Appendix A. Degradates for Consideration in the Human Health Drinking Water Risk Assessment - EFED Report to the ROCKS Committee

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

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

PC Code: 108401
DP Barcode: D340146

MEMORANDUM

Date: **March 27, 2008**

Subject: **Degradates for Consideration in the Human Health Drinking Water Risk Assessment - EFED Report to the ROCKS Committee**

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ROCKS Committee
Health Effects Division

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This memorandum identifies the environmental degradates of thiobencarb and provides data to help inform determinations of which environmental degradates are of risk concern for drinking water assessment in support of human health risk assessment. If you have any questions about this memorandum, please contact William Eckel at 703.305.6451.

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. Sorption, or binding to soil, is a major fate process, especially when thiobencarb is applied to dry-seeded rice. This is shown by the much lower residues found in water when thiobencarb is applied to dry-seeded rice than when it is applied to flooded rice. 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 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 proportion 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. Thiobencarb also degraded under aerobic conditions with calculated half-lives of 27-58 days in soils that typically support rice. Sensitized photodegradation may be an important process in rice paddies with clear water, with the presence of natural photosensitizers, and before the rice plants shade the water.

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 (sensitized, but only 3.9% in non-sensitized) 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 ml/g. The K_{oc} values ranged from 384-6750 ml/g_{oc}. 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 ml/g. The corresponding K_{oc} values ranged from 84-416 ml/g_{oc}. 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. Only thiobencarb sulfoxide and 4-chlorobenzylmethylsulfone were analyzed for in the field study.

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.

In summary, thiobencarb is likely to degrade slowly, unless exposed in the water column to sunlight in the presence of natural photosensitizers. Application to dry rice paddies will result in greater binding to sediment, and therefore less residue in water once the paddies are flooded. Application to wet rice paddies will reduce the amount of binding to sediment, resulting in higher residues in water. Flooding may result in anaerobic conditions, which would significantly slow the rate of degradation.

Major Degradates

The only major degradates (defined as those representing 10% or more of the applied radiation of the parent test substance) identified were 4-chlorobenzoic acid (56% of applied radiation at 30 days) and 4-chlorobenzaldehyde (29.4% at 14 days), both in a sensitized aquatic photodegradation study. Both of these degradates are expected to be soluble and mobile in water. Both should be subject to further degradation by metabolism (based on their simple structures), but the study was terminated at 30 days.

Neither of these degradates was analyzed for in the aquatic field dissipation studies, thus we do not know if their formation in laboratory studies means that they will form in the field. The only degradates measured in the aquatic field were thiobencarb sulfoxide and 4-chlorobenzylmethylsulfone see table below), which is a possible precursor to 4-chlorobenzoic acid and 4-chlorobenzaldehyde.

Minor Degradates

Minor degradates included thiobencarb (TBC) sulfoxide; 2-hydroxyTBC; 3-hydroxyTBC; 4-chlorobenzylalcohol; 4-chlorobenzylmethylsulfone; 4-chloromethylbenzylsulfoxide; bencarb; and desethylTBC. Study details are presented in Table 1 and structures are presented in Table 2.

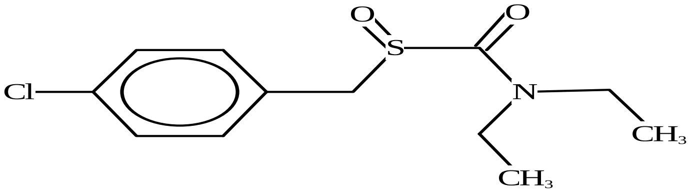
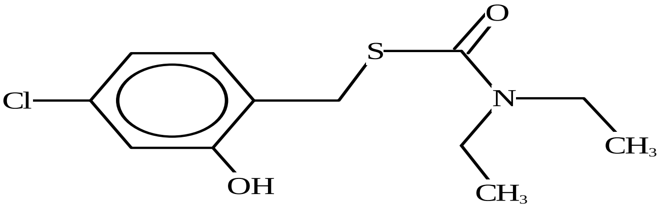
Table 1: Degradate Occurrence Summary for Thiobencarb (TBC)

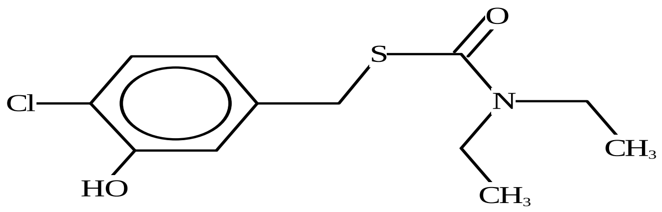
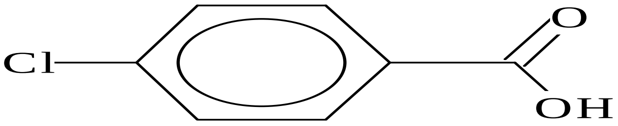
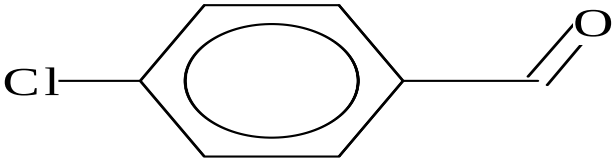
Study MRID	TBC sulfoxide	2-hydroxy TBC	3-hydroxy TBC	4-chloro benzoic acid	4-chloro benz aldehyde	4-chloro benzyl alcohol	4-chloro Benzylmethyl sulfone	4-chloro Benzylmethyl sulfoxide	Bencarb (1)	Desethyl TBC	Half-life
Hydrolysis 41609012											Stable at pH 5,7,9
Aqueous Photolysis 42257801	1.9% @ 25 days max 1.0% @ 30 days last			3.9% @ 30 days max/last	1.8% @ 21 days max 1.8% @ 30 days last	2.5% @ 30 days max/last					190 days
Aqueous Photolysis 42257801 (sensitized)	5% @ 14 days max 1.1% @ 30 days last			**56**% @ 30 days max/last	**29.4**% @ 14 days max 3.7% @ 30 days last	6.7% @ 21 days max 6.2% @ 30 days last			8.3% @ 21 days max 8.1% @ 30 days last		12 days
Soil Photolysis 41215312				1% @ day 9 max 1.1% @ day 21 last							168 days
Aerobic Soil Metabolism 43300401	5.39% @ 56 days max 1.3% @ 366 days last	0.78% @ 3 days max 0.73% @ 56 days last	1.3% @ 120 days max 0.76% @ 231 days last	0.6% @ 120 days max 0.13% @ 366 days last			1.28% @ 366 days max/last	1.92% @ 231 days max/last			56 days (DT50)
Aerobic Soil metabolism 00040925	4.2% @ 28 days max			2.6% @ 7 days max			4% @ 56 days max				15-28 days
Aerobic Aquatic Metabolism 42015301	0.7% @ 0 days max 0.5% @ 30 days last			0.5% @ 7 days max 0.2% @ 30 days last				0.5% @ 0 days max 0.3% @ 30 days last		0.7% @ 21 days max 0.5% @ 30 days last	stable

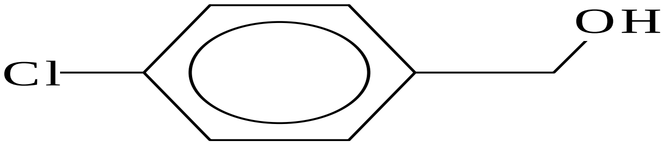
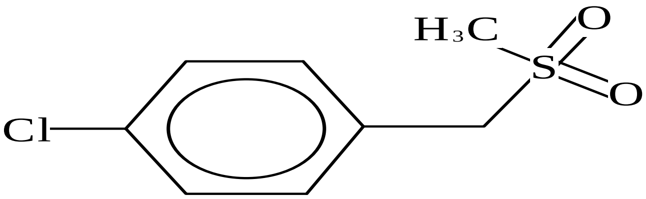
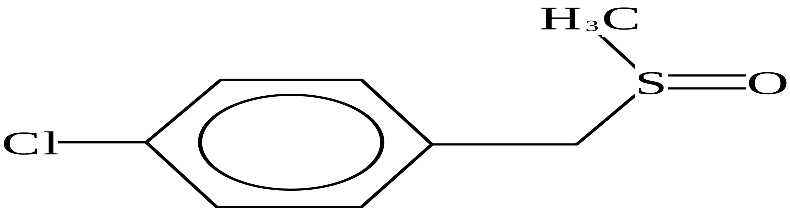
Anaerobic Aquatic Metabolism 43252001		1.1% @ 7 days max 0.8% @ 363 days last	2.1% @ 14 days max 0.7% @ 363 days last	2.2% @ 363 days max/last							5.4 years
Aquatic field Dissipation/wet seeded 43404005	22 ppb, 5% of parent max @ 3 days Nd by 33 days						8 ppb, 1.8% of parent max @ 7-14 days Nd by 60 days				153 days
Aquatic Field Dissipation/dry seeded 42003404	8.9 ppb at 1 day max 1.2 ppb @ 7 days last						5.3 ppb @ 5 days max 1.6 ppb @14 days last				5.8 days from water

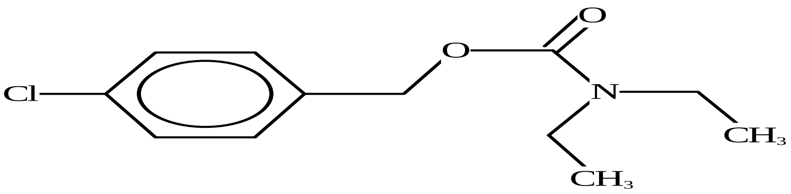
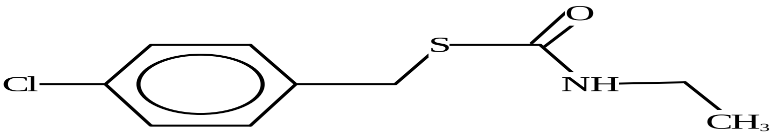
Notes: (1) “Bencarb” = O-[(4-chlorophenyl)methyl]diethylcarbamate

Table 2: Structures of Identified Thiobencarb Degradates

Chemical	Structure
Thiobencarb sulfoxide	
2-hydroxythiobencarb	

3-hydroxythiobencarb	
4-chlorobenzoic acid	
4-chlorobenzaldehyde	

4-chlorobenzyl alcohol	
4-chlorobenzylmethylsulfone	
4-chlorobenzylmethylsulfoxide	

Bencarb	
Desethyl Thiobencarb	

APPENDIX: **Environmental Fate and Transport**

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^{o}C for 30 days. (MRID 41609012)

Photodegradation

In Water

Thiobencarb photodegraded with a calculated half-life of 190 days in a nonsensitized sterile pH 7 aqueous buffer solution at 25 ^{o}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 17.7 % by 21 days, and declined to 12.4 % by 30 days. (MRID 422257801)

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. (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.

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. (MRID 43300401)

The 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)

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)

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. 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. (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. (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)

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)

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). (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. (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))

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. (MRID 42460401)

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.

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 ^{o}C (82 ^{o}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 μg/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. (GLN 164-2, MRID 41722504, 42003404, 43404005).