over 95% of the use of thiobencarb is on rice. The Biological and Economical Assessment Division estimates that approximately 1,190,000 lb of thiobencarb active ingredient are applied on rice annually. Use on rice is divided into three general areas: the Gulf Coast (Texas and Louisiana), the Mississippi River Valley (Arkansas, Mississippi, Louisiana, and Missouri) and the Sacramento and San Juaquin River Valleys in California. A small amount of rice is also grown in Palm Beach and Hendry Counties, Florida.

A much smaller use of thiobencarb is on celery, lettuce, and endive in Florida. The estimated annual use of thiobencarb on these crops is approximately 30,000 lb ai. The majority of these crops are grown in Palm Beach County.

b. Summary of Risk Assessment

Thiobencarb is exceptional as an herbicide in that it poses a risk not only to nontarget plants (as do most herbicides) but also substantial risk to virtually all aquatic and terrestrial wildlife. The ecological risks of the various uses are summarized below.

- Use of liquid formulations pose some acute risk to mammals. The acute risk to birds is minimal.

- Use of liquid formulations pose a high **chronic** risk to birds and mammals. The chronic risk from granular formulations could not be assessed, but it is assumed to be comparable to that of liquid formulations.

- Use of thiobencarb on rice in the southeast US poses a high risk of chronic effects to freshwater and estuarine aquatic invertebrates, including shrimp and mollusks. There is also likely a high risk of chronic effects to fish, but additional data are needed to confirm this. This use of thiobencarb also poses a high risk of acute effects to fish and aquatic invertebrates in certain high-exposure situations.

- Use of thiobencarb on rice in California poses a risk of causing chronic effects to aquatic organisms in the smaller drains and waterways, but not in the larger rivers. Its use poses minimal risk of acute effects to fish and aquatic

invertebrates. Minimal risk of both acute and chronic effects is expected for all estuarine organisms in California.

O Spray drift from aerial application of liquid thiobencarb on rice poses a high risk to nontarget terrestrial and semiaquatic plants. Drift of granular thiobencarb and spraying of liquid thiobencarb applied with ground equipment pose minimal risk to these plants.

O All uses of thiobencarb on rice may pose a risk of killing emerging seedlings of aquatic plants, especially aquatic grasses. Use of thiobencarb on rice may harm aquatic algae in the southeast US and in smaller drains and waterways in California.

O Use of thiobencarb on celery, lettuce, and endive in Florida poses a high risk of causing chronic effects to fish, freshwater invertebrates, and estuarine invertebrates, including shrimp. Additionally, this use poses a high risk of causing acute effects to freshwater and estuarine invertebrates, including oysters and shrimp.

O Use of thiobencarb on celery, lettuce, and endive in Florida poses a high risk to terrestrial plants, semiaquatic plants, and algae. It may also pose a risk to emerging seedlings of vascular aquatic plants.

c. Impacts to Water Resources

(1) Ground Water

Although thiobencarb does exceed several of the criteria for the proposed ground water restricted use rule, the EFED does not consider thiobencarb to be a candidate for restricted use due to ground water concerns. The Agency does not consider use of thiobencarb to be a concern in ground water, nor a human health concern from residues in drinking water that are derived from ground water.

(2) Surface Water

Detections of thiobencarb in water samples were relatively rare in the STORET database of the Office of Water, EPA. Thirty-nine positive detections were reported for 3,130 samples, with a maximum concentration of 0.24 µg/L and a mean concentration of 0.10 µg/L. Surface water concentrations measured in biological field studies were several orders of magnitude greater than this. The field study measurements were taken in surface water that was immediately adjacent to rice fields and were taken soon after thiobencarb was applied. This suggests that high levels of

contamination of thiobencarb in surface water is limited to local areas and for brief time periods.

Unlike the filtered sample results reported in STORET, results reported in the biological field studies may have been from unfiltered samples. As thiobencarb tends to partition more into sediment than water, the presence of suspended sediment in the water samples may have contributed to higher concentrations being reported in the field studies than in the STORET database.

Aquatic EEC modeling for lettuce, endive and celery uses estimated relatively high levels of contamination in surface water. The range of aquatic EECs was 140 µg/L for the 6 lb a.i. application rate and 180 µg/L for the 8 lb a.i. application rate. Thiobencarb is expected to dissipate in pond water at an approximate rate of 0.4-0.6 µg/L/day.

d. Environmental Fate and Risk Characterization

(1) Rice in Southeastern United States

(a) Terrestrial Ecosystems

The main risk from thiobencarb to terrestrial vertebrates (birds, mammals, reptiles, and terrestrial stages of amphibians[3]) is from reproductive and chronic pathological effects. The risk assessment for mammals determined that there is also a risk of acute mortality from all uses of thiobencarb. However, maximum acute RQs for mammals range from less than approximately 0.5 for use on rice to slightly greater than 1 for use on celery. These RQs are much smaller than those for risk of chronic effects to these organisms. In general, the impact to terrestrial ecosystems from acute effects is expected to be of little significance, whereas the impact from chronic effects is considered to be of greater significance.

Use of thiobencarb in the southeast is expected to harm terrestrial vertebrates by causing chronic physiological effects and, in the case of birds, impairing reproduction. The levels that cause chronically toxic effects in both birds and mammals were quite low for a pesticide that is used at high rates (4 to 8 lb ai/A). Furthermore, thiobencarb does not degrade rapidly in the terrestrial environment. The combination of these factors result in EECs remaining at levels that may cause chronic effects for several weeks (Tables B and C). While reproductive and other sublethal effects may result from short-term exposures (one week or less), there is higher certainty that these

[3] No data were available for reptiles or amphibians; therefore, risk to these organisms is inferred from the assessment of risk to birds and mammals.

longer-term exposures will cause these effects. Also, the longer exposure in the environment allows greater opportunity for more organisms to be exposed.

The Biological and Economic Analysis Division (BEAD) estimates the typical use rate of thiobencarb on rice is 3 lb ai/A. Compared to the maximum label rate, use at this rate would decrease exposure levels, and thus the risk quotients, by 25%. Chronic risk quotients for birds and mammals would still be great enough to indicate a high chronic risk.

The timing of application of thiobencarb on rice in the southeast region is from March through June. This corresponds with the breeding season of birds and mammals. Avian reproduction studies have shown that thiobencarb may decrease the number of eggs laid or chicks hatched at dietary concentrations that are similar to environmental concentrations expected in some wildlife food. It thus appears likely reproduction could be impaired in birds that feed in rice fields that have been sprayed with thiobencarb.

For the reasons stated above, the chronic risk to terrestrial organisms is characterized as "high". It is not characterized as "very high" because thiobencarb is only moderately persistent in terrestrial environments and its bioaccumulation is only moderate. Also, except for flooded fields in Louisiana, the use of rice fields by wildlife is not expected to be great during the spring in the Southeast (Gusey and Maturgo, 1973).

Another threat to terrestrial ecosystems in the southeast region is the potential harm to nontarget plants. In this area, thiobencarb is usually applied in a liquid EC formulation which may be sprayed from either aerial or ground equipment. Spray drift from aerial applications are predicted to pose a high risk to some nontarget terrestrial and semiaquatic plants. This may degrade the quality of habitat close to rice fields. This risk may be minimized by applying thiobencarb with ground equipment.

(b) Aquatic Ecosystems

Acute Risk to Fish and Invertebrates

Rice is grown along the Gulf coasts of Texas, Mississippi, and Alabama, often in areas extending many miles inland, as well as in Palm Beach and Hendry counties in Florida. Data from the U.S. National Climatological Data Center (USNCDC) indicates that rainfall in this area is typically around 60 inches per year and that storms of three inches or more occur about once per month. The rice farmer cannot always

retain this volume of water on the paddy[4]. Therefore farmers might apply thiobencarb one day and be forced to release it through the drain gate the next due to unforeseen heavy rains.

Discharges from rice fields following heavy rain events are expected to result in several hundred parts per billion of thiobencarb for short durations in some small estuaries and streams. Monitoring data is available (Section C.1.b.7) showing that these discharges can raise water concentrations in biologically productive estuaries to levels exceeding the LC_{50}'s for fish and aquatic invertebrates. In general, the EFED would expect fish kills and invertebrate kills due to acute exposure to be localized and to be confined to bodies of water near rice fields that have little flow or tidal flushing.[5] During the Matagorda study, there was a fish kill involving menhaden in such an area. The flesh residues of thiobencarb in these fish indicate that thiobencarb may have caused the kill. However, since other pesticides were being used in the area, it is not certain that thiobencarb was the sole cause. The Agency knows of no other fish kills that have been linked to thiobencarb. There is no evidence to suggest that acute risk to fish is a major, widespread problem.

The acute toxicity of thiobencarb to aquatic invertebrates is about the same as that for fish. Some acute mortality of crustaceans[6] and oyster larvae may occur in localized areas near rice fields where high levels of contamination may occur after heavy rainfall. The toxicity to other invertebrates such as corals and jellyfishes (phylum: coelenterata), rotifers (phylum: rotifera; protozoan like organisms which are abundant in freshwater) has not been determined.

Rice is also grown in the Mississippi River Valley. Rainfall data from Little Rock, Arkansas, which is near that state's rice growing area, indicate that the rain may also be heavy in this area; however, the rainfall patterns are somewhat more predictable than in the Gulf area. Because unpredictable spring thunderstorms are less numerous in this region than on the Gulf Coast (Dr. Robert Rohli, personal

---

[4] The rice plant is particularly sensitive to flooding when the stem is long and thin soon after germination. At that time the farmer would try to maintain the water level between 4 to 8 inches. (Personal comm., Dr. Steve Linscombe, LSU).

[5] The rate of flushing refers to how quickly the action of tide and freshwater inputs will purify the estuary. In the Gulf Coast, the difference between high and low tides is only about two feet, which is quite small compared to California or the Northeastern Coast.

[6] Subphylum crustacea, which is comprised of such common animals as shrimps, amphipods(scuds), and copepods, is the most numerous of the marine planktonic animals.

communications, LSU), acute risk to aquatic life resulting from heavy rainfall events would be less here than in the Gulf Coast area.

Chronic Risk to Fish and Invertebrates

Exposure to thiobencarb poses extremely high chronic risk to aquatic organisms, especially for estuarine and freshwater crustaceans in the Gulf Coast region. As mentioned above, heavy rains may result in thiobencarb concentrations in aquatic habitats which greatly exceed chronic toxicity levels of crustacea. Monitoring data from Halls Bayou found concentrations in water at the point of inflow from ricefield drainage of several hundred ppb. This far exceeds the EC_{05} for chronic effects[7] of around 10 ppb for the mysid, and the chronic MATC for the opossum shrimp of 4.5 ppb. High levels are expected to persist long enough in some areas to cause chronic effects. Clearly, the chronic risk to shrimp and other crustaceans is very high and there is potential for high impact on these populations (See Risk to Economically Important Organisms, below). There are also many other types of invertebrates that are important components of the estuarine ecosystem, such as shellfish (phylum: mollusca), corals and jellyfishes (phylum: coelenterata), and rotifers (phylum: rotifera). The chronic toxicity of thiobencarb has not been tested in these species, but it quite possible that thiobencarb would negatively affect their reproduction as it does to crustaceans.

Many species of estuarine crustaceans and other invertebrates are potentially vulnerable to the chronic toxicity of thiobencarb. For example, there are over 100 species of shrimp alone in the Gulf. These creatures would presumably be very vulnerable when they are in estuaries and bayous surrounded by rice fields. For reasons not fully explained, young shrimp mass in the estuaries and streams of the Gulf Coast in the Spring. This is the time when thiobencarb is being applied (see below). Also at great risk are many other crustacean species which are year-round residents in estuaries, including mysids, young blue crabs, many grass shrimp (*Palaemonetes* sp), amphipods (scuds), and isopods (saltwater species related to the garden "sow bug"). These invertebrates serve an important ecological role because they form a fundamental component of the food web. They are important forage for young fish which use estuaries as feeding grounds. Fish whose food web would thus be at stake include drum (sciaenidae; such as redfish and croaker), and flounder such as the Southern flounder.

---

[7] The EC_{05} for chronic effects is the concentration that, based on effects observed in laboratory tests, is predicted to cause a 5% reduction in the reproductive parameters in mysid. This level was estimated using nonlinear regression.

No measured residues from freshwater habitats are available, but they would be expected to be even higher and will dissipate more slowly than in estuaries. This is because freshwater habitats in the southeastern rice-growing region are typically stagnant and lack the tidal flush that is found in estuaries. Reproduction of the waterflea, *Daphnia magna*, is adversely effected at only 3 ppb, making it more sensitive than shrimp and mysids. It is thus clear that thiobencarb can also cause serious harm to freshwater ecosystems.

Risk to Economically Important Organisms

Pink shrimp (*Penaeus duroarum*), brown shrimp (*Penaeus aztecus*), and white shrimp (*Penaeus setiferous*) make up the bulk of the commercial shrimp harvest in the United States. (These and other species in the family Penaeidae are commonly referred to as "penaeids".) The largest harvests are of the brown shrimp. In total, hundreds of millions of tons of shrimp are taken by U.S. ships in the Gulf of Mexico. Overall the shrimp industry is worth billions of dollars to the economy of this country[8].

The natural history of the three commercial shrimp species puts them into a position to receive maximal concentrations of thiobencarb. They breed offshore with each of the females shedding thousands of demersal (sinking) eggs. After hatching, the shrimp larvae and postlarval stages are planktonic. The postlarvae utilize multiple stimuli, including diminished salinity and variations in light, to position themselves in currents so as to be carried into estuaries. In the estuaries they metamorphose to become benthic (bottom dwelling) juvenile shrimp. Some young shrimp are particularly at risk because they migrate for miles up streams that feed the estuaries, even into freshwater[9]. Given that these streams would often be surrounded by rice farms, there is a great hazard to these young shrimp.

Rice growers typically apply thiobencarb beginning in April and ending around June. The young sensitive stages of the commercial shrimp may be exposed to release of thiobencarb in tailwaters, particularly around June, when the arrival of the planktonic larvae begins in the estuaries of the Gulf. The exposure of young commercial shrimp would probably continue beyond June as thiobencarb is considered to be at least moderately persistent in some conditions. In habitats with high turbidity or deep water, the lack of penetration of light could make the rate of photolysis considerably slower than was measured in the laboratory. In these environments, thiobencarb might remain associated with sediments and organic matter on the bottom

---

[8] Economic information provided by Mr. Larry Simpson Director of the Gulf States Marine Fisheries Commission, Ocean Springs, MS.

[9] Information provided by Dr. T. Minello, National Marine Fisheries Service, Galveston, TX.

for several weeks. Being that the juvenile shrimp are benthic, they would be exposed to these contaminated sediments.

The case regarding chronic toxicity to penaeid shrimp is considered strong. However, there is some uncertainty in that the exposures observed in the field are of shorter duration than those in chronic laboratory tests. Even the shortest chronic marine crustacean tests are 28 days long. Monitoring data from all site (other than the flooded paddies themselves) do not show continuous aquatic residues in the range of the mysid LC_{05} (approximately 9 ppb) for a duration this long. On the other hand, it is impossible to know whether the full 28 days are required for adverse effects to occur. Therefore, it is prudent to assume exposure to shrimp and other crustaceans represent a high risk of chronic effects.

Risk to Aquatic Plants

The risk of thiobencarb to aquatic plants is uncertain. Although highly toxic to nontarget plants, thiobencarb appears to act mainly through preventing seed germination and/or early seedling growth. The reproduction of some aquatic plants, especially annuals that reproduce mainly through seeds, may be harmed. This may cause some damage to vegetation growing along the edge of waterways where thiobencarb is discharged.

Thiobencarb is quite toxic to some algae including the very important green algae. There is a high risk of thiobencarb causing some effects, but our current algae toxicity studies cannot be used to judge whether the effects would have permanent impacts on algae populations.

(2) Rice in California

(a) Terrestrial Ecosystems

In the California rice-growing region, thiobencarb is applied mainly in granular form to flooded rice fields. This use of granular thiobencarb is not expected to pose a significant acute risk to birds and mammals. Because of the relatively low toxicity to mammals, the mass of granules required to equal an LD50 substantially reduces the likelihood of significant acute risk to mammals. For example, based on the rat oral LD_{50} of 1080 mg ai/kg, a 100-g mammal has a 50% probability of being killed if it ingests approximately 110 mg of active ingredient in one day. Since thiobencarb granules contain 10% active ingredient, this is equivalent to ingesting 1.1 g of granules in one day. This is much more than a mammal of that size would be expected to ingest incidentally while foraging. Furthermore, most of the granular product would land in standing water and thus would not be available to mammals foraging on land. There is also some use of liquid thiobencarb in California for rice grown with pin-point flood

culture. The acute risk from this use would be similar to that for the southeastern region, that is, there would be an acute risk to mammals but not to birds.

All uses of thiobencarb in California pose a high risk of causing reproductive and chronic physiological effects in terrestrial vertebrates. The characterization of chronic risk from the use of liquid thiobencarb in California is identical to that described above for the Southeast. For use of granular thiobencarb on flooded rice fields, a quantitative assessment of chronic risk could not be performed; however, the EFED considers that exposure of terrestrial vertebrates to granular thiobencarb would be comparable to that of liquid (EC) formulations. Exposure to granular thiobencarb may occur through many routes. The numerous waterfowl and wading bird species that use flooded rice fields in California[10] may ingest granules while foraging for food on the bottom of the pond. Birds, mammals, reptiles, and amphibians that live in the water would also be exposed to thiobencarb dissolved in the water through dermal absorption and by drinking. Furthermore, many terrestrial vertebrates would be exposed to granules that would fall on the ground and vegetation on the levees and around the edge of the field. The Agency therefore characterizes the chronic risk of the use of granular thiobencarb as high, similar to that for use of liquid thiobencarb.

The predominance of the use of the granular formulation in California reduces the risk of harming nontarget terrestrial and semiaquatic plants. Granules generally will fall rapidly from the air without drifting to off-site habitats. Also, as discussed in the risk assessment, the presence of levees around rice fields precludes exposure from runoff into terrestrial habitat. The Agency therefore assumes minimal exposure, and hence minimal risk, to nontarget terrestrial and semiaquatic plants from the use of granular thiobencarb in California. Aerial application of liquid thiobencarb on rice with pin-point flooding is predicted to pose a high risk to these plants; however, this is currently a minor type of use in California.

(b) Aquatic Ecosystems

The state of California has vast acreage of rice in the Sacramento River Basin and some acreage in the San Juaquin River Basin. The State has imposed mandatory holding periods before treated water from farms can be discharged. Holding periods are practical in California because rainfall is quite low and emergency discharges of flood water are generally unnecessary. Monitoring of California waterways indicate

---

[10] Waterfowl species that breed in the California rice-growing region include the mallard, wood duck, cinnamon teal, northern shoveler, gadwall, redhead, ruddy duck, pied-billed grebe and eared grebe. Breeding wading birds include the great egret, snowy egret, green-backed heron, black-crowned night heron, Virginia rail, sora rail, common moorhen, American coot, black-necked stilt, and American avocet.

that water concentrations of thiobencarb rarely reach toxic levels in agricultural drains and never approach toxic levels in the Sacramento and San Juaquin Rivers. Therefore, the Agency concludes that risk to aquatic habitats in California is limited to these agricultural drains in areas with intensive rice production.

(3) Vegetables in Florida

(a) Terrestrial Ecosystems

Thiobencarb is registered for use on celery, lettuce, and endive in Florida. The maximum use rate for these crops is 50-100% greater than that for rice. The risk posed to terrestrial and aquatic organisms is likewise greater. Although these uses are limited in area, the risks they pose to local terrestrial and aquatic ecosystems are extremely high.

Use of thiobencarb on lettuce, celery, and endive poses a risk of causing acute effects to mammals. This risk is somewhat more significant for these crops than for rice. The risk is highest for use on celery, for which the maximum EEC on food items exceeds the estimated rat LC_{50}. Nevertheless, since the RQs are not very large (about 1 or less), this risk is characterized as low to moderate.

In contrast, the risk of reproductive and chronic effects to terrestrial vertebrates is very high. On lettuce, chronic RQs are as high as 14 for birds and 72 for mammals. RQs are even greater for celery, as high as 19 for birds and 57 for mammals. Because thiobencarb is moderately persistent in the terrestrial environment, the high risk from a single application is predicted to persist for one to two months (Tables E and H). The long duration of this exposure increases the certainty that chronic effects will occur, and also provides a greater opportunity for more organisms to be exposed.

Birds, mammals, and reptiles will likely be exposed as they feed in and around these fields. The greatest exposure would likely be to resident ducks and geese and herbivorous small mammals. Because thiobencarb is applied during the spring, these animals would be exposed during the time of breeding. Therefore, serious impairment of reproduction may occur.

For the above reasons, the Agency characterizes the chronic risk to terrestrial vertebrates from use of thiobencarb on celery, lettuce, and endive as very high.

Use of thiobencarb on celery, lettuce, and endive is expected to result in little exposure to nontarget plants from spray drift because aerial application is not allowed on these crops. Nevertheless, the risk assessment indicates that spray drift from ground applications of thiobencarb on celery at 8 lb ai/A poses a risk of harming the

vegetative vigor of nontarget plants. As the RQ was very close to 1, this risk is considered to be of minor importance.

The primary mode of action of thiobencarb in controlling weeds is killing weeds before they emerge. Not surprisingly, then, thiobencarb poses a high risk to emerging seedlings of nontarget plants. Unlike use on rice, use of thiobencarb on vegetable crops in Florida may contaminate soil in off-site terrestrial habitats through runoff. Seedling emergence phytotoxicity studies have shown that some plants, especially grasses, are highly sensitive to thiobencarb at the seedling stage. The primary endpoint effected appears to be mortality of the plant rather than just reduction in growth. Risk quotients based on the EC_{25} for mortality range from 9.5 (terrestrial plants; lettuce and endive) to 88 (semiaquatic plants; celery). Furthermore, the EECs are 5 to 44 times greater than the level predicted to kill 50% of seedlings (i.e. the LC_{50}) of sensitive plants. These results indicate that thiobencarb will kill most or all of the emerging seedlings of sensitive plants exposed to levels equivalent to the EEC.

The exposure to nontarget terrestrial and semiaquatic plants is predicted to occur more from runoff than from spray drift. The exposure from runoff may be overestimated because thiobencarb has a high potential to bind to soil over time. The model used in the risk assessment does not take this soil binding into account. If rainfall occurs within a day or two after application, then exposure from runoff would be great and the high risk predicted by the risk quotients probably would be accurate. If rainfall does not occur for several days, however, then much of the chemical would be bound to the soil at the site of application and would not be transported by runoff. The EFED still believes that a high risk to these plants exists because the RQs are quite high and because heavy rain is frequent and unpredictable in Florida.

The ecological impact of killing emerging seedlings of nontarget plants is largely unknown. It would likely to reduce the number of some sensitive plants, especially annual grasses and herbs. This may alter the composition of the plant community, which may cause unpredictable effects on the ecosystem.

(b) Aquatic Ecosystems

Thiobencarb is used on lettuce, endive, celery and rice in Florida. The total acreage of these crops in Florida is probably less than 40,000 acres (1992 Census of Agriculture). Runoff to surface water will likely cause aquatic concentrations that greatly exceed the Levels of Concern for crustaceans and perhaps fish. Given the very small number of acres on which this pesticide is applied in Florida, risk to aquatic organisms should be quite localized; however, the impact to aquatic habitats within these local areas is likely to be severe.

Most of the use of thiobencarb in Florida is concentrated in Palm Beach and Hendry Counties. These counties lie on the northern edge of The Everglades. Water draining from agricultural fields treated with thiobencarb is likely contributing to the degradation of water quality of northern sections of this very important habitat, including the Loxahatchee National Wildlife Refuge in Palm Beach County.

(3) **Threatened and endangered species**

Protecting threatened and endangered species from thiobencarb will be unusually difficult. Adverse effects are possible for every type of plant and animal. Probably the greatest threat from thiobencarb is to aquatic organisms in freshwater and estuarine habitats near areas with extensive rice production, or near large celery, lettuce and endive farms in Florida. Thiobencarb can clearly cause direct detrimental effects to aquatic organisms, especially small invertebrates. Additionally, thiobencarb may reduce the abundance of phytoplankton and zooplankton which form the base of aquatic food webs. This may cause additional indirect effects to animals at higher trophic levels. It is therefore imperative that thiobencarb be prevented from contaminating critical habitats of threatened and endangered aquatic species. Finally, extreme care should be taken to prevent contamination of the habitat of threatened and endangered plants that occur in areas of Florida where celery, lettuce, or endive is grown.

REFERENCES

Bailey, H. C. 1993. Acute and chronic toxicity of the rice herbicides thiobencarb and molinate to opossum shrimp (*Neomysis mercedis*). Marine Environ. Res. 36:197-215.

Bruce, R. D. and D. J. Versteeg. 1992. A statistical procedure for modeling continuous toxicity data. Environ. Toxicol. Chem. 11:1485-1494.

Borthwick, P. W., J. M. Patrick, Jr. and D. P. Middaugh. 1985. Comparative acute sensitivities of early life stages of atherinid fishes to chlorpyrifos and thiobencarb. Arch. Environ. Contam. Toxicol. 14:??-??

Borthwick, P. W. and G. E. Walsh. 1981. Initial toxicological assessment of Ambush, Bolero, Bux, Dursban, Fentrifanil, Larvin and Pydrin: Static acute toxicity tests with selected estuarine algae, invertebrates, and fish. Publ. No. EPA-600/4-81-076. U.S. Environmental Protection Agency, Washington, DC.

Fletcher, J.S., J.E. Nellessen, and T.G. Pfleeger. 1994. Literature review and evaluation of the EPA food-chain (Kenaga) nomogram, an instrument for estimating pesticide residues on plants. Environ. Toxicol. Chem. 13:1383-1391.

Gusey, W. F. and Z. D. Maturgo. 1973. Wildlife utilization of croplands. Environmental Affairs, Shell Oil Company, Houston, TX.

Kenaga, E.E. 1973. Factors to be considered in the evaluation of the toxicity of pesticides to birds in their environment. Environmental Quality and Safety. 2:166-181.

MacCoy, D., K. L. Crepeau, and K. M. Kuivila 1995. Dissolved pesticide data for the San Joaquin River at Vernalis and the Sacramento River at Sacramento, California, 1991-94. U.S. Geological Survey Open-File Report 95-110, Sacramento, CA..

McEwen, F.L. and G.R. Stephenson. 1979. The use and significance of pesticides in the environment. John Wiley and Sons, Inc., New York. 282 pp.

McKenney, C. L., Jr. 1985. Associations between physiological alterations and population changes in an estuarine mysid during chronic exposure to a pesticide. pp. 397-418. *In* Marine pollution and physiology: Recent advances. F. J. Vernberg, F. P. Thurberg, A. Calabrese, and W. Vernberg (eds.). University of South Carolina Press, Columbia, SC.

Ross, L. J. and R. J. Sava. 1986. Fate of thiobencarb and molinate in rice fields. J. Environ. Qual. 15:220-225.

Smith, G. J. 1993. Toxicology & Pesticide Use in relation to wildlife: Organophosphorus & Carbamate compounds. C. K. Smoley, Boca Raton, FL.

Watanabe, S., S. Watanabe and I. Kazutoshi. 1983. Investigation on the contamination of freshwater fish with herbicides (CNP, chlomethoxynil, benthiocarb and molinate). J. Pesticide Sci. 8:47-53.

Willis, G. H. and L. L. McDowell. 1987. Pesticide persistence on foliage. pp. 23-73. *In* Reviews of Environmental Contamination and Toxicology, Vol. 100. Springer-Verlag, New York.

DATA EVALUATION RECORD 1

CHEM 108401 Thiobencarb §161-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41609012
Chen, Y.S. 1990. Hydrolysis of [phenyl-U-^{14}C]-thiobencarb in water. Laboratory Project ID: MEF-0149/9007557. Unpublished study performed and submitted by Chevron Chemical Company, Richmond, CA. (41609012)

REVIEWED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERCB/EFED/OPP
TEL: 703-305-5925

J. Breithaupt 5/22/96

SIGNATURE:

PEER REVIEWED BY: Stephanie Syslo
TITLE: Environmental Scientist
ORG: ERCB/EFED/OPP
TEL: 703-305-6355

Stephanie Syslo 5/22/96

SIGNATURE:

CONCLUSIONS:

Degradation - Hydrolysis

1. The hydrolysis study is acceptable and satisfies the 161-1 data requirement.

2. ^{14}C-Thiobencarb [S-[(4-chlorophenyl)methyl]diethyl carbamothioate] at 4.3 ppm did not degrade in sterile, aqueous buffer solutions incubated at 25 °C in darkness at pH values of 5, 7, and 9. Therefore, no degradation products were detected. Material balances were acceptable for each pH value and ranged from 89.3-105.6 for the entire study.

METHODOLOGY:

Phenyl-labeled ^{14}C-thiobencarb[S-[(4-chlorophenyl)methyl]diethyl carbamothioate; radiochemical purity 99.8%, specific activity 359,092 MBQ/mmol (41.7 mCi/mMol, Wizard Laboratories)], was made into an acetonitrile solution containing 6142 mg/ml. The buffer solutions (200 ml of pH 5, 7, and 9) were prepared by adding one pHydrion™ buffer capsule to 200 ml of HPLC grade water for each pH, leading to buffer concentrations of 50 mM for all solutions. These buffer solutions were then filter sterilized using a Nalgene™ sterilization unit. An aliquot (140 ul) of the stock (acetonitrile) solution was

added to each buffer solution to obtain an nominal thiobencarb concentration of 4.3 ppm. After solution preparation, 17 10-ml vials were filled with each solution for sampling at 0, 1, 3, 7, 14, 21, and 30 days.

Duplicate samples were analyzed using HPLC with radioactivity detection and TLC/Autoradiography. Identification of radioactivity was confirmed by LC/MS and by HPLC co-chromatography with authentic standards. More details about the analytical procedure may be seen in the Materials and Methods attachments.

DATA SUMMARY:

^{14}C-Thiobencarb [S-[(4-chlorophenyl)methyl]diethyl carbamothioate] at 4.3 ppm did not degrade in sterile, aqueous buffer solutions incubated at 25 °C in darkness at pH values of 5, 7, and 9. Therefore, no degradation products were detected. Material balances were acceptable for each pH value and ranged from 89.3-105.6 for the entire study.

COMMENTS:

None.

DATA EVALUATION RECORD 2

CHEM 108401 Thiobencarb §161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42257801
Chen, Y.S. 1988. Photodegradation of [phenyl-U-^{14}C]-thiobencarb in water. Laboratory Project ID: MEF-0091. Unpublished study performed by Chevron Chemical Company, Richmond, CA, and submitted by Valent U.S.A. Corporation, Walnut Creek, CA, for K-I Chemical U.S.A., Inc.

DIRECT REVIEW TIME = 11

REVIEWED BY: M. Dillman
TITLE: Staff Scientist
ORG: Dynamac Corporation
TEL: 301-417-9800

APPROVED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERCB/EFED/OPP
TEL: 703-305-5925

J. Breithaupt 5/9/96

SIGNATURE:

CONCLUSIONS:

Degradation - Photodegradation in Water

1. This study can be used to fulfill data requirements.

2. Thiobencarb photodegraded with a calculated half-life of 190 days in a nonsensitized sterile pH 7 aqueous buffer solution at 25 °C; the half-life was 12 days in a photosensitized solution. Thiobencarb did not degrade in the nonsensitized dark control. The degradates identified in the nonsensitized and sensitized irradiated solutions were 4-chlorobenzoic acid (4-CB acid), 4-chlorobenzaldehyde (4-CB aldehyde), 4-chlorobenzyl alcohol (4-CB alcohol), and N,N-diethyl-4-(chlorobenzylthio)carbamate S-oxide (thiobencarb sulfoxide). One additional degradate, O-[(4-chlorophenyl)methyl]diethylcarbamate (bencarb), was isolated in the irradiated sensitized solution.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the aqueous photolysis of phenyl ring-labeled [^{14}C]thiobencarb in sterile aqueous buffer solutions at pH 7.

METHODOLOGY:

Uniformly phenyl ring-labeled [^{14}C]thiobencarb (S-4-chlorobenzyl diethylthiocarbamate; radiochemical purity 99.8%, specific activity 41.7 mCi/mMol, Wizard Laboratories), dissolved in acetonitrile, was added at a nominal concentration of 5 ppm to two aliquots (500 mL) of filter-sterilized aqueous pH 7 buffer solution (20 mM phosphate) contained within sterilized borosilicate glass photolysis cells. The final concentration of the acetonitrile cosolvent was 0.1% by volume. One of these solutions was treated with acetone (1% by volume), and served as a photosensitized test sample. Humidified, carbon dioxide-free air was bubbled through each photocell (Figure 2); no attempt was made to trap volatiles. The temperatures of the test solutions were maintained at approximately 25 $\pm$ 1 °C with a refrigerated circulator; the temperatures were monitored continuously with thermistor probes. The test solutions were irradiated with natural sunlight in Richmond, California (37°59'02"N, 122°20'15"W) for 30 days (September 12 through October 12, 1988). Throughout the study, the average daily intensity of the sunlight ranged from 0.0186 to 0.0559 watts/cm^2 (Table III). As a dark control, an additional aliquot of the buffered solution was treated with [^{14}C]thiobencarb and transferred to a brown bottle; this solution was incubated in a constant temperature water bath for 30 days. Duplicate aliquots (5 mL) of the irradiated solution, photosensitized irradiated solution, and dark control solution were collected at 0, 1, 3, 7, 14, 21, and 30 days posttreatment; additional aliquots were collected from the photosensitized irradiated and dark control solutions at 0.5, 2, and 10 days posttreatment, and from the irradiated (nonsensitized) and dark control solutions at 25 days.

Immediately after collection, individual aliquots of the samples were analyzed by LSC. Additional aliquots were analyzed by HPLC using a Phenomenex Ultremex 5C-18 (IP) column with a 5C-18 guard column, eluted with a linear water:acetonitrile:20% acetic acid gradient, and with radioactive flow detection; compounds were identified using MS. Unlabeled reference standards of thiobencarb, thiobencarb sulfoxide, bencarb, 4-chlorobenzyl alcohol, 4-chlorobenzaldehyde, and 4-chlorobenzoic acid were cochromatographed with the samples and visualized by UV (254 nm) detection. Also, aliquots of the samples were analyzed using two-dimensional TLC on silica gel plates developed with chloroform:ethyl acetate (4:1, v:v) in the first direction and benzene (saturated with formic acid):ethyl acetate (3:1, v:v) in the second direction. Radioactive areas on the plates were located by autoradiography; individual areas were then scraped from the plates and analyzed directly by LSC. Reference standards of thiobencarb, thiobencarb sulfoxide, bencarb, 4-chlorobenzyl alcohol, 4-chlorobenzaldehyde, and 4-chlorobenzoic acid were cochromatographed with the samples and visualized under UV light.

DATA SUMMARY:

Uniformly phenyl ring-labeled [^{14}C]thiobencarb (S-4-chlorobenzyl diethylthiocarbamate; radiochemical purity 99.8%), at 5 ppm, photodegraded with a calculated half-life of 190 days in a nonsensitized sterile aqueous pH 7 buffer solution that was irradiated with natural sunlight at approximately 25 ± 1 °C for 30 days; the average daily intensity of the sunlight was 0.0186-0.0559 watts/cm^2. In a photosensitized (1% acetone by volume) solution, the half-life of [^{14}C]thiobencarb was 12 days. In contrast, [^{4}C]thiobencarb did not degrade in the dark control. The degradates identified in the nonsensitized and sensitized irradiated solutions were

4-chlorobenzoic acid (4-CB acid),

4-chlorobenzaldehyde (4-CB aldehyde),

4-chlorobenzyl alcohol (4-CB alcohol), and

N,N-diethyl-4-(chlorobenzylthio)carbamate S-oxide (thiobencarb sulfoxide).

One additional degradate,

O-[(4-chlorophenyl)methyl]diethylcarbamate (bencarb),

was isolated only from the irradiated sensitized solution.

In the non-photosensitized irradiated solution, [^{14}C]thiobencarb decreased from 100-106.6% of the applied radioactivity at 0-7 days posttreatment to 93.3-93.9% at 25 through 30 days (Table VI). The degradate 4-CB acid increased to a maximum of 3.9% of the applied by 30 days posttreatment; 4-CB aldehyde increased to maximums of 1.5-1.8% at 21 through 30 days; 4-CB alcohol increased to maximums of 2.4-2.5% at 25 through 30 days; and thiobencarb sulfoxide increased to maximums of 1.6-1.9% at 14 through 25 days, and was 1.0% at 30 days (Table VI). Unidentified [^{14}C]compounds (up to two compounds) were isolated only once, totalling 0.1% of the applied at 14 days posttreatment.

In the photosensitized (1% acetone by volume) irradiated solution, [^{14}C]thiobencarb was 100% of the applied radioactivity immediately posttreatment, 53.2% at 10 days, 42.7% at 14 days, and 18.8% at 30 days (Table VII). The degradate 4-CB acid increased to a maximum of 56.0% of the applied at 30 days posttreatment; 4-CB aldehyde increased to a maximum of 29.4% at 14 days and was 3.7% at 30 days; 4-CB alcohol increased to maximums of 6.1-6.7% at 14 through 30 days; and thiobencarb sulfoxide increased to maximums of 4.2-5.0% at 10 through 21 days and was 1.1% at 30 days. One degradate not detected in the nonsensitized irradiated solution, bencarb, increased in the sensitized irradiated solution to maximums of 8.0-8.3% of the applied

8/

at 14 through 30 days posttreatment. Unidentified [^{14}C]compounds (up to three compounds) increased steadily to a cumulative maximum of 12.4% of the applied at 30 days posttreatment; individual compounds were each ≤6.1%.

In the dark control, [^{14}C]thiobencarb comprised 100-109.7% of the applied radioactivity during the 30-day incubation (Table V).

Throughout the study, material balances for the nonsensitized irradiated, photosensitized irradiated, and dark control solutions were 100-106.6% of the applied, 100-111.5%, and 100-109.7%, respectively (Table IV).

COMMENTS:

1. Although TLC R_f values and HPLC retention times were provided for all degradates, it appears that only 4-chlorobenzaldehyde, 4-chlorobenzoic acid, and bencarb were identified and quantitated by HPLC analysis, and only 4-chlorobenzyl alcohol and thiobencarb sulfoxide were identified and quantitated by TLC analysis. Example HPLC chromatograms, but not TLC chromatograms, were provided within the study.

2. The temperatures of the test solutions were monitored continuously throughout the study; according to the study author, temperatures remained at 25 ± 1 °C throughout most of the study, although higher and lower temperatures were experienced during the afternoon and night, respectively. The actual temperature measurements were not provided within the study.

3. A preliminary aqueous photolysis study was conducted in which xylene and NaOH scrubbers were used to collect volatiles; since no volatiles were recovered, the trapping solutions were not employed in the definitive study. Additionally, because of losses of substantial radioactivity attributed to the adherence of thiobencarb to quartz photocells in the preliminary study, borosilicate glass photocells were used in the definitive study. The study author stated that the borosilicate glass photocells did not transmit light with wavelengths <288 nm.

4. In order to positively identify photoproducts, a buffer solution containing thiobencarb at 25 ppm was prepared and irradiated in the same manner as the solution used in the definitive study. According to the study author, the HPLC radiochromatograms showed similar degradate distribution between the 5 and 25 ppm solutions, implying that photolysis of thiobencarb is independent of concentration. The data for the 25-ppm solution were not provided.

5. In a laboratory accumulation in fish study (DER 10, MRID 42460401), a similar HPLC system was used for identification of thiobencarb and its degradates. Attempted confirmation of the HPLC results by one-dimensional TLC analysis revealed an additional unknown degradate

which apparently coeluted with desethylthiobencarb in the HPLC system. This unknown degradate was apparently not isolated in this aqueous photolysis study.

6. The study author stated that the detection limit of the HPLC radioactivity detector was approximately 0.5% of the applied radioactivity, and the detection limit for compound identification was approximately 2.5% of the applied.

7. No dark control was provided for the photosensitized (1% acetone) solution.

8. The study author stated that the solubility of thiobencarb in water at pH 7 is approximately 27.5 ppm at 20 °C.

9. The UV absorption spectra of thiobencarb in acetonitrile at 0.0067 mg/mL is provided in Figure 1; no spectra were provided for thiobencarb in the test solution.

10. The proposed photolytic pathway of thiobencarb was detailed in Figure 13.

DATA EVALUATION RECORD 3

CHEM 108401 Thiobencarb §162-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 43300401
Patterson, T. July, 1994. Aerobic soil metabolism of [Phenyl-^{14}C] thiobencarb in soil. Valent Project No. 10210. Unpublished study performed Plant Research Technologies, San Jose, CA, and submitted by Valent, Inc, Walnut Creek, CA.

REVIEWED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERCB/EFED/OPP
TEL: 703-305-5925

J. Breithaupt 5/22/96

SIGNATURE:

PEER REVIEWED BY: Stephanie Syslo
TITLE: Environmental Scientist
ORG: ERCB/EFED/OPP
TEL: 703-305-6355

Stephanie Syslo 5/22/96

SIGNATURE:

CONCLUSIONS:

Metabolism - Aerobic Soil

1. The aerobic soil metabolism data requirement is satisfied with the combination of this study and MRID 00040925, reviewed on 4/29/95. The registrant has now submitted acceptable 162-1 information for the major use sites, CA and LA.

2. ^{14}C-thiobencarb [S-[(4-chlorophenyl)methyl]diethyl carbamothioate] degraded with a registrant-calculated half-life of 89 days (observed half-life of 56 days) in aerobic Stockton clay adobe soil (24 % sand, 30 % silt, 46 % clay, pH 6.1, 40.9 meq/100g CEC, 45.5 % FC, 1.3 g/cm^3 bulk density, and microbial activity of 158 ug formazan/10g soil/day) treated with 3.05 ug/g parent thiobencarb.

   Parent thiobencarb declined to approximately 50 % of applied by 56 days after treatment, and declined to 10.9 % of applied by the end of the study (366 days), (Table XIII). The only non-volatile soil degradate that was present throughout the study was thiobencarb sulfoxide. Thiobencarb sulfoxide reached a maximum of 5.4 % by 56 days, and declined to 0.13 % by 366 days. The other identified non-volatile degradates did not exceed 1.92 % of applied in the study. These included 2- and 3-hydroxy thiobencarb, 4-chlorobenzoic acid, 4-

chloro-benzylmethyl sulfone, and 4-chlorobenzylmethyl sulfoxide (Table XIII). The degradate CO_2 increased to 12.1 % of applied by 56 days, and to 42.6 % of applied by 366 days (Table V). Bound residues increased to 22.3-23.2 % of applied by 120-366 days (Table VII). The mean material balance was 92 % (Table VII).

METHODOLOGY:

A solution was made containing a total of 61.2 ug/160 ul consisting of both labeled (S.A.=32.5 mCi/mm, 86 % radiochemical purity) and unlabeled thiobencarb. An aliquot (160 ul) was added to 20 g of Stockton Clay Adobe soil [≤2 mm diameter size, oven-dry basis, adjusted to approximately 75 % FC, 77 %FC)] in amber glass bottles to obtain a nominal concentration of 3.05 ug/g soil concentration. Stockton Clay Adobe soil has 24 % sand, 30 % silt, 46 % clay, pH 6.1, 40.9 meq/100g CEC, 45.5 % FC, 1.3 g/cm^3 bulk density, and microbial activity of 158 ug formazan/10g soil/day). The amber glass bottles were placed inside a metabolism chamber that was attached to volatility traps for both organics and CO_2. CO_2-free, humidified air was passed through the sample chamber. After incubating duplicate samples in darkness at 25 ± 1 °C for 0, 3, 7, 14, 22, 35, 56, 120, 185, 231, and 366 days after treatment, respectively, the soil samples were extracted. The volatility traps were sampled at 3, 7, 14, 22, 29, 35, 42, 49, 56, 63, 70, 77, 84, 91, 98, 106, 112, 120, 126, 133, 141, 147, 155, 161, 168, 185, 196, 205, 213, 219, 226, 231, 255, 274, 289, 314, 342, and 366 days after treatment. The CO_2 traps were made up to 10 ml in water and counted using LSC. The soil samples were first extracted using acetonitrile:0.01 M HCl (9:1) followed by 0.5 M NaOH in methanol/water (1:1). Radioactivity in the organic extracts was quantified by LSC and characterized by HPLC. Radioactivity remaining in the soil was quantified by combustion and LSC. Confirmation of identity of radioactive residues was by TLC. Additional details about the extraction and analytical procedures may found in the attached materials and methods. Also, the specific chemical, physical, and microbiological properties of the soils used in this study may be seen in the Comments section. The LOQ's of parent thiobencarb and its metabolites may be seen in the Table in Comment 3.

DATA SUMMARY:

^{14}C-thiobencarb [S-[(4-chlorophenyl)methyl]diethyl carbamothioate] degraded with a registrant-calculated half-life of 89 days (observed half-life of 56 days) in aerobic Stockton Clay Adobe soil (24 % sand, 30 % silt, 46 % clay, pH 6.1, 40.9 meq/100g CEC, 45.5 % FC, 1.3 g/cm^3 bulk density, and microbial activity of 158 ug formazan/10g soil/day) treated with 3.05 ug/g parent thiobencarb.

Parent thiobencarb declined to approximately 50 % of applied by 56 days after treatment, and declined to 10.9 % of applied by the end of the study (366 days). (Table XIII). The only non-volatile soil that was present throughout the study was thiobencarb sulfoxide. Thiobencarb sulfoxide reached a maximum of 5.4 % by 56 days, and declined to 0.13 % by 366 days. The other identified degradates did not exceed 1.92 % of applied in the study. These included 2- and 3-hydroxy thiobencarb, 4-chlorobenzoic acid, 4-chloro-benzylmethyl sulfone, and 4-chlorobenzylmethyl sulfoxide (Table XIII). CO_2 increased to 12.1 % of applied by 56 days, and to 42.6 % of applied by 366 days (Table V). Bound residues increased to 22.3-23.2 % of applied by 120-366 days (Table VII). The mean material balance was 92 % (Table VII).

COMMENTS:

1. The registrant used 89 days as a half-life because it had the highest correlation coefficient (r^2=0.98) and took into account the sampling intervals through 231 days. However, the reviewer observed that by 56 days, approximately 50 % of applied thiobencarb had degraded, leading to a calculated half-life of 58 days with a very similar calculated r^2 of 0.97 (Table XVI). Also, the degradate concentrations appeared to be more related to the 58-day instead of the 89-day half-life (Table XII).

2. The biomass content of the soil at the end of the study was not measured. In a 5/2/96 fax, the registrant stated that they expected biomass to decline significantly by the end of the study since they did not add any organic material to the flasks.

3. Storage stability of soil samples was not included in the study. However, it was not necessary since the samples were extracted immediately after the sampling intervals. In the study, the registrant did conduct a storage stability study with acetone and water containing thiobencarb. It was stable for 418 days. See attached fax dated 5/3/96 for a reference.

4. The registrant treated a bulk soil sample and extracted it using the acetonitrile:0.01 M HCl method used for the individual samples. Analysis of the bulk soil extracts was by HPLC and was used to support identification of metabolites (p. 42 of the study).

5. LOQ's for thiobencarb and its metabolites from attached fax dated 5/3/96.

Compound	LOQ (ppm)
Thiobencarb	0.02
2-hydroxythiobencarb	0.02
3-hydroxythiobencarb	0.02
thiobencarb sulfoxide	0.02
4-chlorobenzylmethyl sulfone	0.015
4-chlorobenzylmethyl sulfoxide	0.014
4-chlorobenzoic acid	0.012

DATA EVALUATION RECORD 4

CHEM 108401 Thiobencarb §162-3

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 43252001
Esser, T. and K. Shepler. 1994. Anaerobic Aquatic Metabolism of [phenyl-^{14}C]-Thiobencarb. Laboratory Project ID's: 397W, VP-10505. Unpublished study performed by PTRL West, Inc., Richmond, CA and submitted by Valent USA Corporation, Walnut Creek, CA.

REVIEWED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERCB/EFED/OPP
TEL: 703-305-5925

J. Breithaupt 5/22/96

SIGNATURE:

PEER REVIEWED BY: Stephanie Syslo
TITLE: Environmental Scientist
ORG: ERCB/EFED/OPP
TEL: 703-305-6355

Stephanie Syslo 5/22/96

SIGNATURE:

CONCLUSIONS:

Metabolism - Anaerobic Aquatic

1. The anaerobic aquatic metabolism study is acceptable and the guideline is satisfied. A previously-reviewed study (MRID 00040925, reviewed on 4/29/91) was considered supplemental and upgradeable.

2. ^{14}C-thiobencarb did not degrade significantly in an anaerobic aquatic clay sediment/water system incubated at 25 °C for up to 363 days. The calculated, grossly-extrapolated half-life was 1962 days (5.4 years). The half-lives from a previously-reviewed study (MRID 00040925, reviewed on 4/29/91), were 250 days in a silty clay loam and 350 days in a clay sediment/water system in LA and CA, respectively.

   Mean sediment residues extracted by acetonitrile/HCl increased from 66.2 % at 0 days to 76.6-86.8 % by 7-272 days, and then declined to 64.6 % by 363 days (Table IV). Mean unextracted residues ranged from 6.1-13.2 % in no particular pattern. Mean aqueous residues decreased from 20 % at day 0 to 3.1-7.5 % at 7-272 days, and then increased to 23.3 % of applied by 363 days. Mean volatile residues did not exceed 0.9 % of applied in the study. Mean total recoveries ranged from 94.7-101.3 5 of applied in no particular pattern.

   The identified metabolites in sediment and water were 2-hydroxy thiobencarb, 4-chlorobenzoic acid, and 3-hydroxy thiobencarb at mean levels of <1.1 % of applied.

METHODOLOGY:

Stockton clay adobe sediment (2.0 % OC, CEC 41.9, pH 6.1, Table 1A) was taken from the rice-growing area of California near Nelson, CA. Water was taken from a stream near Corning, CA (pH 7.1, Table 1B). The sediment was not dried, sieved, or processed in any other way. Subsamples of the sediment were oven-dried overnight to determine moisture content.

A water/sediment ratio of 5:1 was obtained by adding sediment (27.6 g moist, 20 g oven dry weight) and 92.6 ml of river water (100 g) into ground glass erlenmeyer flasks with glass inlet and outlet tubes (Figure 6, attached). These flasks were then covered with aluminum foil to protect them from light. The flask contents were made anaerobic by flushing the flasks with nitrogen gas for 8 consecutive days. Glucose was then added to each flask, followed by mixing of the flask contents and placing the flasks in the incubator.

^{14}C-thiobencarb (radiochemical purity of 97.1 %, specific activity of (32.5 mCi/mm) and non-labeled thiobencarb were made into a working solution where 0.72 ml aliquots contained 193 ug of labeled and 799 ug of unlabeled thiobencarb. The 0.72 ml aliquots were then added to duplicate anaerobic flasks that were analyzed after incubation at 25 °C for times of 0, 7, 14, 28, 45, 70, 120, 181, 272, and 363 days. All samples were analyzed for volatiles and soil/water residues except for the 0-day flasks. The samples were centrifuged and the water was analyzed directly. Soil samples were extracted (Figure 7, attached). HPLC, TLC, and LSC were used to analyze soil/water residues and barium chloride was used to analyzed for volatiles in traps. The limit of detection was 10 DPM (>2X background) and the limit of quantitation was 50 DPM (>2X background). Microbial activity was measured at 0 and 272 days. Storage stability was measured for both soil an water. Further details about the analytical methodology may be seen in the attached Materials and Methods from the study. The specific chemical, physical, and microbiological properties of the soils used in this study are found in the attachments.

DATA SUMMARY:

^{14}C-thiobencarb did not degrade significantly in an anaerobic aquatic clay sediment/water system incubated at 25 °C for up to 363 days. The calculated, grossly-extrapolated half-life was 1962 days (5.4 years). Mean sediment residues extracted by acetonitrile/HCl increased from 66.2 % at 0 days to 76.6-86.8 % by 7-272 days, and then declined to 64.6 % by 363 days (Table IV). Mean unextracted residues ranged from 6.1-13.2 % in no particular pattern. Mean aqueous residues decreased from 20 % at day 0 to 3.1-7.5 % at 7-272 days, and then increased to 23.3 % of applied by 363 days. Mean volatile residues did not exceed 0.9 % of applied in the study. Mean total recoveries ranged from 94.7-101.3 5 of applied in no particular pattern.

The identified metabolites in sediment and water were 2-hydroxy thiobencarb, 4-chlorobenzoic acid, and 3-hydroxy thiobencarb at mean levels of <1.1 % of applied (Tables 6 and 8, attached).

pH, Eh, and dissolved oxygen measurements indicated that anaerobic conditions were maintained during the study (Table II, attached). The system was very microbially active, with total CFU's/g of soil of 45,500 at day zero to 89,500 at 272 days (Appendix B).

COMMENTS:

1. The LOQ's for parent thiobencarb in soil and water were 0.0046 ppm and 0.00061-0.0046 ppm, depending on the injection volume into the HPLC.
2. Storage stability was adequate in the sediment, but questionable in the river water. HPLC reanalysis of the 45-day sample 85 days after the original HPLC analysis showed that thiobencarb had degraded to 4-chlorobenzoic acid and thiobencarb sulfoxide. However, this was the only sample in which there were storage problems.

92

DATA EVALUATION RECORD 5

CHEM 108401 Thiobencarb §163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 43150601
Christensen, K.P. 1994. 4-Chlorobenzoic Acid-Determination of the Adsorption and Desorption Properties. Laboratory Project ID: VP-10804. Unpublished study performed by Springborn Laboratories, Inc, Wareham, MA, and submitted by Valent USA Corporation, Walnut Creek, CA.

REVIEWED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERCB/EFED/OPP
TEL: 703-305-5925

SIGNATURE: J. Breithaupt 5/22/96

PEER REVIEWED BY: Stephanie Syslo
TITLE: Environmental Scientist
ORG: ERCB/EFED/OPP
TEL: 703-305-6355

SIGNATURE: Stephanie Syslo 5/22/96

CONCLUSIONS:

Aged Mobility - Leaching and Adsorption/Desorption

1. The batch equilibrium study in this review using the thiobencarb degradate, 4-chlorobenzoic acid, is acceptable and satisfies the aged portion of the 163-1 data requirement.

2. Based on batch equilibrium experiments, [^{14}C]4-chlorobenzoic acid, a degradate of thiobencarb, was determined to be very mobile in sandy loam (pH 5.8, 0.88 % OC), loamy sand (pH 5.6, 0.76 % OC), silt loam (pH 6.0, 0.88 % OC), and clay soil(pH 6.0, 2.0 % OC):calcium chloride solution slurries (1:5, w:v) containing 4-chlorobenzoic acid at approximately 0.03, 0.08, 0.2, and 0.5 mg/L. The slurries were equilibrated in darkness for 5-18 hours at 17-22 °C. Freundlich K_{ads} values were 0.74 for the sandy loam soil, 0.98 for the loamy sand soil, 1.22 for the silt loam soil, and 3.26 for clay soil. The corresponding K_{ocads} values were 84, 128, 138, and 163, respectively. The N values were 1.58, 1.58, 1.56, 1.28, respectively. K_{des} values were 2.19 for the sandy loam soil, 1.94 for the loamy sand soil, 2.44 for the silt loam soil, and 8.31 for the clay soil. The corresponding K_{ocdes} values were 249, 253, 277, and 416, respectively. The N values were 1.58, 1.54, 1.56, 1.18, respectively. Mobility

decreased with increasing clay content, increasing organic matter content, and increasing cation exchange capacity.

METHODOLOGY:

Non-labeled 4-chlorobenzoic acid was made into an 100 ml solution containing 0.5 mg/ml. Labeled 4-chlorobenzoic acid (99 % radiochemical purity, SA =56 mCi/mmol, 794,000 dpm/ug, p.13) was quantitatively transferred to a 50-ml volumetric flask and diluted to volume with acetone to make a 0.0524 mg/ml solution. A calcium chloride solution (0.01 M) was made from reagent grade products and then sterilized by autoclaving. The final solutions made using both labeled and unlabeled 4-chlorobenzoic acid contained 0.5, 0.2, 0.08, and 0.03 mg/L.

Preliminary Study for Adsorption to Glass and Soil.

To determine adsorption to glass, the registrant prepared four centrifuge tubes containing 40 ml of the final solution. After 24 hours of shaking, an aliquot was removed and counted using LSC. A control without radiolabeled 4-chlorobenzoic acid was also prepared. Four tubes/soil (8 g soil in 40 ml solution, Table in Comment 2) were prepared, shaken, and sampled at 5, 18, 24, and 48 hours. After centrifugation, an aliquot (5 ml) of the supernatant from each tube was sampled and counted using LSC. The registrant also conducted a stability test for 4-chlorobenzoic acid following the preliminary study.

Definitive Study

Triplicate samples of 8 g of each soil (oven-dry basis) and 40 ml of test solution at each 4-chlorobenzoic acid concentration of 0.5, 0.2, 0.08, and 0.03 mg/L were put into centrifuge tubes. In addition, three tubes containing only solution at each concentration and one $CaCl_2$ blank were also put into tubes. Following shaking at 125 rpm for the appropriate time intervals (18 hours for the Arkansas, Stockton, and Georgia soils and 5 hours for the Texas soil), and centrifuging and decanting, the supernatants were sampled for radioassay (LSC) as described above. For desorption, fresh 0.01 M $CaCl_2$ with no added pesticide was added to each tube and the tubes were again shaken for the same time intervals as adsorption. After centrifuging and decanting, the supernatants were analyzed using LSC. The soil pellets were then extracted using 50:50 methanol:0.1 M K_2HPO_4 and 1 ml aliquots were combusted to determine extractable residues. The soils were then combusted to determine the amount of bound residues. Further details about the analytical methodology for both the preliminary and definitive studies may be seen in the attached Materials and Methods from the study.

DATA SUMMARY:

Based on batch equilibrium experiments, [^{14}C]4-chlorobenzoic acid, a degradate of thiobencarb, was determined to be very mobile in sandy loam (pH 5.8, 0.88 % OC), loamy sand (pH 5.6, 0.76 % OC), silt loam (pH 6.0, 0.88 % OC), and clay soil(pH 6.0, 2.0 % OC):calcium chloride solution slurries (1:5, w:v) containing 4-chlorobenzoic acid at approximately 0.03, 0.08, 0.2, and 0.5 mg/L. The slurries were equilibrated in darkness for 5-18 hours at 17-22 °C. Freundlich K_{ads} values were 0.74 for the sandy loam soil, 0.98 for the loamy sand soil, 1.22 for the silt loam soil, and 3.26 for clay soil. The corresponding K_{ocads} values were 84, 128, 138, and 163, respectively. The N values were 1.58, 1.58, 1.56, 1.28, respectively. K_{des} values were 2.19 for the sandy loam soil, 1.94 for the loamy sand soil, 2.44 for the silt loam soil, and 8.31 for the clay soil. The corresponding K_{ocdes} values were 249, 253, 277, and 416, respectively. The N values were 1.58, 1.54, 1.56, 1.18, respectively. Mobility decreased with increasing clay content, increasing organic matter content, and increasing cation exchange capacity.

At the termination of the experiment, radioactive material balances for the soil:solution slurries ranged from 83.8 to 107% of the applied. 4-Chlorobenzoic acid was stable in the study in all soils, with 89.9-100 % as parent (Table XII).

COMMENTS:

1. The report did not contain any description of a preliminary study for desorption. However, this was unimportant since 4-chlorobenzoic acid did not degrade significantly in the study. Also, there was no adsorption to glass.

2. The chemical and physical characteristics of the soils and sediment used in this study follow in the Table.

Property	Soil			
Particle Size Distribution	Arkansas silt loam	Stockton Clay Adobe	Georgia loamy sand	Texas sandy loam
Sand (%)	27	18	86	72
Silt (%)	56	27	10	21
Clay (%)	17	55	4	7
Organic Carbon	0.88	2.0	0.76	0.88
pH	6.0	6.0	5.6	5.8
Cation Exchange (CEC, meq/100g)	9.0	40.3	4.9	6.2
Base saturation (% Ca + Mg + Na + K)	60	82	42	57
Bulk Density	1.00	1.21	1.44	1.36
Moisture Content at 1/3 bar	22.3	41.2	3.9	17.6

DATA EVALUATION RECORD 6

CHEM 108401 Thiobencarb §164-2

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 42003404
Lai, J.C. 1991. Field dissipation of Bolero 8EC in rice. Laboratory Project ID: 1641/90/7538. Unpublished study performed by Chevron Chemical Company, Richmond, CA, and submitted by Valent U.S.A. Corporation, Walnut Creek, CA.

DIRECT REVIEW TIME = 27

REVIEWED BY: M. Dillman
TITLE: Staff Scientist
ORG: Dynamac Corporation
TEL: 301-417-9800

APPROVED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERCB/EFED/OPP
TEL: 703-305-5925

J Breithaupt

SIGNATURE:

CONCLUSIONS:

Field Dissipation - Aquatic

1. The study is acceptable and partially satisfies the 164-2 data requirement. The 164-2 data requirement is satisfied with the combination of this study, MRID 43404005, and Ross and Sava (1986).

2. Thiobencarb dissipated with an observed half-life of approximately 36 days in silty clay loam soil in Louisiana that had been planted to rice. The plot was flooded at 7 days posttreatment; thiobencarb dissipated from the floodwater with a registrant-calculated half-life of 5.8 days. Thiobencarb was not detected in the soil below 10 centimeters. The degradates 1-(((4-chlorophenyl)methyl)sulfinyl)-N,N-diethylformamide (thiobencarb sulfoxide) and 4-chlorobenzyl-methylsulfone were detected primarily in the upper 5 cm of the soil and in the floodwater.

METHODOLOGY:

A test plot (245 x 150 feet) of silty clay loam soil (0- to 30-cm depth; 6-16% sand, 53-59% silt, 29-35% clay, 1.1-1.6% organic matter, pH 6.3-6.8, CEC 13.1-16.1 meq/100 g) located in Port Barre,

Louisiana, was planted to rice on April 30, 1990. The plot was divided into five "replicates" (Replicates A-E), and each replicate was divided into 19 subplots (8 x 15 feet). On May 23, 1990, after the rice plants had grown to a height of approximately 6 inches (two to four leaves per plant), thiobencarb (S-4-chlorobenzyl diethylthiocarbamate; Bolero 8 EC, 8 lb ai/gallon, Chevron) was broadcast by airplane at 4 lbs ai/A to the test plot. An untreated plot (100 x 150 feet) of silt loam soil (16% sand, 59% silt, 25% clay, 0.6% organic matter, pH 6.9, CEC 11.8 meq/100 g), also planted to rice, was maintained as a control. A 232-foot buffer zone separated the treated and control plots. On May 26, 1990 (3 days posttreatment), the plots were flush-irrigated; and on May 30, 1990 (7 days posttreatment), the plots were permanently flooded to a depth of 4.5 inches; five additional flood-irrigations were made to maintain the flood levels within the plots for approximately 75 days. Soil samples were collected from the treated plot prior to treatment, at 0, 1, 3, 5, 7, 9, 14, and 28 days, and at 2, 3, 4, 5, 6, 8, and 10 months. The untreated plot was sampled prior to treatment, at 0, 14, and 28 days, and at 2 and 6 months. At each sampling interval, three soil cores were randomly collected from one designated subplot in each of the five replicates of the treated plot using an acetate-lined hydraulic soil corer; cores were collected to a depth of 90 cm (2.5-cm diameter) when the plots were dry and to a depth of 30 cm (2-inch diameter) when the plots were flooded. Five soil cores were collected randomly from the control plot at each sampling interval; the soil samples were stored frozen at approximately -20 C for 20-288 days prior to extraction, and extracts were stored for up to 23, 69, and 25 days prior to analyses for thiobencarb, 1-(((4-chlorophenyl)-methyl)sulfinyl)-N,N-diethylformamide (thiobencarb sulfoxide), and 4-chlorobenzylmethylsulfone, respectively. One water sample (500 mL) from each of the five replicates in the treated plot was collected approximately 3 to 5 cm below the water surface at 0, 1, 3, 5, 7, 10; 14, 21, 28, 42, 56, and 70 days postflooding (7-77 days posttreatment); the control plot was sampled at 0, 7, 14, 28, and 42 days postflooding. Aliquots of inlet water were collected at flood establishment, and at each flood irrigation. Since no runoff occurred during flooding, no runoff samples were collected. Water samples were stored in plastic bottles at approximately -20 C for 27-286 days prior to extraction, and extracts were stored for up to 30 days prior to analysis.

The soil cores were divided into 0- to 5-, 5- to 10-, 10- to 15-, and 15- to 30-cm segments, and further into 30- to 45-, 45- to 60-, 60- to 75- and 75- to 90-cm segments where applicable. Individual soil segments collected from the treated plot were composited across the five replicates to provide three soil samples per sampling interval per depth; the soil cores collected from the control plot were composited to provide one soil sample per sampling interval per depth. Subsamples (50 g) of the composited soil segments were extracted by mixing for 5 minutes with ethyl acetate (150 mL) plus sodium sulfate (pre-rinsed with acetone and ethyl acetate); after the extraction, the supernatant was decanted and filtered through sodium

sulfate. The extract was concentrated (method unspecified), and the resulting residue was dissolved in ethyl acetate using an ultrasonic bath. Aliquots of the ethyl acetate solution were analyzed for thiobencarb by GC with nitrogen-phosphorous detection and for 4-chlorobenzylmethylsulfone by GC with flame-photometric detection. For analysis of 1-(((4-chlorophenyl)methyl)sulfinyl)-N,N-diethylformamide (thiobencarb sulfoxide), an additional aliquot of the ethyl acetate extract was concentrated (method unspecified), and the resulting residue was dissolved in iso-octane:2-propanol (85:15, v:v). An aliquot of the iso-octane:2-propanol solution was immediately analyzed by HPLC using an Ultrasphere Cyano column eluted with iso-octane:methanol:2-propanol (85:10:5 or 90:7:3, v:v:v), and with photo-conductivity detection. Compound identifications and quantitations were achieved by comparison to instrument calibrations using reference standards of thiobencarb, thiobencarb sulfoxide, and 4-chlorobenzylmethylsulfone.

Entire water samples were partitioned with hexane (200 mL) plus sodium chloride (approximately 15 g). The aqueous layer was removed, and the hexane extract was filtered through anhydrous sodium sulfate. The hexane-extracted aqueous solution was partitioned twice with methylene chloride (100 mL); after each extraction, the extracts were filtered through the same sodium sulfate, then combined. The hexane and combined methylene chloride extracts were individually concentrated (method unspecified), and the remaining residues were dissolved in ethyl acetate using an ultrasonic bath. An aliquot of the ethyl acetate solution from the hexane extraction was analyzed for thiobencarb by GC with nitrogen-phosphorous detection; an aliquot of the ethyl acetate solution from the methylene chloride extraction was analyzed for 4-chlorobenzylmethylsulfone by GC with electron capture or flame-photometric detection, and aliquots of the ethyl acetate solutions from both extractions were analyzed for thiobencarb sulfoxide either by GC with nitrogen-phosphorous detection or by HPLC using an Ultrasphere Cyano column or C-18 HS column eluted with iso-octane:methanol:2-propanol (85:10:5 or 90:7:3, v:v:v), and with photo-conductivity or UV (210 nm) detection.

Average recovery efficiencies from soil samples fortified with thiobencarb (0.01-1.0 ppm), thiobencarb sulfoxide (0.01-0.10 ppm), and 4-chlorobenzylmethylsulfone (0.01-0.10 ppm) were 92 $\pm$ 17%, 87 $\pm$ 28%, and 88 $\pm$ 12%, respectively; average recovery efficiencies from fortified water samples (5 ppb) were 97 $\pm$ 14%, 96 $\pm$ 18%, and 99 $\pm$ 8.8%, respectively. Reported sample results were not corrected for recovery efficiencies; soil sample results were expressed on a dry soil basis. Limits of detection were 0.01 ppm in soil and 0.5 ppb in water for each of the three compounds.

DATA SUMMARY:

Thiobencarb (S-4-chlorobenzyl diethylthiocarbamate; Bolero 8 EC, 8 lb ai/gallon), applied as a postemergence broadcast (aerial) treatment

on May 23, 1990, dissipated with a registrant-calculated half-life of 36 days and an observed half-life of approximately 6 days from the upper 5 cm of a plot of silty clay loam soil in Louisiana that had been planted to rice (Figure 3); thiobencarb was not detected in the soil below 10 centimeters. The plot was flooded at 7 days posttreatment on May 30, 1990; thiobencarb dissipated from the floodwater with a registrant-calculated half-life of 5.8 days (Figure 6). The degradates,

1-(((4-chlorophenyl)methyl)sulfinyl)-N,N-diethylformamide (thiobencarb sulfoxide), and

4-chlorobenzylmethylsulfone,

were observed primarily in the upper 5 cm of the soil at maximum average concentrations of 0.16 and 0.03 ppm, respectively (Tables IIA and IIIA); and in the water at 8.9 and 5.2 ppb, respectively (Tables V and VI).

In the 0- to 5-cm soil depth, thiobencarb decreased from 0.67-0.79 ppm (dry soil basis) at 0 days posttreatment to 0.31-0.46 ppm at 3 days, 0.14-0.32 ppm at 7 days, 0.04-0.18 ppm at 9-14 days, 0.01-0.03 ppm at 120 days, and $\leq$0.02 ppm at 150-300 days; thiobencarb was $\leq$0.03 ppm in the 5- to 10-cm depth, and <0.01 ppm below 10 cm (Tables I and IA). In the 0- to 5-cm depth, thiobencarb sulfoxide was 0.06-0.24 ppm (dry soil basis) in all samples collected at 1 and 3 days posttreatment, was 0.13 ppm in one of three samples at 5 days, and was $\leq$0.03 ppm in all other samples and sampling intervals; thiobencarb sulfoxide was $\leq$0.01 ppm at depths below 5 cm at all sampling intervals (Tables II and IIA). In the 0- to 5-cm depth, 4-chlorobenzylmethylsulfone averaged 0.03 ppm (dry soil basis) at 3 and 7 days posttreatment, and was $\leq$0.01 ppm at all other sampling intervals; 4-chlorobenzylmethylsulfone was $\leq$0.01 ppm at depths below 5 cm at all sampling intervals (Tables III and IIIA).

In the floodwater, thiobencarb increased from 6.9-9.1 ppb at 0 days postflooding (7 days after treatment of the soil) to 12.2-14.1 ppb at 3 days, and then decreased to 5.6-10.5 ppb at 7 days, 1.6-2.7 ppb at 14 days, $\leq$1.0 ppb at 28 days, and <0.5 ppb at 42-70 days (Table IV). Thiobencarb sulfoxide increased from 1.6-2.1 ppb at 0 days postflooding to 1.6-13.4 ppb at 1 day (average 8.9 ppb), then decreased to 2.6-5.2 ppb at 3 days, 0.8-1.5 ppb at 7 days, $\leq$0.9 ppb at 14 days, and <0.5 ppb at 21-70 days (Table V). The degradate 4-chlorobenzylmethylsulfone increased from 0.8-2.4 ppb at 0 days post-flooding to 4.8-5.8 ppb at 5 days, then decreased to 1.4-1.8 ppb at 14 days, and <0.5 ppb at 21-70 days (Table VI).

At the time of application, wind speeds were 0-3 miles/hour from the north, the air temperature was 54 F, the soil temperature at a 2-inch depth was 57 F, the relative humidity was 72%, and the cloud cover was 0%; additionally, soil and plant surfaces were moist, and approximately 70% of the soil was covered by foliage. The depth to

the water table was 0-2 feet with very poor subsurface drainage. Throughout the study (5/23/90-3/19/91), air temperatures ranged from 21.6 to 97.5 F, and soil temperatures at the 5-cm depth ranged from 37.2 to 97.2 F. From the time of application to permanent flooding (5/23/90-5/30/90), rainfall and irrigation (flush) totaled 4.1 inches; throughout flooding (5/31/90-7/30/90), rainfall totaled 6.8 inches, and irrigation totaled 22 inches; for the remainder of the study (7/31/90-3/19/91), rainfall totaled 29.6 inches.

COMMENTS:

1. According to the study author, in a soil metabolism study (MRID 00040925; "The soil metabolism of [ring-U-^{14}C]benthiocarb," study not provided for review), 4-chlorobenzylmethylsulfone was the major metabolite under both aerobic and anaerobic conditions. Only this degradate and the degradate thiobencarb sulfoxide were analyzed for in the terrestrial field dissipation study. Depending upon the results obtained for other degradates in the soil metabolism study, it may be necessary for the registrant to investigate the dissipation of other degradates under field conditions.

2. Storage stability data provided within the study for thiobencarb and its degradates in soil (Tables XI-XIII, and table on page 15) were highly variable. Nonetheless, the data served to sufficiently indicate that thiobencarb, thiobencarb sulfoxide, and 4-chlorobenzylmethylsulfone were reasonably stable when stored at -20 C for up to 1 year; additionally, although no explanation was provided by the study author for the exceptionally high variability in the thiobencarb sulfoxide data (page 15), the Dynamac reviewer suspects that there is a significant probability that data for samples 3-I-1 and 3-II-1 were inadvertently confused with data for samples 3-III-1 and 4-I-1.

   Similarly, data from an on-going storage stability study for thiobencarb and its degradates in water (Tables XIV-XVI), although variable, suggest that thiobencarb and 4-chlorobenzylmethylsulfone were stable for up to 181 days in water stored in plastic bottles; thiobencarb sulfoxide appeared to degrade slightly. In the actual dissipation study, water samples were stored for up 286 days prior to analysis; when additional storage stability data for thiobencarb residues in water become available, it should be provided for the longest duration of storage employed within this study.

   In addition, although soil and water extracts were stored for up to 23-69 days prior to analysis, the storage stabilities of thiobencarb and its degradates in the extracts were apparently not investigated.

3. According to the study author, because the volume of water collected at each sampling interval was limited and did not allow for repeat analyses, and because interferences were observed during analysis of the water samples for thiobencarb sulfoxide, results were not

obtained for this compound in seven of the water samples. However, at least one acceptable result was obtained for each sampling interval.

At the 45- to 60-cm depth, 4-chlorobenzylmethylsulfone was 0.02 ppm (wet soil basis) at 3 days posttreatment; however, due to the interferences in the analysis, only one data point was available for this sampling interval and depth. Because it was not detected consistently below 15 cm at any other sampling intervals, 4-chlorobenzylmethylsulfone is not expected to leach significantly beyond a 15-cm depth when thiobencarb is applied under conditions similar to those employed in this study.

4. Descriptions of analytical procedures provided within the study were often vague; specifically, detection methods for all analyses, and mobile phases for HPLC analyses were often not specified appropriately.

5. Rainfall data for the duration of the study was obtained from the actual test site. Additional weather data was obtained from Louisiana State University; the location of the weather data collection site with respect to the location of the test site was not specified within the study.

6. Prior to initiation of the study, the actual concentration of the test material was determined to be 85.6% thiobencarb.

7. The test site was planted to soybeans in 1987, 1988, and 1989. The pesticides bentazon and acifluorfen-sodium were applied (0.50 and 0.25 lb ai/A, respectively) in June, 1987; fluazifop-butyl was applied (0.187 lb ai/A) in June of 1987, 1988, and 1989; and fomesafen was applied (0.375 lb ai/A) in June of 1988 and 1989.

   Immediately prior to application of thiobencarb in this study, the test and control plots were treated with propanil (May 17, 1990) and glyphosate (May 19, 1990) at 4 and 1 lb ai/A, respectively.

DATA EVALUATION RECORD 7

CHEM 108401 Thiobencarb §164-1

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 43404005
Ho, B. 1990. Aquatic Field Dissipation of Bolero 10G in rice. Laboratory Project ID: T-7230. Unpublished study performed by Chevron Chemical Company, Richmond, CA, and submitted by Valent U.S.A. Corporation, Walnut Creek, CA.

REVIEWED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERCB/EFED/OPP
TEL: 703-305-5925

J. Breithaupt

APPROVED BY: William R. Effland, Ph.D.
TITLE: Soil Scientist
ORG: ERCB/EFED/OPP
TEL: 703-305-5738

SIGNATURE: William R. Effland

CONCLUSIONS:

Field Dissipation - Aquatic

1. The study is considered partially acceptable and can be upgraded if the registrant further describes the water management in the study and provides additional storage stability information.

2. Thiobencarb dissipated with an observed half-life of 153 days in Anita clay loam soil in California that had been planted to water-seeded rice. Thiobencarb dissipated from the floodwater with a registrant-calculated half-life of 5 days. Thiobencarb and the metabolites thiobencarb sulfoxide and 4-chlorobenzylmethylsulfone were not detected in the soil below 10 centimeters, with the exception of some sporadic detections that could have been sampling contamination. Residues were primarily associated with the soil, with a 5.6:1 soil:water ratio of residues.

METHODOLOGY:

A flooded (6 inches of water) test plot (250 x 1850 feet) of Anita clay loam soil (28 % sand, 26 % silt, 47 % clay, 3.6 % OC, pH 6.1, CEC of 46 meq/100 g) located in Nelson, CA, was treated on May 27, 1988 with 4 lbs ai/A of 10 G Bolero (40 lbs product/A) by airplane.

feet, followed by further subdivision to 17 subplots of 25 x 125 feet. At the time of application, the rice was at the first germination stage. The registrant also established two additional plots. The first was a tilled, downstream untreated fallow check specifically designed to hold runoff after for six days, which is the time specified by the CDFA. The other plot was a fallow check that would hold the water for another 8 days, prior to off-site release. Soil from the treated plot was sampled to one foot at 0, 1, 2, 3, 4, 5, 7, 10, 14, 21, 30, 60, 92, 187, 272, 368, 457, and 551 days after treatment, and was sampled to two feet at 128 and eight feet at 153 days, respectively. Soil samples were also taken from one of the fallow fields at 15-21 and 27 days after treatment. The water from the treated plot was sampled at 0, 1, 2, 3, 4, 5, 7, 10, 14, 21, 33, 60, and 92 days after treatment, followed by drainage of the treated area into the fallow field. At 14 days posttreatment, some of the paddy water was drained off to the fallow ponds, followed by sampling in the fallow ponds at 15, 16, 17, 18, 19, 21, and 27 days posttreatment. However, the study did not provide information on what happened to the water in the fallow field. At 153 days after treatment, a water sample from eight feet of depth in the treated plot was also taken.

Soil samples were extracted using ethyl acetate followed by the analysis of thiobencarb and thiobencarb sulfoxide by GC/NPD detection. The metabolite 4-chlorobenzylmethylsulfone was analyzed using GC/FPD.

In water, thiobencarb residues were extracted using hexane followed by methylene chloride. As in soil, parent thiobencarb and thiobencarb sulfoxide residues were analyzed by GC/NPD, and the metabolite 4-chlorobenzylmethylsulfone was analyzed using GC/FPD.

The average recovery efficiencies from soil samples fortified with parent thiobencarb, thiobencarb sulfoxide, and 4-chlorobenzylmethyl sulfone at 0.1 ppm were 95, 101, and 100 %, respectively. In water, the method recoveries were 96, 108, and 105 %, respectively. Limits of detection were 0.01 ppm in soil and 0.5 ppb in water for each of the three compounds.

DATA SUMMARY:

Thiobencarb (S-4-chlorobenzyl diethylthiocarbamate; Bolero 10 G), applied broadcast as a granular material in standing water, dissipated with a registrant-calculated half-life of 153 days in Anita clay loam soil and 5 days in water. Thiobencarb was not detected in the soil below 10 centimeters, with the exception of sporadic residues at 0, 1, and 4 days (Table 1). The detected residue was in ground water was 0.001 ppm, twice the detection limit in water of 0.0005 ppm. The detected metabolites were

1-(((4-chlorophenyl)methyl)sulfinyl)-N,N-diethylformamide (thiobencarb sulfoxide), and

4-chlorobenzylmethylsulfone.

There was only one detection of thiobencarb sulfoxide at five days (0.03 ppm) at the 15-30 cm depth (Table 2). There were no observed detections of 4-chlorobenzylmethylsulfone in the treated plot below 10 cm of depth (Table 3).

In the 0- to 5-cm soil depth, parent thiobencarb decreased from an average of 2.23 ppm (1.11-1.74 ppm, dry soil basis) at 0 days posttreatment to an average of 0.03 ppm by 551 days posttreatment in no particular pattern (Table 1). Parent thiobencarb residues were variable in the first 21 days of flooded conditions, ranging from 0.27-2.23 ppm, but they declined steadily after 21 days and past the end of flooding (92 days) until the end of the study. Thiobencarb sulfoxide and 4-chlorobenzylmethylsulfone did not exceed 0.07 and 0.02 ppm in the study, respectively.

In the fallow field, the soil concentrations did not exceed 0.06 ppm for parent thiobencarb, thiobencarb sulfoxide, or 4-chlorobenzylmethyl sulfone. However, they appeared to increase with time, which would be consistent with the evaporation of water from the fallow fields.

In the paddy water, parent thiobencarb residues increased from 266 ppb at 0 days posttreatment to 438 ppb at 3 days, followed by a decline to 1.0 ppb by 92 days of flooding and field drainage (Table 5). Parent thiobencarb residues in water in the fallow field ranged from 1.3-27.9 ppb. Thiobencarb sulfoxide residues in water in the treated field increased from 4.4 ppb at 0 days posttreatment to 22 ppb at 3 days, followed by a decline to non-detectable levels by 33 days (Table 6). Thiobencarb sulfoxide residue concentrations in water in the fallow fields were 1.4-9.8 ppb, and reached non-detectable levels by 27 days. The metabolite 4-chlorobenzylmethyl sulfone increased to 7.9-8.1 ppb by 7-14 days, and then decreased to non-detectable levels by 60 days posttreatment (Table 7). The residue concentrations in water in the fallow fields were 2.1-8.4 ppb in no particular pattern.

COMMENTS:

1. The study did not provide adequate details on water management in the study. The study did not address what happened to the water in the first fallow field.

2. Information on storage stability in soil was incomplete in the study. The registrant conducted a storage stability study for one year. Thiobencarb in soil was shown to degrade in storage to thiobencarb sulfoxide, followed by further degradation to 4-chlorobenzylmethyl sulfone. Parent thiobencarb decreased to 70 % by one year. Thiobencarb sulfoxide increased to 143 %, then decreased to 74 % by one year. 4-Chlorobenzylmethyl sulfone increased to 255 % by one month, followed by a decrease to 82-92 % by 6 months to one year.

However, since the data were extremely variable, the registrant conducted another study, but did not report all of the information for this study because it was not available. At seven months, 95.% of the thiobencarb, 70 % of thiobencarb sulfoxide, and 104 % of 4-chlorobenzylmethylsulfone was still present.

3. In water, 89 % of parent thiobencarb, 40 % of thiobencarb sulfoxide, and 82 % of 4-chlorobenzylmethylsulfone were stil present after 12 months of storage.

DATA EVALUATION RECORD 8

CHEM 108401 Thiobencarb §164-1

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

Literature Article
Ross, L.J. and R.J. Sava. 1986. Fate of thiobencarb and molinate in rice fields. J. Environ. qual. 15:220-225.

REVIEWED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERCB/EFED/OPP
TEL: 703-305-5925

APPROVED BY: William R. Effland, Ph.D.
TITLE: Soil Scientist
ORG: ERCB/EFED/OPP
TEL: 703-305-5738

SIGNATURE:

CONCLUSIONS:

Field Dissipation - Terrestrial

1. The literature study is considered to be supplemental and provides additional information for the purpose of risk assessment.

2. Thiobencarb was predominantly distributed between water (34.5 %) and soil (43 %), with less than 1 % associated with air and vegetation. Thiobencarb water concentrations decreased to 8 ug/L (ppb) by the end of the study (32 days) and soil concentrations decreased to 2330 ug/kg (ppb) by 32 days. Concentrations in water, soil, and vegetation were significantly higher in the holding period (0-6 days) than in the postholding period (8-32 days). Water and vegetation concentrations were stable in the holding period and only declined with time during the postholding period. In contrast, soil concentrations did not change significantly in either period. The mass balance (including air, water, soil, and vegetation) increased from 41 % at 0 days after treatment to 67-70 % by 2-6 days after treatment and then decreased to 26-27 % by 16-32 days after treatment.

METHODOLOGY:

The authors studied two commercial rice fields in the Sacramento Valley of CA. Thiobencarb was applied at 4 lbs ai/A using fixed-wing aircraft into standing water when rice plants had not yet emerged (1-3 leaf growth stage). Water was held at 10.4 inches of depth for 6 days with no inflow or outflow (stagnant water). After 6 days, the field was rapidly drained and water depth was then maintained at 6.8 inches of depth with intermittent inflow and outflow. Water temperatures averaged 28 °C (82 °F) for 30 days. Water, soil, and vegetation samples were collected from four pads within each rice field. The pads were located at the field inlet and outlet and two randomly-chosen points in between. Samples were taken at -1, 0, 2, 4, 8, 16, and 32 days after application near the pads and where the water flow was slower. ANOVA was used to examine the dynamics of herbicide dissipation. Air, water, soil, and vegetation were analyzed using GC.

DATA SUMMARY:

Thiobencarb was predominantly distributed between water (34.5 %) and soil (43 %), with less than 1 % associated with air and vegetation. Thiobencarb water concentrations at 0, 2, 4, 6, 8, 16, and 32 days after treatment were 79. 567, 576, 515, 367, 56, and 8 ug/L, respectively. Soil concentrations of thiobencarb were 3250, 2880, 3350, 3860, 2020, 2260, and 2330 ug/kg (ppb), respectively. Thiobencarb vegetative concentrations were 78, 691, 1750, 1360, 1280, 796 and 169 ug/kg (ppb), respectively, leading to a regression-calculated half-life of 8.5 days. Thiobencarb air concentrations at 0, 1, 2, and 3 days after treatment were 1.4, 0.9, 0.8 and 0.43 ug/m^3, respectively. The calculated half-life in air was 2.2 days. The flux rates were 37, 8, 16, and 6 ng/cm^2 h^{-1} at 0, 1, 2, and 3 days after treatment, respectively. Concentrations in water and on vegetation were significantly higher in the holding period (0-6 days) than in the postholding period (8-32 days). Water and vegetation concentrations were stable in the holding period and only declined with time during the postholding period. In contrast, soil concentrations did not change significantly in either period. The mass balance (including air, water, soil, and vegetation) increased from 41 % at 0 days after treatment to 67-70 % by 2-6 days after treatment and then decreased to 26-27 % by 16-32 days after treatment.

The authors quoted Seiber et al., 1986 as saying that the vapor pressure at 20 °C is 2.0 x 10^{-5} Pa, and the Henry's Law constant is 1.7 x 10^{-7} atm m^3/mol. They used a water solubility of 30 ppm, which is consistent with the 27.5 ppm

solubility from the registrant. The authors also speculated that volatility from granular material lying on leaves and floating slicks on the water surface led to higher air concentrations at day zero than on subsequent days.

COMMENTS:

None

DATA EVALUATION RECORD 9

CHEM 108401 Thiobencarb §165-3

FORMULATION--12--EMULSIFIABLE CONCENTRATE (EC)

STUDY ID 43148201
Green, C.A. 1994. Accumulation of thiobencarb and metabolites in crops irrigated with water treated with Bolero 8 EC herbicide. Valent ID No. V-93-10610; A & L Mid West Laboratories, Inc. ID No. 3-288-0859 and 3-288-0861; Chemtec ID. No. R33-93. Unpublished study performed by Valent USA Corporation, Dublin, CA; A & L Mid West Laboratories, Inc, Omaha, NE; and Chemtec, Chico, CA. Unpublished study submitted by Valent USA Corporation, Walnut Creek, CA.

DIRECT REVIEW TIME = 57

REVIEWED BY: K. Ferguson
TITLE: Task Leader
ORG: Dynamac Corporation
TEL: 301-417-9800

APPROVED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERCB/EFED/OPP
TEL: 703-305-5925

J. Breithaupt 5/22/96

SIGNATURE:

CONCLUSIONS:

Accumulation - Irrigated Crops

1. The study is acceptable and satisfies the 165-3 data requirement for thiobencarb.

2. Thiobencarb (S-4-chlorobenzyl diethylthiocarbamate) was detected (≤0.07 ppm) in the tops of table beets grown in plots of clay soil in California that were sprinkler-irrigated five times at 8- to 13-day intervals with water containing thiobencarb (Bolero 8 EC, 85% emulsifiable concentrate) at approximately 200 ppb. Thiobencarb was not detected (<0.01 ppm) in either the beet root or in tomato fruits grown under similar conditions. In addition, the potential degradate 4-chlorobenzylmethyl sulfone was not detected in beet tops or roots, or in tomato fruits. In the 0- to 6-inch depth of the treated soil, thiobencarb and the degradate thiobencarb sulfoxide were 0.04-0.13 and ≤0.02 ppm, respectively, at all sampling intervals, with no apparent pattern of accumulation or decline.

METHODOLOGY:

Three plots (each 100 x 40 feet) of clay soil (26% sand, 28% silt, 46% clay, 1.4% organic matter, pH 7.0, CEC 30 meq/100 g) located near Richvale, California, were planted to lettuce, table beets, or tomatoes on June 25, 1993 (Figure D.2). Three additional plots (each 100 x 40 feet), separated from the test plots by a 100-foot wide buffer of corn, were planted as described and designated as controls. The tomato plants were replanted on July 12, 1993. Because of crop failure, the lettuce was reseeded on July 12, 1993; this seeding also failed. The well water used for irrigation (pH 7.6, total hardness 135 mg/L) was collected prior to and following the study, and irrigation ditch water was collected prior to the application of thiobencarb. Thiobencarb (S-4-chlorobenzyl diethylthiocarbamate; Bolero 8 EC, 85% emulsifiable concentrate, Valent USA) was mixed into irrigation water at 200 ppb, and applied to the crops via sprinkler five times, at 8- to 13-day intervals, between August 6 and September 16 (8/6, 8/19, 8/30, 9/7, and 9/16). Approximately 1-inch of water (7270 gallons) containing 8 mL of the formulated thiobencarb was applied to the test plots during each irrigation event [page 97]. To establish the application rate, aliquots of the treated irrigation water were collected for analysis following mixing and prior to irrigation. Each plot was divided into 25 subplots (each 8 x 20 feet) for the purpose of sampling. Three soil cores (2.5-cm diameter, 0- to 6-inch depth) were collected from each plot prior to and at the time of crop planting, prior to the first irrigation, 1 day after each of the first four irrigations, and 1 and 5 days after the fifth irrigation. Duplicate samples of the fruit from tomatoes in the treated plots and single samples of the tomatoes in the untreated plots were collected prior to treatment, 1 day after the third irrigation, and 1 and 5 days after the fifth irrigation (25, 42, and 46 days after the initial irrigation). Duplicate samples of the beets (tops and roots) in the treated plots and single samples in the untreated plots were collected prior to treatment, 1 day after the third irrigation and 5 days after the fifth irrigation. The samples were stored on ice in a cooler between collection and arrival at the field laboratory.

Water samples were shipped frozen (initial samples) or refrigerated to the analytical laboratory; in general, water samples were analyzed within 8 days of collection. Soil and crop samples were stored frozen for approximately 24 hours prior to being shipped frozen to the analytical laboratory. Soil samples were stored frozen for up to 123 days prior to analysis. Crop samples were stored frozen for 44 to 119 days prior to analysis.

All water samples were analyzed for thiobencarb using Method RM-16W-4. Aliquots of the water were partitioned with a mixture of hexane and NaCl by shaking for 2 minutes. The hexane layer was filtered through anhydrous sodium sulfate, then concentrated to dryness by rotary evaporation. The resulting residues were dissolved in ethyl acetate, and aliquots of the ethyl acetate solutions were analyzed

using GC with a nitrogen-phosphorus detector. Sample chromatograms were compared to those of a thiobencarb standard chromatographed under the same conditions. The limit of detection for thiobencarb was ≤0.004 ppm. Recovery efficiencies from water samples fortified with thiobencarb at 0.01 or 0.2 ppm were 93-107% of the applied.

Soil samples were analyzed for thiobencarb and the degradate thiobencarb sulfoxide using Method RM-16A-5S. Soil was extracted with a mixture of ethyl acetate and sodium sulfate by mixing for 5 minutes. The extract was filtered through anhydrous sodium sulfate, then concentrated to dryness by rotary evaporation. The resulting residues were dissolved in ethyl acetate, and aliquots of the ethyl acetate solutions were analyzed for thiobencarb using GC as described. Additional aliquots of the ethyl acetate solutions were concentrated to dryness, and the resulting residues were dissolved in acetonitrile:water (30:70, v:v) and analyzed for thiobencarb sulfoxide by HPLC using an Adsorbosphere C-18 column eluted with a gradient of acetonitrile:water (30:70 to 90:10); the column was equipped with UV (210 nm) detection. Sample chromatograms were compared to those of a thiobencarb sulfoxide standard chromatographed under the same conditions. The limits of detection for thiobencarb and thiobencarb sulfoxide were 0.01 ppm. Recovery efficiencies from soil samples fortified with thiobencarb at 0.1 ppm were 96-127% of the applied; recovery efficiencies from soil samples fortified with thiobencarb sulfoxide at 0.1 ppm were 76-100%.

Crop samples were analyzed for thiobencarb and the potential degradate 4-chlorobenzylmethyl sulfone using Method RM-16A-5. Crop tissues were ground with dry ice when necessary, then extracted three times with ethyl acetate by blending for 5 minutes; after each extraction, the extract was filtered through glass wool and anhydrous sodium sulfate. The extracts were combined, then concentrated to dryness by rotary vacuum evaporation at ≤40 C. The resulting residues were mixed with hexane:acetonitrile (2:1, v:v) by shaking for 1 to 2 minutes. The acetonitrile was drained from the mixture, and the hexane was re-extracted twice with additional acetonitrile. The acetonitrile extracts were combined and concentrated to dryness in a heated (≤40 C) waterbath. The resulting residues were dissolved in hexane and filtered through an alumina column. Thiobencarb was eluted from the column with ether:hexane (15:85); 4-chlorobenzylmethyl sulfone was eluted from the column with acetone:ether (25:75). The column eluates were concentrated to near dryness on a vacuum rotary evaporator, dissolved in acetone, and concentrated to dryness on a vacuum rotary evaporator. The dried thiobencarb residues were dissolved in hexane, and aliquots of the solutions were analyzed using GC as described. The dried 4-chlorobenzylmethyl sulfone residues were dissolved in ethyl acetate, and aliquots were analyzed using GC with flame-photometric detection (in the sulfur mode) and/or electron-capture detection. The limits of detection for thiobencarb and 4-chlorobenzylmethyl sulfone were 0.01 ppm. Recovery efficiencies from crop samples fortified with thiobencarb at 0.02 or 0.1 ppm were 70-93% of the applied; recovery

efficiencies from crop samples fortified with 4-chlorobenzylmethyl sulfone at 0.02 or 0.1 ppm were 70-97%.

DATA SUMMARY:

Thiobencarb (S-4-chlorobenzyl diethylthiocarbamate) was detected (≤0.07 ppm) in the tops of table beets grown in plots (100 x 40 feet) of clay soil in California that were sprinkler-irrigated five times at 8- to 13-day intervals with water containing thiobencarb (Bolero 8 EC, 85% emulsifiable concentrate) at approximately 200 ppb (Table C). Thiobencarb was not detected (<0.01 ppm) in either the beet root or in tomato fruits grown under similar conditions (Tables B and D). In addition, the potential thiobencarb degradate 4-chlorobenzylmethyl sulfone was not detected in beet tops or roots, or in tomato fruits.

In the 0- to 6-inch depth of the treated soil 1 day following each irrigation, thiobencarb ranged from 0.05 to 0.13 ppm; in the treated soil 5 days following the fifth irrigation, thiobencarb was 0.04-0.05 ppm (Table I). Thiobencarb sulfoxide was ≤0.02 ppm in the treated plots at all sampling intervals.

During the treatment period, the concentration of thiobencarb in the irrigation water ranged from 189 to 233 ppb (excluding outliers; Table A). Throughout treatment (8/6/93 to 9/21/93), the air temperatures ranged from 50 to 100 F, and the soil temperatures (depth not specified) ranged from 67 to 87 F. No precipitation was received during this period; the site received approximately 5 inches of irrigation water. The depth to the water table was 15-25 feet, and there was no subsurface drainage.

COMMENTS:

1. The study author stated that the selection of analytes for the crops in this study was based on results previously obtained in metabolism studies for thiobencarb in celery and rice (Accession No. 072984 and MRID 42384701), in which thiobencarb and 4-chlorobenzylmethyl sulfone were identified as possible residues in crops. The selection of analytes for the soil in this study was based on results obtained in a field dissipation study (MRID 42003404), in which thiobencarb and thiobencarb sulfoxide were identified as soil residues. The irrigation water was analyzed for thiobencarb only, since it was sampled almost immediately after mixing and was used immediately after sampling.

2. Thiobencarb was detected at 0.03-0.06 ppm in the 0- to 6-inch depth of the soils prior to treatment, and at 0.03-0.08 ppm in the untreated soils during the period of treatment. Thiobencarb sulfoxide was detected at up to 0.05 ppm in the soil prior to treatment and up to 0.04 ppm in the untreated soils during treatment. The study author stated that the test plots had been fallow for the preceding 3 years, but that the adjacent field was planted to rice.

and had been treated with thiobencarb in 1993. It could not be determined if the measured residues were the result of contamination of the test site or of interference by other soil components with the analyses. The presence of thiobencarb and thiobencarb sulfoxide in the untreated soil did not appear to affect the study results, since residues in the plant tissues were lower than those detected in the soil.

3. The study author suggested that the low concentrations of thiobencarb in three irrigation water samples were a result of improper handling following sampling; two of the samples arrived at the analytical laboratory at room temperature rather than refrigerated, and "degradation of thiobencarb from heat is likely" [page 24]. No similar indication of improper handling was noted for the third atypical sample.

4. The study author stated that the stability of thiobencarb and thiobencarb sulfoxide during 180 days of frozen storage in soil and water matrices had been established in MRID 42003404, and that the recommended holding time for water samples stored under refrigeration was $\leq$7 days [page 19]. To supplement the frozen stability data to include crops, an ancillary experiment was conducted to determine the stability of thiobencarb and the degradate 4-chlorobenzylmethyl sulfone in tomatoes, table beet tops, and table beet roots during frozen storage. Ten subsamples of the macerates of each commodity were weighed (25 g) into plastic bags and treated with 0.1 ppm of thiobencarb and 0.1 ppm of 4-chlorobenzylmethyl sulfone. Two samples of each crop were analyzed immediately, the remainder were stored frozen at -20 C until analysis. After 29-32, 61-62, and 92-93 days of frozen storage, duplicate samples were removed from the freezer. At each sampling interval, a freshly fortified sample was analyzed with the stored samples. The frozen and fresh samples were extracted and analyzed as described. There was no apparent degradation of thiobencarb and 4-chlorobenzylmethyl sulfone during approximately 3 months of frozen storage. For thiobencarb, the adjusted percent recovery from the frozen samples was 88-107% of the applied for tomatoes, 65-99% for beet tops, and 77-107% for beet roots. For 4-chlorobenzylmethyl sulfone, the adjusted percent recovery from the frozen samples was 100-118% of the applied for tomatoes, 90-125% for beet tops, and 93-106% for beet roots.

   The study author stated that the frozen storage stability study is ongoing, and that results through 6 months will be submitted when available.

5. Both initial and replant seedings of lettuce failed to mature. The initial planting failed prior to the initiation of the treatment, so the failure of the crop appeared to be unrelated to the presence of thiobencarb in the irrigation water. Field notes provided with the study attribute the lettuce failure to weather conditions.

6. A preliminary study was conducted to establish the necessary mixing time, and the concentration obtained, for the thiobencarb tank mix. It was determined that a 2-hour mixing would ensure a homogeneous treatment solution, and that an application of 1.1 mL Bolero 8EC per 1000 gallons of water would provide a treatment solution of 200 ppb.

7. The plots were irrigated with untreated water on 6/28, 7/12, and 7/26/93. Irrigation ditch water was collected prior to the application of thiobencarb, but not during treatment. It could not be determined if the sites were irrigated with sufficient water to have standing water on the plots for any length of time.

8. The units for the cation exchange capacity were not reported, but were assumed by the Dynamac reviewer to be "meq/100 g".

9. The slope of the test site was not reported.

DATA EVALUATION RECORD 10

CHEM 108401 Thiobencarb §165-4

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 42460401
Thacker, J.D., K.A. Strauss, and G.J. Smith. 1992. Thiobencarb: A metabolic fate study with the bluegill (Lepomis macrochirus). Laboratory Project ID: 263E-101. Unpublished study performed by Wildlife International Ltd., Easton, MD, and submitted by Valent U.S.A. Corporation, Walnut Creek, CA, for K-I Chemical U.S.A., Inc.

DIRECT REVIEW TIME = 30

REVIEWED BY: M. Dillman
TITLE: Staff Scientist
ORG: Dynamac Corporation
TEL: 301-417-9800

APPROVED BY: J. Breithaupt
TITLE: Agronomist
ORG: ERCB/EFED/OPP
TEL: 703-305-5925

J. Breithaupt 5/22/96

SIGNATURE:

CONCLUSIONS:

Laboratory Accumulation - Fish

1. The study is acceptable and satisfies the 165-4 data requirement for thiobencarb.

2. Thiobencarb residues accumulated in juvenile bluegill sunfish exposed to [^{14}C]thiobencarb at 0.05 mg/L, with maximum bioconcentration factors of 128x, 639x, and 411x for edible (muscle) tissue, nonedible tissue, and whole fish, respectively. The degradates 4-chlorobenzylmethylsulfoxide, thiobencarb sulfoxide, desethylthiobencarb, and 2-hydroxythiobencarb were identified in edible and nonedible tissue. By day 3 of the depuration period, 93-95% of the accumulated [^{14}C]residues were eliminated from the tissues.

METHODOLOGY:

Flow-through aquatic exposure systems were prepared using four 55-L Teflon-lined polyethylene aquaria filled to a volume of 45 L. Aerated, filtered well water (pH 7.3-8.2, total hardness 144-160 mg/L

as $CaCO_3$, and alkalinity 186-200 mg/L as $CaCO_3$) was provided to each aquarium at a rate of 10 turnovers per day. The aquaria were immersed in a temperature-controlled water bath (enclosed in a plexiglass ventilation hood) maintained at 22 ± 1 C under fluorescent lamps on a 16-hour photoperiod. Two of the aquaria (Chambers A and B) were continuously treated at a nominal concentration of 0.05 mg/L with uniformly phenyl ring-labeled [^{14}C]thiobencarb (S-4-chlorobenzyl diethylthiocarbamate; radiochemical purity >99%, specific activity 32.5 mCi/mMol, New England Nuclear), dissolved in N,N-dimethylformamide. The two remaining aquaria (Chambers A and B) were continuously treated with pesticide-free N,N-dimethylformamide (0.048 mL/L), and served as untreated solvent controls. The flow-through systems were allowed to equilibrate for 3 days prior to addition of the fish. Triplicate water samples (5 mL) were collected from each of the aquaria in the treated and control systems at 1 and 2 days before initiation of the exposure period.

Juvenile bluegill sunfish (Lepomis macrochirus; mean length 43 mm, mean weight 2.05 g) were maintained in culture tanks for 14 days prior to initiation of the exposure period. After the holding period, 450 fish were transferred to each of the four test aquaria. Duplicate or triplicate water samples (1 L) and five fish were collected from both aquaria in the treated and control systems after 0, 0.3, 1, 3, 7, 10, 14, 21, and 28 days of exposure. Following the 28-day exposure period, the water in each aquarium was replaced with pesticide- and solvent-free water (method unspecified) for a 14-day depuration period. During the depuration period, triplicate water samples (1 L) and five fish were collected at 0.3, 1, 3, 7, 10, and 14 days. For metabolite identification, duplicate water samples (1 L) were collected immediately after initiation of the exposure period, after 14 and 28 days of exposure, and after 7 and 14 days of depuration; 45 fish were collected after 14 and 28 days of exposure, and after 7 and 14 days of depuration.

Analysis of fish tissues: At each sampling interval, four of the five fish were divided into edible (muscle) and nonedible tissue, then composited and homogenized according to tissue type; the remaining fish was homogenized for whole-fish analysis. For determination of total [^{14}C]residues, triplicate subsamples of the tissue samples (edible, nonedible, and whole fish) were analyzed by LSC following combustion.

The additional fish samples collected for metabolite identification were composite as edible and nonedible tissue. Subsamples (approximately 25 g) of the composite tissues were extracted three times with acetone (3 mL/g tissue); after each extraction, the slurries were centrifuged, and the supernatants were decanted and combined. The combined acetone extracts were concentrated under vacuum; the remaining oily residue was redissolved in acetonitrile, and the solution was extracted three times with hexane. After each extraction, the hexane layers were removed and combined. Aliquots of the acetonitrile solution and the combined hexane extracts were

analyzed separately by LSC. The solutions were concentrated under vacuum, and aliquots were analyzed by HPLC using an LC-18-DB column eluted with a nonlinear acetonitrile:water gradient in 1% acetic acid (by volume), and with UV (230, 240, and 260 nm) detection. For compound identification, the samples were cochromatographed with a mixed reference standard of thiobencarb and the degradates desethylthiobencarb, 4-chlorobenzylmercaptan, 4-chlorobenzylmethylsulfone, 4-chlorobenzylhippuric acid, 4-chlorobenzaldehyde, 4-chlorobenzoic acid, 4-chlorobenzylmethylsuflide, 4-chlorobenzylmethylsulfoxide, 4-chlorobenzylalcohol, and thiobencarb sulfoxide; for quantitation, HPLC eluate fractions were collected at 1-minute intervals and analyzed by LSC. The remaining tissue pellets were extracted three times with methanol:water (2:1, v:v; 2 mL/g tissue); after each extraction, the slurries were centrifuged, and the supernatants were decanted and combined. Aliquots of the combined methanol:water extracts were analyzed by LSC, and subsamples of the tissue pellets were analyzed by LSC following combustion. After LSC analysis, the methanol:water extracts were concentrated under vacuum, then diluted with acetonitrile; aliquots of the acetonitrile solutions were analyzed by HPLC as described above. For confirmation of compound identities, aliquots of acetonitrile, hexane, and methanol:water extracts of edible and nonedible fish tissues were analyzed by one-dimensional TLC on Si250F plates developed in chloroform:ethyl acetate (4:1, v:v); unlabeled reference standards of thiobencarb and various degradates were cochromatographed with the samples and visualized by UV. Radioactive areas on the TLC plates were located by autoradiography (Figure 2). In an attempt to identify an unknown degradate isolated in TLC analysis, the combined acetonitrile extracts of the nonedible tissue collected after 28 days of exposure were prepared for HPLC analysis by TLC on preparatory plates developed in chloroform:ethyl acetate (4:1, v:v); radioactive areas corresponding to the unknown degradate and desethylthiobencarb were extracted from the plate (method unspecified), and aliquots of the extracts were analyzed by HPLC using a reverse phase, microbore C-18 column eluted with a linear acetonitrile:water gradient; the HPLC eluate was continuously analyzed by MS.

For characterization of non-extractable [^{14}C]residues as acid- and base-hydrolyzable, subsamples (1 g) of the extracted tissue pellets were further extracted with 1 N HCl by continuous shaking and heating at 80 C. After extraction for 1 hour, the slurries were centrifuged, and the supernatants were removed and filtered. After three rinses with deionized water, the remaining pellets were extracted with 6 N NaOH by intermittent shaking and heating at 80 C. After extraction for 21-24 hours, the slurries were centrifuged, and the supernatants were removed and filtered. Aliquots of the HCl and NaOH extracts were analyzed by LSC, and subsamples of the remaining tissue pellets were analyzed by LSC following combustion (Figure 3).

Analysis of water samples: For determination of total [^{14}C]residues, triplicate aliquots of one of the water samples collected at each sampling interval were analyzed directly by LSC; unused water samples

were stored at -14 C. The additional water samples collected for metabolite identification were acidified to a pH of approximately 2 and partitioned three times with methylene chloride (100 mL); after each extraction, the organic layers were removed and combined. Aliquots of the combined methylene chloride extract and remaining water layer were analyzed by LSC. The combined extracts were concentrated under vacuum. The remaining water layer was extracted through a C-18 solid phase extraction cartridge, and residues were eluted from the cartridge with acetone (3 mL). The acetone eluate and methylene chloride extract were combined, and evaporated under vacuum; the remaining residue was diluted with acetonitrile. An aliquot of the acetonitrile solution was analyzed by LSC; an additional aliquot was analyzed by HPLC as described above using an LC-18-DB column eluted with a nonlinear acetonitrile:water gradient in 1% acetic acid (by volume), and with UV (230, 240, and 260 nm) detection (Figure 1).

DATA SUMMARY:

[^{14}C]Thiobencarb residues accumulated in juvenile bluegill sunfish exposed to uniformly phenyl ring-labeled [^{14}C]thiobencarb (S-4-chlorobenzyl diethylthiocarbamate; radiochemical purity >99%) at a nominal concentration of 0.05 mg/L for 28 days under flow-through conditions. Maximum bioconcentration factors were 128x, 639x, and 411x for edible (muscle) tissue, nonedible tissue, and whole fish, respectively (Tables 8 and 9). Maximum mean concentrations were 5.86 mg/kg for edible tissue (28 days), 25.8 mg/kg for nonedible tissue (3 days), and 15.3 mg/kg for whole fish (1 day). Four degradates,

4-chlorobenzylmethylsulfoxide,

thiobencarb sulfoxide,

desethylthiobencarb, and (tentatively)

2-hydroxythiobencarb,

were identified in the edible and nonedible fish tissues.

Based on HPLC analyses of extracts from the edible tissues, [^{14}C]thiobencarb was 1.81 and 1.75 mg/kg after 14 and 28 days of exposure, respectively; based on analysis of extracts from the nonedible tissues, [^{14}C]thiobencarb was 3.40 and 4.99 mg/kg after 14 and 28 days of exposure, respectively (Tables 16 and 17). After 14 and 28 days of exposure, 4-chlorobenzylmethylsulfoxide was 0.38 and 0.71 mg/kg, respectively, in the edible tissues and 1.01 and 1.33 mg/kg, respectively, in the nonedible tissues. After 14 and 28 days of exposure, thiobencarb sulfoxide was 0.09 and 0.20 mg/kg, respectively, in the edible tissues and 0.86 and 1.56 mg/kg, respectively, in the nonedible tissues. Based on TLC

characterization and HPLC quantitation of extracts from the edible tissues, desethylthiobencarb plus an unknown, tentatively identified by HPLC-MS as 2-hydroxythiobencarb, were a combined total of 0.64 and 1.25 mg/kg after 14 and 28 days of exposure, respectively; based on analysis of extracts from the nonedible tissues, the combined total was 8.34 and 7.01 mg/kg after 14 and 28 days of exposure, respectively.. After 28 days of exposure, uncharacterized extractable [^{14}C]residues (reportedly distributed across approximately 15 individual compounds) were 1.74 and 4.85 mg/kg in the edible and nonedible tissue, respectively. Also, after 28 days of exposure, unextractable [^{14}C]residues were 0.21 and 1.04 mg/kg in the edible and nonedible tissue, respectively. In the edible tissues, 33.6-35.9% of the unextractable [^{14}C]residues were acid-hydrolyzable, and 63.1-65% were base-hydrolyzable; in the nonedible tissues, 47.1-54.0% of the unextractable [^{14}C]residues were acid hydrolyzable, and 44.1-50.4% were base-hydrolyzable (Table 12).

By day 0.3 of the depuration period, the concentration of accumulated [^{14}C]residues decreased by 83% in the edible tissue, and by 65-66% in the nonedible tissue and whole fish; by day 3, the concentration of [^{14}C]residues decreased by 93-95% in all fish tissues and the whole fish (reviewer-calculated from Tables 8 and 9).

HPLC characterization results for the acetonitrile extracts of treated water samples collected throughout the study were reportedly "unremarkable"; actual data were not provided. Throughout the exposure period, mean [^{14}C]residues in the treated water of the two test aquaria were 0.027-0.055 mg/L (Table 8). Throughout the entire study, the temperature of the water in the four aquaria (treated and control) ranged from 21.5 to 22.3 C, the dissolved oxygen content was 3.4-8.2 mg/L, and the pH was 7.3-8.2.

COMMENTS:

1. Unidentified extractable [^{14}C]residues that totaled up to 1.74 mg/kg in the edible tissue and 4.85 mg/kg in the nonedible tissue were not individually quantified. According to the study authors, these [^{14}C]residues were distributed over approximately 15 unknowns in HPLC analysis.

2. According to the study authors, no data were provided for HPLC characterization analysis of the water samples because the data were "unremarkable". In the aqueous photolysis study submitted concurrently (Study 1, MRID 42257801), thiobencarb degraded only slightly (half-life of 190 days) in an aqueous solution (pH 7) which was irradiated in natural sunlight for 30 days; additionally thiobencarb is stable to hydrolysis. Consequently, it is reasonable to expect that thiobencarb did not degrade in the test water for this fish accumulation study.

3. Throughout the study, fish were fed commercial flaked fish food; excess feed was siphoned from the test chambers approximately 30 minutes after feeding. Feeding and sampling schedules were coordinated so that the digestive tracts of the fish could clear for at least 4 hours prior to sampling.

4. On day 15 of the exposure period, 100 fish were removed from each aquaria to minimize overcrowding; additionally, dissolved oxygen content dropped below 60% of saturation at day 10 in three of the aquaria and at day 27 in solvent control chamber B. All of the mortalities (8-13% by the end of the depuration phase) were attributed to either overcrowding or low dissolved oxygen content; mortalities in the treated aquaria were not considered to be treatment-related.

5. The average method detection limit for LSC was 25.9 cpm; limits of quantitation were 0.009 mg/L in water (5 mL sample), and 0.21 mg/kg in tissue (0.08 g sample). The approximate detection limit for HPLC analysis was 0.0021 ug.

6. Forty-one percent of the [^{14}C]residues extracted from edible tissues collected after 14 days of depuration could not be accounted for after HPLC analysis. The study authors stated that it is likely that the [^{14}C]residues were distributed at undetectable levels across the approximately 15 unidentified metabolites observed in the extracts from the exposure phase; of the [^{14}C]residues extracted from the nonedible tissues collected after 14 days of depuration, 90% were accounted for after HPLC analysis.

7. A proposed metabolic pathway for thiobencarb has been detailed in Figure 11.

8. The nominal test concentration of thiobencarb (0.05 mg/L) is <1/10th of the reported LC_{50} of 1.3 mg/L in fish.

9. The phenyl ring-labeled [^{14}C]thiobencarb was diluted (2.08 mg:106.2 mg) with unlabeled thiobencarb (purity 96.9%, Chevron Chemical) prior to use.

Note: A DER for molinate is attached to the end of this DER.

DATA EVALUATION RECORD
AQUATIC INVERTEBRATE LIFE CYCLE TEST
GUIDELINE 72-4(B)

1. **CHEMICAL**: Thiobencarb PC Code No.: 108401

2. **TEST MATERIAL**: Technical grade thiobencarb
Purity: Not reported

3. **CITATION**

Authors:	Bailey, Howard C.
Title:	Acute and chronic toxicity of the rice herbicides thiobencarb and molinate to Oppossum shrimp (*Neomysis mercedis*)
Publication Date:	1993
Laboratory:	SRI International
Sponsor:	California State Water Resources Control Board
MRID No.:	43976801

4. **REVIEWED BY**: F. Nicholas Mastrota, Biologist, ERCB

Signature: **Date:** 4/15/96

5. **PEER REVIEW BY**: Robert K. Hitch, Ecologist, ERCB

Signature: **Date:** 4/23/96

6. **STUDY PARAMETERS**

Age of Test Organism:	Not reported
Definitive Test Duration:	56 days
Study Method:	Flow-through
Type of Concentrations:	Mean measured

7. **CONCLUSIONS**: This published paper provides supplemental information on the chronic toxicity of thiobencarb to saltwater shrimp and shrimp-like species. It is best described as a shrimp early life-stage test. This test is scientifically sound, but does not satisfy the guideline requirements for a aquatic invertebrate life-cycle test since effects on reproduction were not evaluated. The results show that chronic exposure to thiobencarb at concentrations greater or equal to 6.2 µg/L can significantly reduce the survival of young opossum shrimp.

Results Synopsis
NOEC: 3.2 µg ai/L LOEC: 6.2 µg ai/L
MATC: 4.5 µg ai/L

LOEC's for specific effects
Larvae Survival: 6.2 µg ai/L
Growth (Length): Not determined

8. ADEQUACY OF THE STUDY

A. Classification: Supplemental.

B. Rationale: The test was not a life-cycle test and have several grave deviations from the guidelines for a life-cycle aquatic invertebrate test (GLN 72-4b). The experiment design was similar to that used for a fish early life-stage test (GLN 72-4a), but it cannot be used to fulfill this guideline since the test species was not a fish. Also, the published paper was lacking some information required for analyzing this study.

C. Repairability: None.

8. MAJOR GUIDELINE DEVIATIONS:

1) The experimental design was not a life-cycle test. Adult shrimp were not paired. Instead, gravid shrimp were selected from the parental stock and placed into test solutions to provide offspring. The young were then maintained in the test solutions until the termination of the test, at which time their survival and length were recorded. Thus, this study examines developmental effects rather than reproductive effects. Although the experimental design is scientifically sound, it is not acceptable for fulfilling the data requirement for the life-cycle aquatic invertebrate test with an aquatic invertebrate (guideline 72-4b).

2) The endpoints measured differed from those required for the life-cycle aquatic invertebrate test. Survival data was recorded on the young rather than the adult organisms, and survival of males and females were not recorded separately. Although the number of young produced was measured, this measure does not reflect effects on reproduction since the females were already gravid when they were first exposed. The dry weights were not measured for either the first or second generation. The lengths of the young alive at the end

of the study were measured, but not separately for males and females. Also, results on length were only reported for concentrations that did not have a significant decrease in survival. A reduction in survival should not preclude the analysis of effects on length.

3) The duration of the acclimation period was not reported.

4) Therefore, there was an insufficient number of test organisms per treatment level. The ASTM guidelines for a mysid life-cycle toxicity test (E 1191-90) states that at least two compartments should be placed in each two replicate chambers at each treatment level, and at least 15 organisms should be placed in each of these compartments. This means that there should be at least 60 organisms per treatment level. In the present test, two replicate test chambers were used without compartments, and 15-20 shrimp were placed in each chamber. Therefore, only 30-40 organisms were used per treatment level.

5) Summary statistics were only reported on a per treatment level basis. Summary statistics for each replicate is needed to confirm statistical analysis.

6) The dilution water was dechlorinated tap water, which is not recommended since dechlorination is usually not complete.

7) A serial diluter system was not used to deliver test concentrations. Instead, separate solutions were prepared for each of five test concentrations which were delivered to test chambers from Mariotte bottles.

8) Crystallizing dishes were used for test vessels. These dishes are not designed for this purpose and may not be appropriate. The volume of these dishes was not reported.

9) The flow rate was approximately 2 volumes/24 h, whereas it should have been 5 to 10 volumes/24 h.

10) Quality assurance and GLP compliance statements were not provided.

11) Observations for clinical signs of toxicity were not reported.

10. MATERIALS AND METHODS:

A. Biological System:

Guideline Criteria	Reported Information
Species: An estuarine shrimp species, preferably *Americamysis bahia*.	Opossum shrimp (*Neomysis mercedis*)
Duration 28 days/one generation	56 days
Source (or supplier)	Montezuma Lough, Sacramento-San Joaquin Delta, CA
Parental Acclimation 1) Parental stock must be maintained separately from the brood culture in dilution water and under test conditions. 2) Mysids should be in good health.	Parental stock was maintained in dilution water and under test conditions.
Parental Acclimation Period At least 14 days	Not reported
Chamber Location: Treatments should be randomly assigned to test chamber locations.	Adult gravid shrimp were randomly assigned to treatments. Young produced within each treatment level were pooled and then randomly distributed between the two replicate test chambers.
Duration of the Test: A mysid test must not be terminated before 7 days past the median time of 1st brood release in the control treatment.	Test was terminated 56 days after gravid adults were placed into treatment solutions.

Guideline Criteria	Reported Information
Brood Stock: Test started with mysids: 1) from only one brood stock or 2) from brood stock which has not obtain sexual maturity or had been maintained for > 14 days in a laboratory with same food, water, temperature, and salinity used in the test.	The brood stock was a wild population from the Sacramento-San Joaquin Delta. The duration of acclimation was not reported.
Distribution: **No. of mysids before pairing:** Minimum of 15 mysids per compartment, 2 compartments per chamber, 2 chambers per concentration for a total of 60/level. **No. of mysids after pairing:** ≥ 20 randomly selected pairs/treatment (excess males should be held in separate compartment to replace paired males).	There were two replicate chambers per treatment level. Each chamber held 3 adult gravid shrimp during the first 14 days, and 15-20 young thereafter. During the first 14 days, water from each chamber drained into a second tier chamber that was used to hold the young produced by the gravid females. There were a total of 30-40 shrimp per level (excluding adults). No mysids were paired.
Pairing: 1) Should be conducted when most of the mysids are sexually mature (usu. 10-14 days after test initiation). 2) Should be paired on the same day	Shrimp were not paired. Instead, gravid shrimp were selected from the parental stock and placed into test solutions to provide offspring.
Feeding: 1) Mysids should be fed live brine shrimp nauplii at least once daily. 2) 150 live brine shrimp nauplii per mysid per day or 75 twice a day is recommended.	Shrimp were fed *Artemia* nauplii once daily. Algal and vitamin supplements were also provided three times per week.

Guideline Criteria	Reported Information
Counts: Live adult mysids should be counted 1) at initiation, 2) at pairing, 3) and daily after pairing. 4) Live young must be counted and removed daily. 5) Missing or impinged animals should be recorded.	Counts of adult shrimp were not recorded. Young produced were counted and removed to a separate chamber daily for the first 14 days. Thereafter, the number of young surviving were counted daily.
Controls: Survival in any control chamber (between pairing and test termination) must not be less than 70%.	Survival was not reported per chamber. Overall, the control chambers had 80% survival.
Controls: Negative control and carrier control (when applicable) are required.	The test included a negative control. (No carrier was used.)

Comments: *Neomysis mercedis* is a small, primarily estuarine, crustacean found along the Pacific Coast of North America.

B. Physical System:

121

Guideline Criteria	Reported Information
Test Water: 1) May be natural (sterilized and filtered) or a commercial mixture; 2) During the test, difference between highest and lowest measured salinities must be less than 10 $^{0}/_{00}$ (parts per thousand). Should be measured daily. 3) Salinity should be between 15 and 30 $^{0}/_{00}$. 4) Measured pH should be between 7.6 and 8.2. Must not deviate by more than one unit for more than 48 hours. Should be measured at the beginning, end of test and weekly. 5) Water must be free of pollutants. 6) DO must be measured @ each conc. @ least once a wk. (see details in ASTM)	The test water was artificial sea water prepared from tap water dechlorinated with activated carbon filters. Salinity: Not reported Conductance: 3500 µmhos pH: 6.9 - 7.9 DO: 7.9 - 9.4 mg/L
Test Temperature: 1) Mean measured temperature for each chamber at test termination should be within 1°C of selected test temperature. 2) Each individual measured temperature must be within 3°C of the mean of the time-weighted averages. 3) For mysid shrimp, 27°C is recommended. 4) Whenever temp. is measured concurrently in more than one test chamber the highest & lowest temp. must not differ by more than 2°C.	Test temperature ranged from 17.5 to 18.5 °C
Photoperiod: Recommend 16L/8D.	16 h light / 8 h dark

Guideline Criteria	Reported Information
Dosing Apparatus: 1) Intermittent flow proportional diluters or continuous flow serial diluters should be used. 2) A minimum of 5 toxicant concentrations 3) with a dilution factor not greater than 0.5 and controls should be used.	Diluters were not used. Separate solutions were prepared for each of five test concentrations. Test solutions were delivered to test chambers from Mariotte bottles.
Toxicant Mixing: 1) Mixing chamber is recommended but not required; 2) Aeration should not be used for mixing; 3) It must be demonstrated that the test solution is completely mixed before intro. into the test system; 4) Flow splitting accuracy must be within 10%.	Since a diluter system was not used, there were no mixing chambers.
Test Vessels: 1) Material: all glass, No. 316 stainless steel, or perflorocarbon plastic 2) Size: 250 ml with 200 ml fill volume is preferred; 100 ml with 80 ml fill volume acceptable 3) 90 or 140 mm inside dia. glass Petri dish bottoms with collars made of 200 - 250 um mesh screen.	Crystallizing dishes, 150 mm x 75 mm, were used for test vessels. The depth or volume was not reported.
Covers 1) Renewal: Test vessels should be covered with a glass plate. 2) Flow-through: Openings in the test compartments should be covered with nylon mesh or stainless steel screen.	Not reported.

Guideline Criteria	Reported Information
Flow Rate: 1) Flow rates should provide 5 to 10 volume additions per 24 hr. 2) Flow rate must maintain DO at or above 60% of saturation and maintain the toxicant level. 3) Meter systems calibrated before study and checked twice daily during test period 4) Renewal must not drop below 50% for more than 48 hours.	The flow rate was approximately 2 volumes/24 h
Aeration: 1) Dilution water should be aerated to insure DO concentration at or near 100% saturation. 2) Test tanks may be aerated.	Aeration was not mentioned, but the DO levels were adequate (86-100%).

C. **Chemical System**:

Guideline Criteria	Reported Information
Concentrations: 1) Minimum of 5 concentrations and a control, all replicated, plus solvent control if appropriate. 2) Toxicant conc. must be measured in one tank at each toxicant level every week. 3) One concentration must adversely affect a life stage and one concentration must not affect any life stage. 4) The measured conc. of the test material of any treatment should be at least 50% of the time-weighted average measured conc. for >10% of the duration of the test. 5) The measured conc. for any treatment level should not be more than 30% higher than the time-weighted average measured conc. for more than 5% of the duration of the test.	Test concentrations: 0, 3.2, 6.2, 12.8, 23.5, and 53.4 µg/L Test solutions were sampled weekly. The concentrations of test material was measured using gas chromotagraphy with TSD detection. The CV for measured concentrations was 9.6.
Solvents: 1) Should not exceed 0.1 ml/L in a flow-through system. 2) Following solvents are acceptable: triethylene glycol, methanol, acetone, ethanol.	Aqueous solutions without solvents were used.

11. REPORTED RESULTS:

Guideline Criteria	Reported Information
Quality assurance and GLP compliance statements were included in the report?	No

Guideline Criteria	Reported Information
1) At least 75% of the paired 1st generation females in the control produced young or 2) the average number of young produced by the 1st generation females in the control(s) was more than 3.	Not applicable.
Data Endpoints must include: 1) Survival of first-generation mysids Female Male 2) Number of live young produced per female 3) Dry weight of each first-generation mysid alive at the end of the test Female Male 4) Length of each 1st generation mysid alive at the end of the study Female Male 5) Incidence of pathological or histological effects; 6) Observations of other effects or clinical signs.	Data Endpoints were: 1) Number of young produced per gravid female 2) Mortality of young over 42 days following the 14-day hatching period 3) Mean survival times of young 4) Length of survivors
Raw data included? (Y/N)	No

Effects Data:

Measured Toxicant Conc. (µg/L)	45-Day Percent Mortality	Average Survival Time for Young (days)	Mean Total Length (mm)
Control	80	31	8.4 (SD = 1.8)
3.2	75	29	7.4 (SD = 1.5)
6.2	60	25	
12.8	40	20	
23.5	0	2	
53.4	8	8	

Toxicity Observations: Not reported.

Statistical Results:

Endpoint	Method	NOEC	LOEC
Average survival time for young	Mantel-Cox test	3.2 µg/L	6.2 µg/L
Number of young produced	Dunnett's test	≥ 53.4 µg/L	Not determined
Length	Dunnett's test	≥ 3.2 µg/L	Not determined

Comments:
1) The average survival time at the 6.2 µg/L was marginally significant (P=0.06). Considering the concentration response shown, this was considered a significant treatment-related response.
2) Significant difference in length, compared to the control, was only tested at the 3.2 µg/L test level. There was no significant effect at this level. Although the NOEC and LOEC for effect on length can not be determined, it is clear that this endpoint is not more sensitive than survival time.

12. Reviewer's Statistical Results:

Comments: Statistical results could not be verified since this was a published paper that only provided summary data.

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

SUBJECT: Transmittal of DERs for Acute and Chronic mysid toxicity studies with Thiobencarb--Sh# 108401 (A response to barcode D197655). PRAT Case # 816135.

OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

From: Robert K. Hitch, Ecologist, RKH 7/18/96
Environmental Risk Characterization Branch
Environmental Fate and Effects Division

THRU: Nick Mastrota, Peer Reviewer and Thiobencarb Team Leader
Environmental Risk Characterization Branch
Environmental Fate and Effects Division

THRU: Elizabeth Leovey, Ph.D., Chief,
Environmental Risk Characterization Branch
Environmental Fate and Effects Division

TO: Mark Wilhite, PM 51,
Special Review and Reregistration Division

Please find attached DERs for the following studies:

1. Acute mysid toxicity (MRID 00079117)

2. Chronic mysid toxicity (MRID 00079117)

We judge study #1 to be "Supplemental". It can not fill the requirement 72-3(c) for an acute "estuarine or marine toxicity study with a shrimp". The most important deficieny of the study is that the test organisms were too old.

We judge study #2 to be "Supplemental". It can not fill the requirement 72-4(b) for an Aquatic Invertebrate Life Cycle Study. Another study will have to be provided. The most important deficieny of the study was that controls were not replicated. Recently submitted raw data (MRID 430317-01) did not repair the lack of replication problem. Because of lack of control replication, NOEL's and Geometric means could not be determined. The NOEL's and Geometric means are among the most important endpoints of the chronic mysid study. We converted the study to a regression of dose against effects and we were able to derive the 28 day EC05's for mortality and reproduction so the study is judged "Supplemental".

Attachment: Two (2) Data Evaluation Records (DER's).

136

DATA EVALUATION RECORD[1]

1. **CHEMICAL:** Bolero (thiobencarb). Shaughnessey No. 108401.

2. **TEST MATERIAL:** Bolero® Technical; S-(4-chlorobenzyl)-N,N-diethylthiocarbamate; Lot No. H9028; 95.1% active ingredient (ai); a light orange liquid.

3. **STUDY TYPE:** 72-1 and 72-4. Mysid Acute Toxicity Test and Mysid Life-Cycle Toxicity Test. Species Tested: *Mysidopsis bahia*.

4. **CITATION:** Hollister, T. 1979. Acute and Chronic Toxicity of Bolero® Technical to Mysid Shrimp (*Mysidopsis bahia*). Report No. BP-79-9-141. Prepared by EG & G Bionomics, Pensacola, FL. Submitted by Valent USA Corporation, Walnut Creek, CA. EPA MRID Nos. 79117 (Report) and 430317-01 (Raw Data).

5. **REVIEWED BY:**

Robert K. Hitch, Ecologist, ERCB
Environmental Fate and Effects Division
Signature: Robert K. Hitch
Date: July 18 96

6. **APPROVED BY:**

Nick Mastrota, Peer Reviewer and Thiobencarb Team Leader
Environmental Fate and Effects Division
Nick Mastrota
7-18-96

7. **CONCLUSIONS:** The acute test is scientifically sound but does not meet the requirements for an acute toxicity test using mysids. Test mysids were much older than recommended by the guidelines. No additional study is needed as another mysid study is in ERCB files.

The chronic study provides scientifically sound data when analyzed by regression analysis but does not meet the guideline requirements for a mysid life-cycle toxicity test. We could not determine whether there was true replication in

---

[1]This review was originally writen by Rosemary G. Mora of KBN Engineering (Signed 5 April 1994). The U.S. EPA slightly modified Ms. Mora's text to indicate that some valid information could be derived from the Chronic study via regression analysis and that therefore it should be classified as "Supplemental". Ms. Mora had originally called the chronic study "Invalid" because the controls did not seem to have been replicated.

either the dilution water control or the solvent control and the test concentrations were highly variable during the test. Dry weight of mysids was not measured at test termination and the test organisms were also older than the recommended age. Based on the author's mean measured concentrations, the 96-hour LC_{50} was 288 µg/l. Using the author's data in a regression analysis, the best estimate of the EC05 for reproduction was 9.8 ppb (95%C.I. 1.6 -61 ppb ppb and slope 2.49). The best estimate for the 28 day LC05 was 9.9 (95% C.I. 0 to 24.1 ppb (slope 1.34). Computer printouts from the regression analyses runs are attached.

8. **RECOMMENDATIONS**: N/A.

9. **BACKGROUND**:

10. **DISCUSSION OF INDIVIDUAL TESTS**: N/A.

11. **MATERIALS AND METHODS**:

A. **Test Animals**: *Mysidopsis bahia* were obtained from laboratory cultures. The cultures were maintained in flowing, natural seawater. The mysids used for the acute study were 6-8 days old; those used in the chronic study were 24-48 hours old.

B. **Test System**: Two tests were performed during the course of this study. These tests are henceforth referred to as the acute and chronic tests.

In each test, an intermittent-flow proportional diluter delivered test solutions to test aquaria containing 8 l of test solution. Each aquarium was divided into two separate sections. The flow rate provided ≥3 volume additions to each aquarium per day. Two retention chambers (glass petri dishes with 15-cm high nylon screen collars) were placed in each of two test vessels per treatment. One aquarium was used for the controls (i.e., one section for the solvent control and the other section for the dilution water control).

The target test temperature was 25 ±1°C. The dilution water was filtered (10 µm) natural seawater collected from Big Lagoon, a Gulf of Mexico estuary, Pensacola, FL.

A stock solution (22,000 mg/l for the acute and chronic test) was prepared by dissolving appropriate amounts of the test substance in acetone.

C. **Dosage:** Ninety-six-hour and 28-day flow-through tests. Based on the results of a static acute toxicity test, five nominal concentrations (65, 108, 180, 300, and 500 µg/l) were selected for the acute test. Based on the results of the acute toxicity test, five nominal concentrations (13, 22, 36, 60, and 100 µg/l) were selected for the chronic test. In addition, a dilution water control and a solvent control (21 ml acetone/l) were included in each test. The acetone concentration in the solvent control was the same as that present in the highest test concentration.

D. **Design:** The investigators put five mysids into each test container (a floatng petri dish with a Nitex screen collar). There were 20 mysids per treatment; 10 mysids per control. For the chronic test there is a controversy about whether there was water exchange between the "replicate" test containers in the blank and in the solvent controls. The diagram on the raw data sheet shows no partitions separating test chambers A1 and A2. If this was the case then the two control test chambers (which were labeled A1 and A2) might influence each other via disease, parasitism (etc) and they would, therefore not be true replicates. Dr. Brent Solomon of Valent Corp sent a Fax on Sept. 1995 (attached) indicating that there might have been two separate aquaria for the blank control and two more for the solvent control. However, the raw data show clearly that there were only 10 mysids total in the blank control and 10 mysids total in the solvent control instead of 20 in each as was the case for the treatments. For the treatments it is clear that there were duplicate aquaria.

The mysids were fed brine shrimp nauplii once daily during the chronic test.

Observations of mortality were recorded every 24 hours in both tests. In the chronic test, the time to formation of brood pouches and the number of offspring were also recorded daily. After hatching occurred, a maximum of 10 juveniles (F_1) were isolated within each duplicate test container for continued exposure and observation.

Temperature, dissolved oxygen concentration (DO), salinity, and pH were measured periodically during both tests. Samples were collected from each test vessel on days 0 and 4 for the acute test and on days 0, 4, 7,

11, 14, 18, 21, 25, and 28 for the chronic test. The samples were analyzed to determine exposure concentration using gas chromatography.

E. **Statistics:** For the acute test, the 72- and 96-hour LC_{50} and their 95% confidence interval were calculated using the computer program by Stephan (1977 and 1978).

For the chronic test, analysis of variance and Williams' test were used to determine significant differences in survival and offspring per female between the solvent control and treatments. Survival data were arcsine square-root percentage transformed before the analysis.

12. **REPORTED RESULTS:**

Acute Test

Mean measured concentrations were 40, 94, 177, 235, and 510 µg/l which represent 62-102% of nominal concentrations (Table 1, attached).

No mortality occurred in the dilution water control or the solvent control (Table 4, attached). The 96-hour LC_{50} was 288 µg/l with a 95% confidence interval of 237-356 µg/l.

During this test, the test solutions had a pH of 7.9, a temperature of 25 ±1°C, a salinity of 25-28 parts per thousand (ppt), and a DO of 87-94% of saturation.

Chronic Test

Mean measured concentrations were 11, 19, 30, 50, and 96 µg/l which represent 83-96% of nominal concentrations (Table 2, attached).

Cumulative mortality in the dilution water control and solvent control was 10% at test termination (Table 6, attached). "There appeared to be a meaningful delay in time to brood pouch formation in mysids exposed to a test concentration of 96 ppb" (Table 6, attached). The average number of offspring of mysids exposed to measured concentrations of 50 and 96 ppb was significantly less than that of the solvent control (Table 7, attached). Due to the delay in time to release of offspring at 96 ppb, the F_1 mysids at 96 ppb were exposed for only 2 days post-hatch. No mortality of F_1 mysids occurred in any treatment during post-hatch exposure.

During this test, the test solutions had a pH of 7.6-8.0, a temperature of 25 ±1°C, a salinity of 16-26 ppt, and a DO of 71-101% of saturation.

13. **STUDY AUTHOR'S CONCLUSIONS/QUALITY ASSURANCE MEASURES:** "Based on a chronic laboratory toxicity test, the effect of Bolero Technical on reproduction of mysid shrimp appeared to be significant in mean measured concentrations ≥30 ppb."

This study was conducted before the GLP guidelines were promulgated and would be exempt from GLP requirements.

14. **REVIEWER'S DISCUSSION AND INTERPRETATION OF STUDY RESULTS:**

A. **Test Procedure:** ASTM guidelines (1990) were used to evaluate the chronic test and the SEP to evaluate the acute test. Study weaknesses were as follows:

The mysids must be <24 hours old at test initiation. For the acute study the mysids were 6-8 days old; for the chronic study the mysids were 24-48 hours old.

For both tests, there appears to have been no replication of the blank and solvent controls.

For the chronic study, the mysids were not separated into mating pairs at the time of sexual maturation. Consequently, the ratio of males to females was not one to one. Only females which produced brood pouches were used to determine the number of young per female.

Dry weight was not determined at termination of the chronic test.

During the chronic test, the F_1 were placed in the replicate vessel for continued exposure. F_1 mysids should have been removed daily.

Table 2 indicates that the mean measured concentrations for the chronic test were derived from 8 measurement periods, however, the text and the raw data indicate 9 measurement periods. The reviewer calculated the mean measured concentration from the raw data as 15.6, 18.4, 29.9, 46.4, and 87.1 µg/l. In addition, the measured concentrations were highly variable during the chronic test (pages 242-250, attached). The highest measured concentration ranged from 1.7 to 8.2 times the lowest measured concentration at the same level.

1-11

The photoperiod and the size of the test vessels were not reported for the studies.

B. **Statistical Analysis:** For the acute test, R. G. Mora of KBN used EPA's Toxanal computer program to verify the 96-hour LC_{50} and obtained similar results (printout, attached).

For the chronic test, Robert Hitch of the U.S.EPA evaluated reproduction and survival using nonlinear regression (EFED Nuthatch program) and SAS probit analysis, respectively. Use of the traditional analysis of variance techniques, was not possible since the controls may not have been replicated. Without Analysis of Variance the NOEC and LOEC could not be determined. However, it was possible to use the chronic data in regressions of dose against response. Using the regression techniques, the best estimate of the EC05 for reproduction was 9.8 ppb (95%C.I. 1.6 -61 ppb ppb and slope 2.49). The best estimate for a 28 day LC05 was 9.9 (95% C.I. 0 to 24.1 ppb using the SAS probit procedure; slope 1.34). Computer printouts from the regression analyses runs are attached.

C. **Discussion/Results:** The acute test is scientifically sound but does not meet the requirements for an acute toxicity test using mysids. Test mysids were much older than the current recommended protocols. The chronic study does not meet the guideline requirements for a mysid life-cycle toxicity test, but it provides "supplemental" data. Both the dilution water control and the solvent control did not have true replicates and test concentrations were highly variable during the test. In addition, dry weight was not determined at test termination and test organisms were older than recommended by ASTM guidelines. Based on the author's mean measured concentrations, the 96-hour LC_{50} was 288 µg/l *Mysidopsis bahia*.

D. **Adequacy of the Study:**

(1) **Classification:** Supplemental for the acute test and Supplemental for the chronic test.

(2) **Rationale:** For the acute test, the test organisms were much older than required. For the chronic test, it was unclear whether there is true replication in either the dilution water control or the solvent control, measured concentrations

were highly variable and dry weights of the mysids were not determined at test conclusion.

(3) **Repairability:** No.

15. **COMPLETION OF ONE-LINER FOR STUDY:**

REFERENCE:

ASTM. 1990. Standard Guide for Conducting Life-Cycle Toxicity Tests with Saltwater Mysids. ASTM Designation: E 1191-90.

Nuthatch

THIOBEN : thiobencarb

Williams Test

!!!Williams: not implemented for 1 degrees of freedom.

Dose	Isotone Means
0	4.9
11	4.15
19	4.15
30	3.9
50	1.4
96	1.2

Estimates of EC%

Parameter	Estimate	95% Bounds Lower	95% Bounds Upper	Std.Err.	Lower Bound /Estimate
EC5	9.8	1.6	61.	0.29	0.16
EC10	14.	2.9	64.	0.24	0.21
EC25	24.	8.2	71.	0.17	0.34
EC50	45.	23.	88.	0.10	0.51

Slope = 2.49 Std.Err. = 0.819

Goodness of fit: p = 0.11 based on DF= 3.0 1.0

THIOBEN : thiobencarb

Observed vs. Predicted Treatment Group Means

Dose	#Reps.	Obs. Mean	Pred. Mean	Obs. -Pred.	Pred. %Control	%Change
0.00	2.00	4.90	4.83	0.0660	100.	0.00
11.0	1.00	3.90	4.53	-0.625	93.6	6.39
19.0	1.00	4.40	3.99	0.414	82.5	17.5
30.0	1.00	3.90	3.24	0.662	67.0	33.0
50.0	1.00	1.40	2.20	-0.802	45.5	54.5
96.0	1.00	1.20	1.00	0.198	20.7	79.3

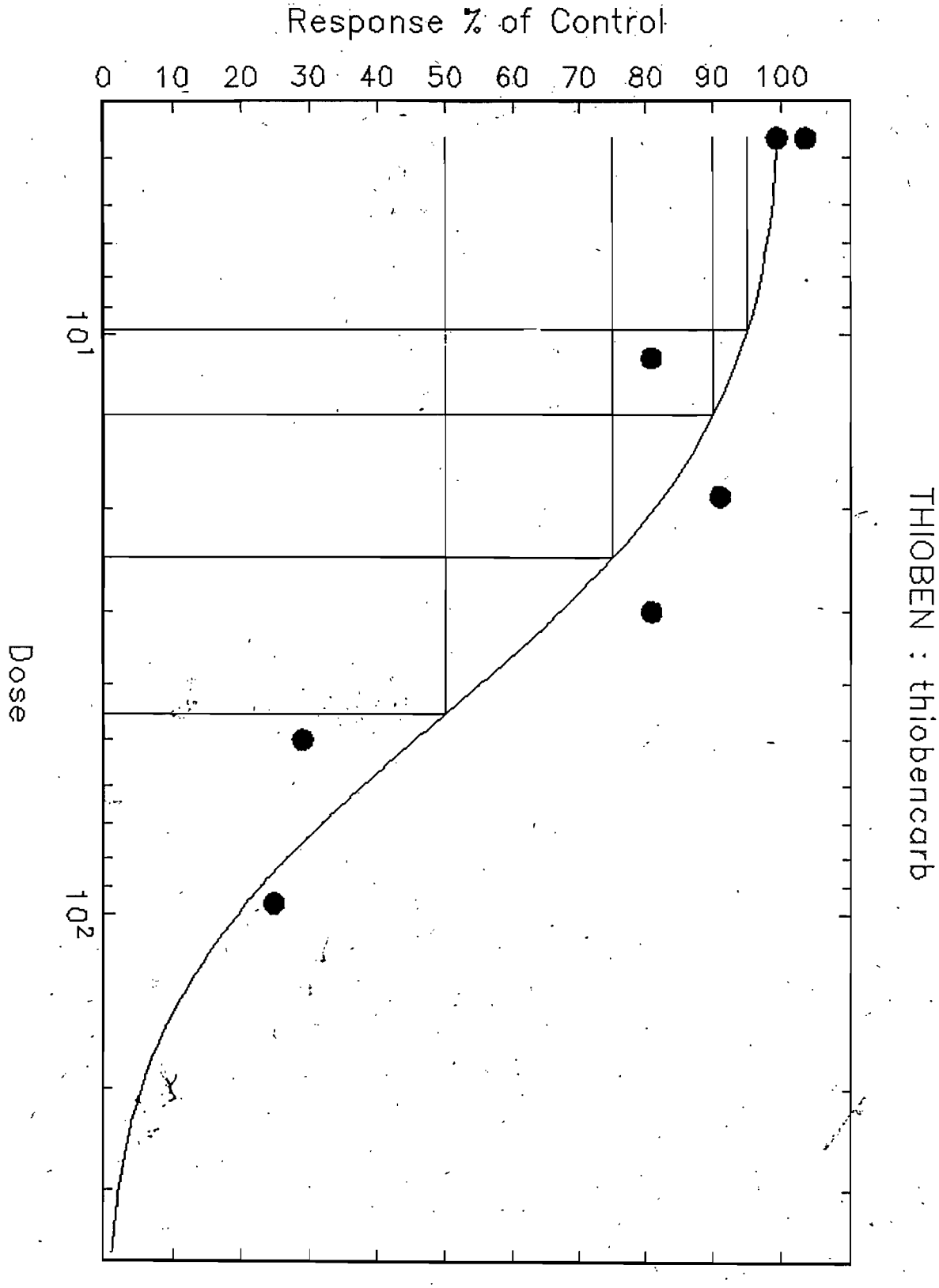
!!!Warning: EC5 not bracketed by doses evaluated.
Toxicity measurement for continuous endpoints, using weighted nonlinear regression, weighting proportional to predicted means.

Reference

R.D. Bruce and D.J. Versteeg. 1992. A statistical procedure for modeling continuous toxicity data. Env. Tox. and Chem. 11:1485-1494.

Input file: THIOBEN

Raw data:


Response % of Control
0 10 20 30 40 50 60 70 80 90 100
Dose
10^1
10^2
THIOBEN : thiobencarb

Program: Nuthatch Date: 1/18/96

Toxicity measurement for continuous endpoints, using weighted nonlinear regression, weighting proportional to predicted means.

Reference

R.D. Bruce and D.J. Versteeg. 1992. A statistical procedure for modeling continuous toxicity data. Env. Tox. and Chem. 11:1485-1494.

Input file: THIOBEN

Raw data:

```
thiobencarb
6
2
1
1
1
1
1
    0
4.8
5.0
    11
3.9
    19
4.4
    30
3.9
    50
1.4
    96
1.2
```

```
options linesize=72;
data;
input chem $ dose n res;
Cards;
 0 20 2
 11  20 3
 19  20 4
 30  20 5
 50  20 6
96 20 9
proc print; run;
proc probit log10 c=0.1;
var dose n res; run;
```

SAS 15:19 Thursday, May 2, 1996 1

OBS	CHEM	DOSE	N	RES
1	0	20	2	11
2	19	20	4	30
3	50	20	6	96

OBS	DOSE	N	RES
1	0	20	2
2	11	20	3
3	19	20	4
4	30	20	5
5	50	20	6
6	96	20	9

Probit Procedure

Iter	Ridge	LogLikelihood	INTERCPT	Log10(DOSE)
0	0	-74.4326608443	0	0
1	0	-56.92782526267	-1.740040621	0.7005315899
2	0	-55.79546911028	-2.597145992	1.1393017327
3	0	-55.71687861562	-2.935041806	1.3223596118
4	0	-55.71551318304	-2.987472757	1.3507455707
5	0	-55.71551248233	-2.98869108	1.3514035832

Probit Procedure

Data Set =WORK.DATA2
Dependent Variable=RES
Dependent Variable=N
Number of Observations= 5
Number of Events = 27 Number of Trials = 100

Log Likelihood for NORMAL -55.71551248

Last Evaluation of the Gradient

INTERCPT	Log10(DOSE)
0.000001799	0.000002188

Probit Procedure

Last Evaluation of the Hessian

	INTERCPT	Log10(DOSE)
INTERCPT	27.034629	44.989031
Log10(DOSE)	44.989031	77.150132

Goodness-of-Fit Tests

Statistic	Value	DF	Prob>Chi-Sq
Pearson Chi-Square	0.0527	3	0.9968
L.R. Chi-Square	0.0530	3	0.9968

Response Levels: 2 Number of Covariate Values: 5

Probit Procedure

NOTE: Since the chi-square is small (p > 0.1000), fiducial limits will be calculated using a t value of 1.96.

Probit Procedure

Variable	DF	Estimate	Std Err	ChiSquare	Pr>Chi	Label/Value
INTERCPT	1	-2.9886911	1.118105	7.144912	0.0075	Intercept
Log10(DOS)	1	1.35140358	0.661873	4.168898	0.0412	

C=0.1000

Estimated Covariance Matrix

	INTERCPT	Log10(DOSE)
INTERCPT	1.250159	-0.729013
Log10(DOSE)	-0.729013	0.438075

Probit Procedure

Probit Model in Terms of Tolerance Distribution

MU	SIGMA
2.211546	0.739971

Estimated Covariance Matrix for Tolerance Parameters

	MU	SIGMA
MU	0.092136	0.097166
SIGMA	0.097166	0.131344

Probit Procedure
Probit Analysis on Log10(DOSE)

Probability	Log10(DOSE)	95 Percent Fiducial Limits	
		Lower	Upper
0.01	0.49012	-27.67886	1.09960
0.02	0.69183	-22.65028	1.20965
0.03	0.81981	-19.46157	1.28123
0.04	0.91609	-17.06422	1.33648
0.05	0.99440	-15.11546	1.38271
0.06	1.06106	-13.45802	1.42333
0.07	1.11950	-12.00608	1.46025
0.08	1.17183	-10.70745	1.49472
0.09	1.21943	-9.52795	1.52761
0.10	1.26323	-8.44397	1.55965
0.15	1.44461	-3.99452	1.73080
0.20	1.58877	-0.65217	2.06076
0.25	1.71244	1.12194	3.43717

Probit Procedure
Probit Analysis on Log10(DOSE)

Probability	Log10(DOSE)	95 Percent Fiducial Limits	
		Lower	Upper
0.30	1.82350	1.50589	5.88248
0.35	1.92642	1.64700	8.36309
0.40	2.02408	1.73659	10.76126
0.45	2.11856	1.80751	13.09729
0.50	2.21155	1.86980	15.40377
0.55	2.30453	1.92784	17.71451
0.60	2.39902	1.98410	20.06520
0.65	2.49667	2.04034	22.49672
0.70	2.59959	2.09817	25.06062
0.75	2.71065	2.15941	27.82864
0.80	2.83432	2.22659	30.91197
0.85	2.97848	2.30393	34.50694
0.90	3.15986	2.40020	39.03127

Probit Procedure
Probit Analysis on Log10(DOSE)

Probability	Log10(DOSE)	95 Percent Fiducial Limits	
		Lower	Upper
0.91	3.20367	2.42332	40.12417
0.92	3.25126	2.44839	41.31149
0.93	3.30359	2.47591	42.61708
0.94	3.36203	2.50658	44.07527
0.95	3.42869	2.54149	45.73842
0.96	3.50700	2.58242	47.69248
0.97	3.60328	2.63263	50.09486
0.98	3.73126	2.69922	53.28856
0.99	3.93298	2.80388	58.32253

Probit Procedure
Probit Analysis on DOSE

Probability	DOSE	95 Percent Fiducial Limits	
		Lower	Upper
0.01	3.09111	2.0948E-28	12.57773
0.02	4.91847	2.2373E-23	16.20510
0.03	6.60408	3.4549E-20	19.10866
0.04	8.24306	8.6253E-18	21.70109
0.05	9.87191	7.6655E-16	24.13854
0.06	11.50954	3.4832E-14	26.50498
0.07	13.16748	9.8609E-13	28.85699
0.08	14.85365	1.9613E-11	31.24042
0.09	16.57393	2.9652E-10	33.69876
0.10	18.33304	3.5977E-9	36.27894
0.15	27.83651	0.0001013	53.80274
0.20	38.79451	0.22275	115.01733
0.25	51.57542	13.24148	2736

Probit Procedure
Probit Analysis on DOSE

Probability	DOSE	95 Percent Fiducial Limits	
		Lower	Upper
0.30	66.60465	32.05427	762913
0.35	84.41503	44.36040	230725155
0.40	105.70032	54.52466	5.77115E10
0.45	131.38934	64.19626	1.25108E13
0.50	162.75934	74.09723	2.53381E15
0.55	201.61912	84.69217	5.18219E17
0.60	250.61989	96.40543	1.16197E20
0.65	313.81380	109.73472	3.13847E22
0.70	397.72904	125.36452	1.14979E25
0.75	513.62842	144.34934	6.73962E27
0.80	682.84410	168.49653	8.1653E30
0.85	951.64941	201.33902	3.21324E34
0.90	1445	251.30513	1.07466E39

Probit Procedure
Probit Analysis on DOSE

Probability	DOSE	95 Percent Fiducial Limits	
		Lower	Upper
0.91	1598	265.04695	1.33096E40
0.92	1783	280.79742	2.04877E41
0.93	2012	299.16210	4.14075E42
0.94	2302	321.05217	1.18924E44
0.95	2683	347.92469	5.4754E45
0.96	3214	382.31076	4.92583E47
0.97	4011	429.16924	1.24411E50
0.98	5386	500.28762	1.94341E53
0.99	8570	636.61957	2.10152E58