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

OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

July 8, 2004

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MEMORANDUM

TITLE: Tier I Aquatic Exposure Assessment for Section 3 for Penoxsulam

SUBJECT: Tier I Drinking Water Concentrations (Surface and Ground Water) of the Combined Residues of the Rice Herbicide, Penoxsulam (CAS # 219714-96-2) and the Metabolites: BSTCA (3-[[[2-(2,2-difluoroethoxy)-6-(trifluoromethyl)phenyl]-sulfonyl]amino]-1H-1,2,4-triazole-5-carboxylic acid); 5-OH-penoxsulam (2-(2,2-difluoroethoxy)-N-(5,6-dihydro-8-methoxy-5-oxo[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide); SFA (2-(2,2-difluoroethoxy)-N-(iminomethyl-6-(trifluoromethyl)-benzenesulfonamide); sulfonsmide (2-(2,2-difluoroethoxy)-6-(trifluoromethyl)-benzenesulfonamide); 5,8-diOH (2-(2,2-difluoroethoxy)-6-trifluoromethyl-N-(5,8-dihydroxy-[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)benzenesulfonamide); and 2-amino TCA (2-amino-1,2,4-triazole carboxylic acid).

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This memo presents **Tier 1 Estimated Drinking Water Concentrations** (EDWCs) for the postemergence herbicide, penoxsulam, when used on rice crops. Applying the method outlined in the current EFED interim policy for calculating ***both*** the Tier I estimated ecological effects concentrations (EECs) and the drinking water concentrations (EDWCs) resulting from the use of pesticides on rice crops produced an ***upper bound screening estimation***, using the lowest K_d value (0.13) for a non-sand soil, of ***45 ppb*** (ug/L) ***in paddy waters***. The estimated EEC calculated in accordance with the EFED interim policy should be used for both acute and chronic EECs, as well as for both aquatic ecological risk assessments and for drinking water exposure (EDWCs) in human health risk assessments.

Modeling ground water concentrations using the standard Tier 1 model, SCI-GROW, estimated ***combined residue ground water concentrations (EDWCs) of 5.86 ppb*** (ug/L). Ground water concentrations were estimated for parent-only (EECs) of at 0.67 ppb (ug/L). However, EFED does not regard ground water contamination from a pesticide applied to rice to be a significant route of dissipation.

<u>Method for Estimating Aquatic Surface Water Concentrations</u>

EFED does not currently have an approved higher tier model for estimating aquatic concentrations resulting from pesticides use on rice crops. An interim policy has been issued by EFED Division Director, Steven Bradbury on October 29, 2002. This policy outlines a method of estimating screening level concentrations in surface water to support regulatory decisions for pesticides used in rice agriculture that require ecological and human health risk assessments. The guidance document can be located on the f-drive of the LAN at <u>F:\USER\SHARE\Policies, Guidance, and Formats\EFED Policies\Final Policies\Rice Policy Memo</u>.

The policy establishes a method for calculating estimated environmental concentrations (EEC's) and estimated drinking water concentrations (EDWCs) for the use of pesticides in rice paddies until a more complete rice modeling method becomes available. EECs and EDWCs are estimated by applying the total annual application to the paddy and partitioning the pesticide between the water and the paddy sediment according to a linear or K_d partitioning model. The EEC/EDWC (μg. L^{-1}) represents the dissolved concentration occurring in the water column and the concentration in water released from the paddy. Movement of pesticide on suspended sediment is not considered. The equation to use for this calculation is:

$$EEC = \frac{10^9 M_T}{V_T + m_{sed} K_d}$$

where M_T is the total mass of pesticide in kg applied per ha of paddy, V_T is 1.067×10^6 L ha^{-1} which is the volume of water in a paddy 4 inches (10.16 cm) deep, and includes the pore space in a 1 cm sediment interaction zone. The mass of sediment, m_{sed}, is the amount found in the top 1 cm interaction zone and is 130,000 kg ha^{-1} when the sediment bulk density was assumed to be 1.3 kg L^{-1}, a standard assumption for the bulk density of surface horizons of mineral soils (Brady, 1984; Hillel, 1982). The 10^9 constant converts the units of mass from kg to μg. For chemicals that have a valid K_{oc}, the K_d can be calculated using a sediment carbon content of 2% (K_{oc}*0.02). An organic carbon content of 2% represents a typical value for a high clay soil that might be used to grow rice in the Mississippi Valley or Gulf Coast regions. Both K_d and K_{oc} should be estimated according to the methods recommended for other surface water models in EFED's Input Parameter Guidance (USEPA, 2002).

The estimated EEC/EDWC value should be used for both acute and chronic EECs as well as for aquatic ecological risk assessments and for drinking water exposure in human health risk assessments, EDWCs. EECs/EDWCs calculated by this method are screening estimates, and as such may exceed the true values found in the environment the great majority of the time. Based on preliminary assessment of rice monitoring data, predicted pesticide concentrations as derived above (assuming a 1 cm sediment interaction zone) exceed the observed peak pesticide concentrations. These EECs/EDWCs are expected to exceed concentrations actually measured in the paddy, because degradation processes and dilution with uncontaminated water outside the paddy is not considered.

It is worth emphasizing that the result of this calculation does not represent a concentration that we would expect to find in drinking water, as it represents paddy discharge water. Rather, it represents an upper bound on the drinking water concentrations, and is therefore suitable for use in screening assessments. The concentrations found at drinking water facilities impacted by rice culture would be expected to be less than this value (in some cases much less) because of the aforementioned degradation processes, dilution by water from areas in the basin not in rice culture, and the fact that less than 100% of the rice paddies in a specific area are likely to be treated with a given pesticide.

When the level of concern in a risk assessment is not exceeded using an EEC/EDWC calculated by this screening method, there is high confidence that there will be little or no risk above the level of concern from exposure through water resources. However, because of the uncertainties associated with this method, when a level of concern is exceeded it cannot be determined whether the exceedance will in fact occur or whether this method has overestimated the exposure. While this method is conservative, it does represent the exposure experience by aquatic organisms whose habitat lies close to the discharge from the paddies during and shortly after discharge.

The size of the area and length of time for which the estimate is reasonable depends upon how fast the pesticide degrades, the rate of removal onto uncontaminated bed sediments, and the nature of the local stream network. EFED is working to develop more refined methods for drinking water estimation for rice pesticides. To further characterize the nature of the risk for a particular chemical, it is necessary to have information on the specific agronomic practices for that use, dissipation rates in the environment (degradation, volatilization, dilution), and site specific pesticide usage data. For drinking water, there is an undetermined number of people on drinking water facilities which are downstream from rice growing areas. These areas would includes certain basins in California, Texas, and Louisiana. There is also substantial rice culture in Arkansas, Mississippi, and Missouri, but there are no identified surface water source drinking water facilities downstream from rice cultural areas in these states.

<u>Estimated Aquatic Concentrations of Penoxsulam in Rice Paddy Water</u>

Applying the method outlined in the current EFED interim policy for calculating both estimated environmental concentrations (EEC's) and estimated drinking water concentrations (EDWCs), using the lowest K_d value for a non-sand soil, which would result from the use of pesticides on rice crops which has been outlined above, produced an upper bound screening estimation of ***45 ppb*** (ug/L) ***in paddy waters***. This estimated EEC/EDWC should be used for the estimated acute and chronic exposure concentrations, for both aquatic ecological risk assessments and for drinking water exposure in human health risk assessments. An EEC/EDWC value of 43 ppb (ug/L) was calculated from the average K_d value for non-sand, non-volcanic soils/sediments, and excluding Canadian soils which are not typical of rice growing regions.

Individual EEC/EDWC values calculated from adsorption/desorption data submitted for the individual soil/sediment systems for non-sand, non-volcanic soils/sediments appears in Table 3 below. K_d values for submitted non-sand, non-volcanic soils/sediments are also tabulated below. EEC/EDWC values were not calculated for those excluded test systems. Mobility data submitted for three penoxsulam transformation products (including BSTCA and 5-OH-penoxsulam) indicates that the three degradates examined are of generally equivalent mobility when compared to the parent compound, penoxsulam.. Therefore, EDWCs were estimated using submitted adsorption/desorption data for the parent compound.

<u>Penoxsulam Residues of Toxicological Concern in Surface Derived Drinking Water</u>

On March 19, 2004, the Health Effects Division MARC determined that six penoxsulam transformation products (see Table B1 below) should be included with the parent compound in the risk assessment for water. However, the EFED interim policy for estimating surface water concentrations does not consider degradation of the pesticide. ***The result of not considering degradation in the risk assessment is the same as considering all degradation products to be of toxicological concern.*** Therefore, applying current EFED policy produces an even more conservative screening estimate than the inclusion of these six individual degradation products.

<u>Estimated Aquatic Concentrations of Penoxsulam in Ground Water</u>

Modeling screening level aquatic concentrations using SCI-GROW (input parameters Table 2) produced estimated ***ground water concentrations of 5.9 ppb*** (ug/L) for the ***combined residues of penoxsulam and the six degradates identified by HED to be of toxicological concern***. Mobility data submitted for three penoxsulam degradates indicated a mobility approximately equivalent to the parent compound, so the K_{oc} value for penoxsulam was used as the combined residue input values.

Ground water concentrations for assessing ecological risk (EECs) were estimated for parent-only at 0.67 ppb (ug/L). However, EFED does not regard ground water contamination from a pesticide applied to rice to be a significant route of dissipation.

Table 1. Penoxsulam Residues of Human Toxicological Concern

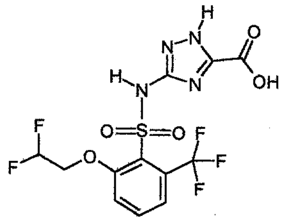
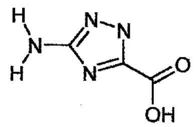
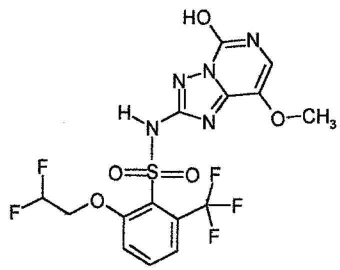
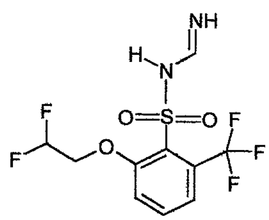
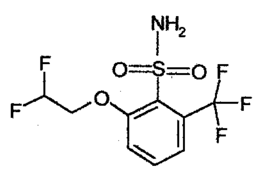
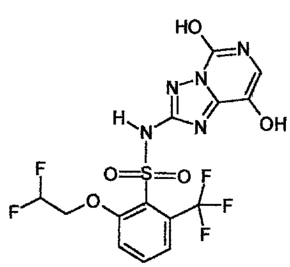
Degradate Name	Structure	Maximum %	Study Type
BSTCA 3-[[[2-(2,2-Difluoroethoxy)-6-(trifluoromethyl)phenyl]-sulfonyl]amino]-1H-1,2,4-triazole-5-carboxylic acid		39.4%* *Maximum % of applied reported at study termination indicating that amounts may have continued to increased with time	aerobic aquatic metabolism
2-amino TCA 2-amino-1,2,4-triazole carboxylic acid		85%*	aqueous photolysis
5-OH-penoxsulam 2-(2,2-Difluoroethoxy) -N-(5,6-dihydro-8-methoxy-5-oxo[1,2,4] triazolo[1,5-c] pyrimidin-2-yl)-6-(trifluoromethyl) benzenesulfonamide		62.6%	aerobic soil metabolism
SFA 2-2,2-Difluoroethoxy)-N-(iminomethyl-6-(trifluoromethyl)-benzenesulfonamide		14.7%*	aerobic soil metabolism
Sulfonamide 2-(2,2-Difluoroethoxy) -6-(trifluoromethyl)-benzenesulfonamide		33.0%*	aerobic soil metabolism
5,8-diOH 2-(2,2-Difluoroethoxy) -6-trifluoromethyl-N-(5,8-dihydroxy-[1,2,4] triazolo[1,5-c] pyrimidin-2-yl) benzenesulfonamide		11.0%*	anaerobic aquatic metabolism

Table 2. Combined Penoxsulam and Degradate Residue Environmental Fate Input Parameters for SCIGROW :

Parameters	Values & Units	Sources
Application Rate (1 application)	0.044 lbs. a.i./acre/season	Product Label
Organic Carbon Partition Coefficient	13	Lowest Non-Sand K_{oc} MRID 458308-01
Combined Residue Aerobic Soil Metabolism Half-life	410 days	Calculated from Combined Residues MRID 458307-24
Parent-Only Aerobic Soil Metabolism Half-life	116 days	MRID 458307-24

Table 3. Estimated Surface Water EECs for Penoxsulam Used on Rice Crops

Soil/Sediment Type	Soil/Sediment Source	K_d	K_{oc}	EEC in ppb
Silt loam	Arkansas	0.37	40	43.9
Silty clay sediment	Arkansas	1.4	1100	39.2
Clay loam	California	0.49	20	43.3
Loam	North Dakota	0.45	20	43.5
Sandy clay loam	Japan	0.56	40	43.0
Silty clay loam	Italy	2.0	250	37.1
Sandy loam	Italy	0.32	46	44.2
Sandy clay loam	United Kingdom	0.16	13	45.0
Silty clay loam	France	0.48	66	43.4
Sandy loam	Brazil	0.51	35	43.2
Clay loam	Brazil	0.64	14	42.6
Sandy clay loam	**Brazil**	**0.13**	**13**	**45.2**
All soils	***average Kd***	***0.92***	***average EEC***	***41.3***
All soils	***median Kd***	***0.54***	***median EEC***	***43.1***
Sand	North Carolina	0.27	76	Not calculated
Loam (volcanic)	Japan	0.59	22	Not calculated
Loam (volcanic)	Japan	4.7	310	Not calculated
Loam (volcanic)	Japan	1.6	200	Not calculated
Clay loam	Canada	1.4	73	Not calculated
Clay loam	Canada	0.67	19	Not calculated

Suggested Alternate Method of Estimating Aquatic Concentrations

Dow Agrosciences has submitted a document (MRID 458308-11) that addresses modeling of ecological and human drinking water exposure for the use of penoxsulam on rice. However, the estimated surface water concentrations from the more conservative, EFED Interim Rice Model were used, as indicated by current policy. Ground water concentrations suggested by Dow were estimated using inappropriate input parameters for the SCI-GROW model. However, EFED does not regard ground water contamination from a pesticide applied to rice to be a significant route of dissipation. EFED notes that (1) the registrant used field dissipation half-lives instead of laboratory metabolism half-lives for estimating both surface water and ground water concentrations, and (2) that the lowest partitioning coefficient from a non-sand, non-volcanic soil was not used. Additionally, (3) the six degradates identified to be of toxicological concern were not considered for human drinking water concentrations.

SCIGROW
VERSION 2.3

ENVIRONMENTAL FATE AND EFFECTS DIVISION
OFFICE OF PESTICIDE PROGRAMS
U.S. ENVIRONMENTAL PROTECTION AGENCY
SCREENING MODEL
FOR AQUATIC PESTICIDE EXPOSURE

SciGrow version 2.3
chemical:penoxsulam combined residues
time is 7/ 7/2004 16:12:32

Application rate (lb/acre)	Number of applications	Total Use (lb/acre/yr)	Koc (ml/g)	Soil Aerobic metabolism (days)
0.044	1.0	0.044	1.30E+01	410.0

groundwater screening cond (ppb) = 5.86E+00

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Ground and Surface Water Contamination Modeling of Penoxsulam Applied to Rice (MRID 45830811)

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Conclusions: Dow Agrosciences has submitted modeling that addresses both ground and surface water contamination from Penoxsulam applied to rice. For ground water, the registrant used SCI-GROW and generated EECs of 0.0014 and 0.0042 ug/L. For ecological effects from surface water (Table 1 in Dow document), the highest estimated concentrations for ecological effects occurred in wet-seeded rice in Louisiana on the Gulf Coast. The highest peak concentration was 0.518 ug/L, which declined to <0.001 ug/L by 72 days after application. For drinking water, the highest peak concentration in the Index Reservoir from all scenarios was 0.26 ug/L, and the maximum chronic (365-day average) concentration was 0.005 ug/L. This concentration also occurred in the water-seeded rice grown on the Gulf Coast in Louisiana. While the Dow modeling used proper approaches and assumptions, the estimates are of questionable value due to the use of inappropriate values for both degradation and partitioning, and because the residues identified by HED as being of toxicological concern were not considered in the calculated half-life estimates.

Ground Water Contamination from Penoxsulam Use on Rice

Dow provided modeling of ground water using the SCI-GROW model, which they state is not relevant to applied compounds in rice fields because of relatively impermeable layers that hold a flood. This conclusion is consistent with the molinate and thiobencarb REDs, However, the registrant did calculate ground water concentrations of 0.0014 and 0.0042 ug/L assuming wet-seeded and dry-seeded rice, respectively, using the SCI-GROW model as an "extremely conservative Tier I EEC." EFED notes that the registrant used field dissipation half-lives instead of laboratory aerobic soil metabolism half-lives as an input into the model, which may be inappropriate. Even so, EFED does not regard ground water contamination from a pesticide applied to rice to be a significant route of dissipation.

Ground Water Inputs

- Application Rate–0.045 lb ai/A
- No. Apps–1
- Koc (l/kg)–90
- $T_{1/2}$ (for wet-seeded rice)–6.5 days (average total system half-life from water-seeded aquatic field dissipation studies)
- $T^{1/2}$ (for dry-seeded rice)–14.6 days (average total system half-life from dry-seeded aquatic field dissipation studies)

Surface Water Modeling of Penoxsulam

Modeling Approaches

Interim Rice Model

EFED has used different modeling approaches for rice tailwater runoff to date. The first appproach, known as the Interim Rice Model, includes only sorption as a dissipation process. It provides a conservative Tier I estimate of the concentration of an applied pesticide in surface water with the following assumptions:

- Sorption is the only dissipation process the model considers
- 100 % of perfectly-normal application is applied to flooded field, reaches the flood water, and instantaneously partitions between water and soil
- No degradation, drift, volatility, foliar interception, runoff, or leaching occurs in the field
- The field is drained the day of application

Refined Modeling used for Propanil RED

Dry-seeded Rice

EFED modeled the dissipation of propanil in the field by incorporating both degradation (aerobic soil and aerobic aquatic metabolism) and partitioning between water and soil. For dry-seeded rice, the refined modeling used for propanil estimates the concentration in paddy water 10 days after the day of application to a non-flooded field. Most of the rice grown in the U.S. is produced using this cultural practice, and is primarily located in the lower Mississippi River Delta and in southeastern Texas. This modeling approach provides a maximum concentration in paddy water, which can be held for up to 78 days. It also predicts concentrations for ecological effects to organisms living at the edge of the rice paddy. Required water-holding times to reduce aquatic exposure below a given level of concern can be estimated. The assumptions for dry-seeded rice and application to non-flooded soil include:

- 100 % of perfectly-normal application reaches the soil and instantaneously sorbs to the soil
- Degradation occurs by aerobic soil metabolism (average $T_{1/2}$=46 days) and by aquatic field dissipation (average $T_{1/2}$=4.4 days) for non-flooded and flooded fields, respectively.
- No drift, volatility, foliar interception, runoff, or leaching occurs in the field
- Flooding over the entire field is instantaneous
- The field is flooded 10 days after the day of application, followed by aquatic field dissipation and immediate partitioning between soil and water.
- No outflow or overflow from the fields occurs after flooding.
- For ecological effects, the concentration of paddy water was used as exposure to aquatic organisms
- For drinking water, the paddy water was drained to the Index Reservoir, diluted, and then degraded using aerobic aquatic metabolism.

Water-Seeded Rice

Water-seeded rice is grown in southwestern Louisiana and in California. The primary method of water-seeded rice production in Louisiana that uses propanil is called "delayed flood rice." The pregerminated seeds are dropped into standing water, which is drained 1-2 days later. A permanent flood is established about 3-4 weeks after planting and is held for about 10 weeks in the first crop. The modeling assumes that the compound is applied before the permanent flood, and the water is drained 28 days after herbicide application due to a rainfall event causing overflow. California uses the "permanent flood" method of producing rice. Pregerminated seeds are dropped into standing water which is NOT normally drained until a postemergence herbicide is applied about 30 days later. After treatment with a herbicide, a 4-inch flood is reestablished and later increased to 8 inches of depth in Mid-July to ensure proper seed formation. It is drained about 2-3 weeks prior to harvest. The maximum surface water concentration is that achieved on the day of application, and the later concentrations for 78 days are predicted assuming aerobic aquatic metabolism of the pesticide. The modeling assumptions used in the propanil modeling follow:

- 100 % of perfectly-normal application reaches flooded soil and instantaneously partitions between the soil and floodwater
- Degradation occurs by aquatic field dissipation half-life of 4.4 days
- No drift, volatility, foliar interception, runoff, or leaching occurs in the field
- Flooding over the entire field is instantaneous
- The flood water is released 28 days later for southern Louisiana and 78 days in California.
- No outflow or overflow from the fields occurs after flooding prior to release.
- For ecological effects, the concentration of paddy water was used as exposure to aquatic organisms
- For drinking water, the paddy water was drained to the Index Reservoir, diluted, and then degraded using aerobic aquatic metabolism

Deviations from Propanil Modeling

For surface water, Dow used the modeling approach from the propanil RED and cyhalofop butyl Section 3 documents with some modifications. Dow noted that EFED has no official Tier II model for surface water exposure from pesticides applied to rice. While most of these modifications were reasonable and scientifically sound, the registrant used "average" aerobic soil metabolism half-lives prior to flooding instead of upper 90th CB values. The registrant also used "average" aquatic field dissipation half-lives instead of aerobic aquatic metabolism half-lives. The use of field dissipation half-lives is questionable because they incorporate the results of many dissipation processes. The registrant justified the use of field dissipation half-lives because penoxsulam degrades by both abiotic and biotic processes. If two or more routes are used as separate model inputs, use of field dissipation values as a model input may "double count" one or both, leading to predicted EECs that are unrealistically low.

Drinking Water from Surface Water

For drinking water derived from surface water, Dow drained all the fields at once into the Index Reservoir and calculated peak and annual mean values for acute and chronic exposure. The peak concentration leaving the fields was divided by two (2) because the volume of water from the rice paddies and the volume of the Index Reservoir were very similar. The chronic exposure were determined by degrading the peak concentrations from California (continuous flood rice), the Mississippi Delta (dry-seeded rice), and South Louisiana (pinpoint flood or delayed flood rice) for one year to get an annual mean concentration for each location.

Ecological Effects and Drinking Water Model Predictions

Based on the modeling results (Table 1 in Dow document), the highest estimated concentrations for ecological effects occurred in wet-seeded rice in Louisiana on the Gulf Coast. The highest peak concentration was 0.518 ug/L, which declined to <0.001 ug/L by 72 days after application. For drinking water, the highest peak concentration in the Index Reservoir from all scenarios was 0.26 ug/L, and the maximum chronic (365-day average) concentration was 0.005 ug/L. This concentration occurred in the water-seeded rice grown on the Gulf Coast in Louisiana. The Dow estimates are of questionable value due to the use of inappropriate values for both degradation and partitioning, and because the residues identified by HED as being of toxicological concern were not considered in the calculated half-life estimates.