U. S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, DC 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

April 28, 1997

MEMORANDUM

SUBJECT: Registration: NC Food/Feed Use; Environmental Fate Data; **Cloransulam-Methyl** (XDE 565); Chemical Code 129116; DP Barcodes D223558 and D223560; PRAT Case 039560; Data Sponsor: DowElanco (062719)

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The EFED Environmental Fate Science Chapter for the Section 3 registration of cloransulam-methyl is attached. The chapter includes both the environmental fate assessment and surface and ground water assessments, along with supporting information. Recommendations for label advisories pertaining to potential contamination of ground and surface waters are included in the Water Assessment section.

Available fate data indicate that cloransulam-methyl is highly mobile in the environment. The major routes of dissipation appear to be metabolic transformation, leaching, and photolysis in water and, to a lesser extent, on soil. The initial transformation of cloransulam-methyl involves modifications of functional groups while the structural "backbone" of the chemical remains intact. Three major transformation products -- cloransulam, 5-hydroxy-cloransulam, and 5-hydroxy-cloransulam-methyl -- appear to be mobile, more persistent than the parent, and potentially phytotoxic. Cloransulam-methyl had a transformation half-life of 2 to 4 weeks in the soil under laboratory conditions. The degradation half-life (involving breakdown of cloransulam-methyl and structurally-similar products) was on the order of 1 to 2 months.

Cloransulam-methyl and its structurally-similar transformation products exhibit characteristics similar to those pesticides that are known to leach to ground water or to reach surface waters via

spray drift and runoff. Leaching through the soil to ground water will likely be a competing process with runoff in a dissolved phase to surface waters. Weather and site factors that affect runoff and leaching processes will greatly influence the routes of movement for cloransulam-methyl and its transformation products. Because the primary routes of transformation of cloransulam-methyl (metabolism and photolysis) are not likely to be dominant below the surface layer, the actual persistence of the chemical in the subsurface and ground water may be significantly greater. Due to concerns about the mobility and persistence of cloransulam-methyl and its structurally-similar, biologically active transformation products, EFED is requesting that a prospective ground water monitoring study be conducted.

The environmental fate data requirements for the use of cloransulam-methyl as a broad-leaf herbicide on soybeans have been satisfied through acceptable studies or data waivers, except for terrestrial field dissipation (Guideline No. 164-1) and prospective ground water study (166-1). The terrestrial field dissipation study is considered supplemental because the samples were apparently stored frozen for an unspecified period of time with no storage stability data provided (another study indicated that cloransulam methyl residues decreased in extractability with time in frozen storage). The registrant can upgrade this study to acceptable by submitting the appropriate storage stability data and, if dictated by the results of this study, make any adjustments as needed in the terrestrial field dissipation results.

ENVIRONMENTAL FATE ASSESSMENT OF CLORANSULAM-METHYL

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CHEMICAL INFORMATION

Common Name: Cloransulam-methyl; XDE-565; DE-565

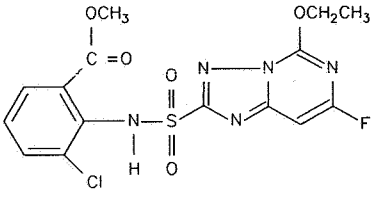
Chemical Name: N-(2-carboxymethyl-6-chlorophenyl)-5-ethoxy-7-fluoro[1,2,4]triazolo[1, 5-c] pyrimidine-2-sulfonamide

Chemical Code: 129116

CAS Number: 147150-35-4

Trade Names: FirstRate Herbicide

Structure:



Formulations: water-dispersible granular

Physical/Chemical Properties (at 20°C unless otherwise noted; from 436689-33):

Molecular formula:	$C_{15}H_{13}O_5N_5SClF$	Molecular weight:	429.82
Physical state:	Solid		
Vapor pressure:	4×10^{-14} Pa (3×10^{-16} mm Hg) (estimated at 25°C)		
Water Solubility:	3 ppm at pH 5; 180 ppm at pH7; 3400 ppm at pH 8.5 16 ppm in deionized water		
pK_a:	4.81		
Log K_{ow}	1.12 (pH 5.0); -0.365 (pH 7.0); -1.24 (pH 8.5); -0.572 (distilled)		

USE PATTERN

This triazolopyrimidine sulfonanilide herbicide is used to control broadleaf weeds in soybeans (food/feed use). It can be applied to the soil surface or incorporated preemergence or postemergence. Cloransulam-methyl works by inhibiting the acetolactate synthase (ALS) enzyme (MRID 436689-33). According to the proposed label for FirstRate, the herbicide will be applied by ground spray at maximum rates of 44 g a.i./ha (0.040 lb a.i./A) preemergence (incorporated or surface) or 17.5 g a.i./ha (0.016 lb a.i./A) postemergence (proposed label). Only one application will be made per season.

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ENVIRONMENTAL FATE ASSESSMENT

Laboratory and field data indicate that cloransulam-methyl is highly mobile in the environment. The major routes of dissipation appear to be metabolism, leaching, and photolysis in water and, to a lesser extent, on soil. Hydrolysis may be an important mode of dissipation in alkaline environments. The initial transformation of cloransulam-methyl involves modifications of functional groups while the structural "backbone" of the chemical remains intact. The three transformation products -- cloransulam, 5-hydroxy-cloransulam, and 5-hydroxy-cloransulam-methyl -- appear to be mobile, more persistent than the parent, and potentially phytotoxic[1]. Later degradation involves cleavage of the sulfonamide bridge or a break in the triazolopyrimidine ring and requires more energy (from photolysis) or special conditions (alkaline hydrolysis or anaerobic metabolism). Cloransulam-methyl had a transformation half-life of 2 to 4 weeks in the soil under laboratory conditions. The degradation half-life (involving breakdown of cloransulam-methyl and structurally-similar products) was on the order of 1 to 2 months. In field studies, half of the parent dissipated from the surface in less than 8 days (DT_{50}).

Microbial transformation and photolysis occur in the surface layer of the soil, but may not be major factors if the chemical leaches to the subsurface, where hydrolysis or other slower degradation processes may become important. So, while cloransulam-methyl and its structurally-similar transformation products are likely to be only of slight persistence in the surface, the chemical may be more persistent when leached into the subsurface. The extent of persistence in subsurface layers with low metabolic activity and in ground water is uncertain.

The registrant should be commended for the effort put into providing a better understanding of the environmental fate characteristics of cloransulam-methyl. In addition to the basic guideline requirements, the registrant submitted a supplemental aerobic metabolism and desorption study on 16 soils that better defines the factors influencing the fate of the parent and its structurally-similar transformation products. The use of radiolabeled materials in the field dissipation study allowed for a better tracking of the residues in the environment and for the detection and identification of the residues at the low application rates.

Persistence

Degradation: The susceptibility of cloransulam-methyl to hydrolysis is pH-dependent. The parent was stable at pH 5 (half-life >365 days), degraded slowly at pH 7 (half-life of 4 to 8 months), and hydrolyzed rapidly at pH 9 (half-life of 3 days) (MRID 430034-32). Cloransulam-methyl photolyzed rapidly in water (pH 7), with a half-life of 22 minutes (MRID 437154-02). Photolysis on soil occurred more slowly, with half-lives, corrected for metabolism, of 30 to 70 days (MRID 437600-01).

Metabolism: Under aerobic conditions, the transformation of cloransulam-methyl in soil was initially rapid but slowed over time. Structurally-similar transformation products were

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[1]The registrant refers to internal non-GLP phytotoxicity tests which show that cloransulam has herbicidal potential, but at a lower level than the parent cloransulam-methyl. These studies have not been evaluated by the Agency.

formed before the breakdown of the sulfonamide bridge or triazolopyrimidine ring occurred. Because of the concern for potential phytotoxicity of these similar transformation products (cloransulam, 5-OH-cloransulam-methyl, and 5-OH-cloransulam), half-life estimates are given for both the initial transformation of parent cloransulam-methyl (calculated by the registrant unless otherwise noted) and for the degradation of the parent and structurally-similar transformation products (calculated by the EPA reviewer).

With a nonlinear, two-compartment kinetic model[2], the apparent transformation half-life in aerobic soils was estimated at 9 to 13 days (16 to 21 days using a first-order model for the first 56 days; 67 to 72 days using a first-order model for the entire 357-day study period). The amount of time required for 50% of the parent to transform (DT_{50}) was 9 to 15 days and, for 90% (DT_{90}), 49 to 72 days (MRID 430034-33). Over time, the parent and its transformation products may be adsorbed more tightly on soil and/or organic matter. In a supplemental aerobic metabolism study on 16 soils, the transformation half-live of cloransulam-methyl ranged from 13 to 30 days (MRIDs 430034-34 and 432166-01). The transformation half-life of cloransulam-methyl under anaerobic aquatic conditions was approximately 16 days (MRID 437154-03). The combined residues (cloransulam-methyl and structurally-similar products) degraded with a half-life of 1 to 2 months in laboratory studies. While the transformation half-lives of cloransulam-methyl showed no correlation with pH in the 16 soils, the degradation half-lives of the combined residues were correlated with pH, increasing as the pH decreased (MRIDs 430034-34 and 432166-01). This suggests that the parent and its structurally-similar products may be more persistent in acidic soils.

Transformation Products: The structurally-similar transformation products *cloransulam* (37-38% at 28 days), *5-hydroxy-cloransulam-methyl* (17% at 14 days) and *5-hydroxy-cloransulam* (11-21% after 120 days) occurred in aerobic and anaerobic metabolism studies. *Sulfonamide (ASTP)* (27% at 30 days) and *cloransulam-methyl fluorethenyl* (49-54% at 365 days) were found in anaerobic conditions. Cloransulam-methyl fluorethenyl appears to be persistent under anaerobic conditions. *Sulfonic acid (TSPA)* was the major photolytic degradate in the soil photolysis study (peak concentration of 22% at the end of the study). *Sulfinic acid*, which was detected in the aqueous photolysis study (23% at the end of the study), should oxidize rapidly to TSPA in natural waters. *Cloransulam-methyl imidate* and *cloransulam-methyl acetic acid* were associated with the hydrolysis of cloransulam-methyl (Appendix A).

Mobility

Cloransulam-methyl is highly mobile while the major transformation products also appear to be mobile in soils. In batch equilibrium studies, the parent had Freundlich K_{ads} values of 0.15 to 1.49 ml/g and K_{des} of 0.27 to 1.25 ml/g; cloransulam had K_{ads} values of 1.1 to 2.3 ml/g

[2] The two-compartment model splits the parent into two differentially-reacting soil compartments and the half-life is estimated from the combined reaction rates of the two components. The model was described by Alexander and Scow, based on the work of Hamaker and Goring. Such an approach may not be unreasonable considering the initial reaction appears to be a transformation into structurally-similar products before breakdown of the sulfonamide bridge or triazolopyrimidine ring occurs. Additionally, the parent and transformation products that are adsorbed tighter in the soil with time may degrade at a different rate than in solution.

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and K_{des} values 1.6 to 2.8 ml/g. Cloransulam-methyl, cloransulam, cloransulam-methyl acetic acid, 5-OH-cloransulam-methyl, and 5-OH-cloransulam all had low desorption coefficients when aged for up to 3 months under aerobic conditions. Median non-Freundlich desorption coefficients (apparent K_ds), calculated from simple ratios of material extracted to material remaining on soil, ranged from 0.2 ml/g initially to 1.8 ml/g after 3 months for the parent. Initial median K_ds for the four degradates ranged from 0.2 to 0.7 ml/g; three-month median K_ds ranged from 0.4 to 1.2 ml/g. In general, sorption increased with time. The K_{ads} and K_d values were correlated with pH (increasing with decreasing pH) but not with organic carbon, clay content, or cation exchange capacity. (MRIDs 430034-35 and 432166-02).

The pK_a (4.81) and increasing solubility with increasing pH (chemical data summarized in 436689-33) indicate that cloransulam-methyl will be an anion under typical pH conditions found in the field. Because the anion exchange/adsorption capacity is typically negligible at the natural pH of most soils (Sposito, 1989; p. 172), very little of the cloransulam methyl applied to the soil is likely to be adsorbed to soil exchange sites.

Field Dissipation

Cloransulam-methyl dissipated relatively rapidly from the upper 15 cm of bare-ground plots in Indiana and Mississippi, with DT_{50}s (the time in which 50% of the 0-day concentration dissipated from the upper 15 cm) of 5 to 8 days and DT_{90}s of less than 45 days. Dissipation rates did not follow first-order kinetics. The transformation products detected in the study -- cloransulam, 5-OH-cloransulam-methyl, 5-OH-cloransulam, sulfonamide (ASTP), and sulfonic acid (TPSA) -- indicate that metabolism and photolysis are likely to be major routes for transformation of cloransulam-methyl in the field. The timing of rainfall or irrigation in relation to dissipation at each site and lab mobility data suggest that leaching may also play an important role in the dissipation of cloransulam-methyl from the surface layer. Radioactive residues were detected as deep as 90 cm (maximum sample depth) in IN and 45 cm in MS (MRID 437160-02).

Accumulation

With a low reported octanol/water coefficient (log K_{ow} ranges from 1.12 at pH 5.0 to -1.24 at pH 8.5), cloransulam-methyl is not expected to accumulate significantly in fish.

Subsurface Persistence

The primary transformation pathways for cloransulam-methyl -- microbial breakdown (metabolism) and photolysis -- are dominant in the surface layer of the soil but may not be major factors if the chemical leaches to the subsurface, where light does not penetrate and microbial populations are substantially reduced. In such instances, hydrolysis or other slower degradation processes may become important. So, while cloransulam-methyl and its transformation products are likely to be only of slight persistence in the surface, the chemicals may become more persistent when leached into the subsurface.

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WATER RESOURCE ASSESSMENT

Environmental fate data suggest that cloransulam-methyl has the potential to leach to ground water and to reach surface waters through spray drift and runoff. Cloransulam-methyl is a new chemical and monitoring data are not available to determine actual concentrations in water. Therefore, the assessment for the potential to contaminate ground and surface waters is based on the environmental fate characteristics of the chemical. Cloransulam-methyl and its structurally-similar transformation products exhibit characteristics similar to those pesticides that are known to leach to ground water or to reach surface waters via spray drift and runoff. Leaching through the soil to ground water will likely be a competing process with runoff in a dissolved phase to surface waters. Weather and site factors that affect runoff and leaching processes will greatly influence the routes of movement for cloransulam-methyl and its transformation products. Because the primary routes of transformation of cloransulam-methyl (metabolism and photolysis) are not likely to be dominant below the surface layer, the actual persistence of the chemical in the subsurface and ground water may be significantly greater. Due to concerns about the mobility and persistence of cloransulam-methyl and its structurally-similar, biologically active transformation products, EFED is requesting that a prospective ground water monitoring study be conducted.

Ground Water

Existing environmental fate studies show that cloransulam-methyl has a number of characteristics in common with pesticides that are known to leach to ground water. The low K_{ads} and K_{des} values suggest that cloransulam-methyl is highly mobile while the pK_a of 4.81 indicates that it will be an anion under typical pH conditions found in the field and thus be susceptible to leaching. Terrestrial field dissipation studies also suggest a potential for leaching. Dissipation in the two field sites closely followed potential leaching rainfall/ irrigation events and low concentrations of residues were detected at depths of 45 to 90 cm.

While the initial transformation half-lives of cloransulam-methyl suggest slightly persistent in the surface layer (laboratory $t_{1/2}$ values of 9 to 15 days in aerobic soils; field DT_{50} of 9 to 13 days), two factors suggest longer persistence and a greater concern:

(1) The three major transformation products (cloransulam, 5-OH-cloransulam-methyl, and 5-OH-cloransulam) are structurally-similar and may have herbicidal activity. These products are similar in mobility and more persistent than the parent. The degradation half-life of the combined residues of the parent cloransulam-methyl and its similar transformation products is approximately 1 to 2 months under aerobic soil conditions.

(2) The influence of the primary degradation pathways for cloransulam-methyl (metabolism and photolysis) are likely to diminish as the chemical leaches into subsurface soil layers and to ground water. In such instances, hydrolysis or other slower processes may become the primary degradation pathways, resulting in greater persistence. The actual fate of cloransulam-methyl and its transformation products in subsurface and ground water is not known.

EFED recommends a ground water label advisory for cloransulam methyl. The following label language is appropriate:

> *This chemical and its transformation products demonstrate the properties and characteristics associated with chemicals detected in ground water. The use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground-water contamination.*

Due to concerns about the mobility and the potential persistence of cloransulam-methyl and its structurally-similar, biologically active transformation products in the subsurface and ground water, EFED is requesting that the registrant conduct a prospective ground water monitoring study. Small-scale prospective ground-water monitoring studies offer the prospect of better defining the scenarios and conditions under which cloransulam-methyl and its structurally similar transformation products may leach to ground water. The monitoring study should be designed to provide direct information on the behavior of the pesticide in the vadose zone, and include detailed soil characterization, hydrogeologic data, and accurate usage data. Guidance in developing the study protocols may be found in the "Guidance for Small-Scale Ground-Water Monitoring Studies: Workshop Draft" of March 1995.. With low application rates (44 g a.i./ha or 0.040 lb a.i./A), concentrations of cloransulam-methyl that could reach ground water may drop below current analytical limits of detection. The registrant needs to use methods that allow for as low a limit of detection as possible.

Surface Water

Cloransulam-methyl may contaminate surface water through spray drift associated with ground application or in the dissolved phase during runoff. The persistence of cloransulam-methyl and structurally-similar transformation products (degradation $t_{1/2}$ of 1 to 2 months for aerobic soil metabolism; $DT_{50} \leq 13$ days in the field) suggest that residues may be available for transport for weeks to months after application. Cloransulam, 5-OH-cloransulam-methyl, and 5-OH-cloransulam may have some degree of herbicidal activity and could contribute to off-site impacts on non-target terrestrial and aquatic plants. With a low soil/water partitioning coefficient ($K_{ads} < 1.5$, predominantly < 0.5), cloransulam-methyl and its transformation products will predominantly be dissolved in runoff water rather than adsorbed to the eroded soil or sediment. In the terrestrial field dissipation study (MRID 437160-02), 2 to 11% of the applied parent was recovered in the runoff collection traps. However, the study was not specifically designed to monitor runoff and additional interpretations of these results are not possible. Leaching through the soil to ground water will likely be a competing process with runoff to surface waters. Weather and site factors that affect runoff and leaching processes will greatly impact the degree to which cloransulam-methyl will be susceptible to transport to surface waters via runoff.

Photolysis is likely to be the primary route of dissipation of cloransulam-methyl in surface waters (aquatic photolysis $t_{1/2}$ of 22 minutes). The major photolytic degradates -- sulfinic acid (TSPA) and sulfonic acid (ASTP) -- result from a cleavage of the sulfonamide ring. Therefore, photolysis will probably result in the breakdown of the structurally-similar transformation products as well. Dissipation in water will likely depend on the physical

components of the water affecting light penetration, such as sediment loading and depth. Cloransulam-methyl should not persist in clear, shallow water bodies. Hydrolysis is not expected to be a major route of dissipation, except at alkaline pH's ($t_{1/2}$ of 3 days at pH 9). No data is available for aerobic aquatic metabolism; under anaerobic aquatic conditions, cloransulam-methyl transformed with a half life of 16 days while the transformation products were more persistent. Cloransulam increased in concentration through 65 days before declining with a half-life of 45 days; 5-OH-cloransulam increased through 273 days before declining with a half-life of 60 days; cloransulam-methyl fluorethenyl increased to >50% of the applied by the end of the study and appears to be persistent under anaerobic conditions. Because of a low octanol/water partitioning coefficient (log K_{ow} ranges from 1.12 at pH 5.0 to -1.24 at pH 8.5), cloransulam-methyl is not expected to accumulate significantly in fish.

The low soil-water partitioning coefficients suggest that cloransulam-methyl and its transformation products will be primarily associated with the water column rather than the sediments. Aged aerobic soil metabolism and adsorption/desorption studies indicate that cloransulam-methyl residues become more tightly bound on soil with time. However, no data is available to determine whether this holds true with sediments in water.

Uncertainties in the surface water assessment include lack of information on aerobic aquatic metabolism, assumptions regarding spray drift (the surface water is assumed to receive a constant 1% of the applied as drift from ground spray), and the adequacy of the K_{oc} model to predict partitioning of the chemical in mineral soils (Freundlich partitioning coefficients were not significantly correlated with organic carbon contents of the soils). Data on the persistence of some cloransulam-methyl transformation products is also inadequate.

Cloransulam-methyl is a new chemical and is not regulated under the Safe Drinking Water Act; therefore, no Maximum Contaminant Level (MCL) has been established for it. Its mode of action (ALS inhibitor) is specific to plants and the chemical has a low toxicity profile for humans, mammals, or other animals. The primary impacts from drift and runoff of cloransulam-methyl will be on non-target terrestrial and aquatic plant species.

If a decision is made to require labeling for cloransulam-methyl to minimize runoff and drift impacts, EFED recommends the following wording:

This chemical can contaminate surface water through spray drift.

Under some conditions, this chemical may also have a high potential for runoff into surface water (primarily via dissolution in runoff water), for several weeks post-application. Vulnerable conditions include poorly draining or wet soils with readily visible slopes toward adjacent surface waters, frequently flooded areas, areas over-laying extremely shallow ground water, areas with in-field canals or ditches that drain to surface water, areas not separated from adjacent surface waters with vegetated filter strips, and areas over-laying tile drainage systems that drain to surface water.

Generic Estimated Environmental Concentrations in Surface Waters

GENEEC is a screening model that can be used to provide an upper-bound ("worst case") estimate of environmental concentrations (EECs) on a high exposure site. The GENEEC program uses basic environmental fate values and pesticide label information to estimate the EECs following the treatment of a 10 ha field. The runoff event occurs two days after the last application (in the case of cloransulam-methyl, the only application). The model calculates the concentration of pesticide in a one-hectare, two-meter deep pond. It takes into account adsorption to the soil or sediment (using K_{OC} values), soil incorporation (cloransulam-methyl was assumed to be applied to the surface without incorporation), degradation in soil before runoff (based on aerobic soil metabolism studies), and degradation within the water body (hydrolysis, photolysis, and aquatic metabolism studies). The model also accounts for direct deposition of spray drift onto the water body (assuming 1% of the application rate for ground spray applications in the case of cloransulam-methyl).

The maximum EEC for cloransulam-methyl is based on the maximum pre-emergent single application rate of 44 g/ha (0.040 lb/A) applied to the bare-ground surface. The following environmental fate parameters were used in the model:

> Solubility = 180 ppm (pH 7); K_{OC} = 43 (taken from one of the adsorption studies, even though the K_{ads} values of cloransulam-methyl do not appear to be correlated with organic content, especially during the initial contact with the soil); Hydrolysis $t_{1/2}$ = 231 days (pH 7); Photolysis in water $t_{1/2}$ = 0.015 days. Aerobic aquatic metabolism was assumed to be stable in the absence of such data (although evidence from other metabolism studies would suggest that cloransulam-methyl would be susceptible to metabolism in water). Two aerobic soil metabolism half-lives were used. For the parent chemical, a maximum transformation half-life of 28 days was selected (from one of the supplemental metabolism studies). A degradation half-life of 61 days was chosen to include both cloransulam-methyl and the structurally-similar metabolites which may have some herbicidal activity, albeit at a lower level.

The maximum EECs for cloransulam-methyl and for the parent and structurally-similar metabolites are shown below.

GENERIC EECs (IN PPB)

	PEAK GEEC	AVERAGE 4 DAY GEEC	AVERAGE 21 DAY GEEC	AVERAGE 56 DAY GEEC
Cloransulam-methyl	1.83	1.13	0.28	0.10
Cloransulam-methyl & similar products	1.88	1.16	0.28	0.11

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DETAILED INFORMATION ON SUPPORTING ENVIRONMENTAL FATE STUDIES

Environmental fate studies on hydrolysis, aerobic soil metabolism, and mobility/ adsorption-desorption were reviewed for an earlier EUP application for cloransulam-methyl (also referred to as XDE-565). These DERs can be found in the 12/23/95 memorandum from A. Clem to R. Taylor and E. Allen. Studies on photolysis (water and soil), anaerobic aquatic metabolism, and terrestrial field dissipation were reviewed for the first time for this Section 3 registration. These DERs are included in Appendix B. Additional data evaluation for the supplemental aerobic soil metabolism and desorption study originally reviewed in 1995 is also included in Appendix B.

Cloransulam methyl contains both an aniline and a triazolopyrimidine ring. Unless otherwise noted, separate studies were conducted using ^{14}C labels for each of the rings. In most instances, the concentrations of the parent and the degradates were similar for both ring studies and the results are shown as a range.

A. Degradation

161-1 Hydrolysis

Hydrolysis of *cloransulam-methyl* is pH-dependent, with rates increasing as pH increases. In sterile buffer solutions, the parent was relatively stable at pH 5 (4% degraded after 30 days; half-life >365 days); degraded slowly at pH 7 (18% degraded after 30 days; extrapolated half-life of 4 to 8 months), and hydrolyzed rapidly at pH 9 (half-life of 3 days, with 80% degraded after 7 days).

Three transformation products were identified in the study. *Cloransulam methyl imidate* [N-(2-carbomethoxy-6-chlorophenyl)-2-N-ethylimido-3-(1,2,4)-triazoloacetic acid-5-sulfonamide] reached a maximum of 25-29% of the applied after 3-5 days at pH 9 before decreasing to 21% after 7 days. It also reached a maximum of 8-10% after 30 days at pH 7. *Cloransulam-methyl acetic acid* [N-(2-carbomethoxy-6-chlorophenyl)-3-(1,2,4)-triazoloacetic acid-5-sulfonamide] was at a maximum of 49-54% after 7 days at pH 9 and 3-4% after 30 days at pH 7. *5-OH cloransulam-methyl* [N-(2-carbomethoxy)-7-fluoro-5-hydroxy(1,2,4)-triazolopyrimidine-2-sulfonamide] peaked at 5-6% after 7 days at pH 9 (MRID 430034-32).

161-2 Photodegradation in Water

Cloransulam-methyl, at a concentration of 1 ug/ml, photolyzed rapidly in pH 7 buffer solutions exposed to natural sunlight near noon on a clear summer day in Indianapolis, IN. Parent concentrations declined from 93-96% of the applied radioactivity to 40-43% after 20 minutes and 9-11% after 60 minutes. In contrast, cloransulam-methyl did not degrade in the dark during that time period. The first-order degradation rate constant was 56.25 da^{-1} and the half-life was 18 minutes (22 minutes adjusted for an "average" summer day at 40°N Latitude). Absorbance spectra indicate that cloransulam-methyl absorbs light strongly at wavelengths below 280 nm, with an

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absorbance tail extending to 340 nm.

Cloransulam-methyl sulfinic acid [5-ethoxy-7-fluoro(1,2,4)tirazolo(1,5c) pyrimidine-2-sulfinic acid] was the major transformation product, increasing to a maximum of 23% after 60 minutes. The sulfinic acid, formed by the cleavage of the sulfonamide bridge and the loss of the phenyl ring, should oxidize readily to cloransulam-methyl *sulfonic acid* (TPSA) in natural waters. Six other degradates did not exceed 10% of initial concentrations. Four of these were believed to form by Cl loss, ester hydrolysis, and loss of SO_2 (cleavage of the sulfonamide bridge and recombination of the phenyl and triazolopyrimidine rings) (MRID 437154-02).

161-3 Photodegradation on Soil

Triazolopyrimidine- (TP) and aniline- (AN) labeled *cloransulam methyl*, applied to soil and exposed to simulated sunlight (xenon lamp), degraded with respective half-lives of 13 and 28 days on irradiated samples and 16 and 67 days on dark control samples. The resulting half-lives, corrected for aerobic metabolism and adjusted to "sunlight equivalent" days at 40°N Latitude, were 70 and 30 days. Differences between the two label studies may be partly due to the lower light intensity and lack replications in the 0-8 day samples of the AN label study.

Parent concentrations declined from 90-96% of the applied radioactivity to 43-60% after 15 days, and 15-45% after 30 days of irradiation. The amount of CO_2 increased to 8-9% after 30 days of irradiation, compared to <3% in dark controls. One transformation product in the TP study, *TSPA (*cloransulam-methyl sulfonic acid), increased to a maximum of 14 to 18% after 22 days before declining to 5-10% after 30 days. Three additional transformation products -- ASTP (cloransulam-methyl sulfonamide), cloransulam, and 5-OH cloransulam-methyl -- occurred in the dark control at similar or greater concentrations than in the irradiated samples (MRID 437600-01).

161-4 Photodegradation in Air

Because of the low reported vapor pressure (3×10^{-16} mm Hg), cloransulam-methyl is not expected to be volatile. Therefore, fate studies on the photodegradation of cloransulam-methyl in air will not be required.

B. Metabolism

162-1 Aerobic Soil Metabolism

The aerobic soil metabolism of *cloransulam-methyl* does not follow first-order kinetics. An initially-rapid transformation into structurally-similar products slowed over time, with later degradation involving a breakdown of the sulfonamide bridge or triazolopyrimidine ring. Detectable levels of the parent remained at the end of the 357-day study. With a first-order kinetics model, the transformation half-life of cloransulam-

methyl was 16 to 21 days for the first 56 days of the study and 67 to 72 days for the entire 357-day study period. Degradation half-lives calculated by the EPA reviewer for the phenyl-sulfonamide-triazolopyrimidine structure (combining the parent cloransulam-methyl with cloransulam, 5-OH-cloransulam-methyl, and 5-OH-cloransulam) ranged from 50 to 60 days. A non-linear, two-compartment model estimated a transformation half-life of 9 to 13 days for the parent. The two-compartment model splits the parent into two differentially-reacting soil compartments and the half-life is estimated from the combined reaction rates of the two components. The model was described by Alexander and Scow, based on the work of Hamaker and Goring. As expected, the two-parameter model provides a better fit of the experimental data than would a linear first-order half-life prediction, although it slightly underestimates concentrations at 150 to 350 days. Such an approach may not be unreasonable considering the initial reaction appears to be a transformation into structurally-similar products before breakdown of the sulfonamide bridge or triazolopyrimidine ring occurs. The parent and transformation products that are adsorbed tighter in the soil with time may degrade at a different rate than in solution.

Applied to two soils (Cecil loamy sand and Hanford loam) at a concentration of 60-70 ppb, cloransulam-methyl declined to 39-56% of the applied after 14 days, 22-36% after 21 days, 10-15% after 56 days, and 2% after 357 days. *Cloransulam* reached a maximum of 21-37% between 28 and 56 days and was at 10-14% at 357 days. *5-OH cloransulam methyl* peaked at 8-16% at 28 days and was at 2-6% after 357 days. *5-OH cloransulam* peaked at 11% between 129 and 224 days in the Hanford loam but was $\leq$ 4% in the Cecil loamy sand. Unextracted residues increased throughout the study to 44-56% in the Hanford loam and 74-78% in the Cecil loamy sand. A mild acid extraction released more identifiable residues (see table below), suggesting that a portion of the residues may be adsorbed by the soil more tightly with time (MRID 430034-33). These adsorbed residues may degrade at a slower rate, partially explaining the non-linear transformation rate.

Residue	1st Extract	Mild Acid Extraction	Total % of Applied
cloransulam-methyl	1 - 3	1 - 2	3 - 5
cloransulam	9 - 12	6 - 17	14 - 29
5-OH-cloransulam-methyl	2 - 14	0 - 3	4 - 14
5-OH-cloransulam	1 - 10	0 - 9	8 - 11

In a supplemental study, cloransulam-methyl transformed with apparent first-order half-lives of 13-28 days in 16 soils incubated for up to 55 days. Cloransulam, 5-OH-cloransulam-methyl, 5-OH-cloransulam, and CO_2 were identified as transformation products. The results of this study reinforce those of MRID 430034-33 above (MRID 430034-34 with additional data provided by MRID 432166-01). The degradation half-life of the combined residues (cloransulam-methyl and structurally-similar products) was 26-61 days. While the transformation half-lives of cloransulam-methyl showed no correlation with pH on the 16 soils, the degradation half-life of the combined structurally-similar residues was correlated with pH, increasing as the pH decreased (r^2 value of 0.40). This suggests that the parent and its structurally-similar products may be more persistent in acidic soils.

162-2 Anaerobic Soil Metabolism

An anaerobic aquatic metabolism study has been submitted in place of the anaerobic soil metabolism study to fulfill this data requirement.

162-3 Anaerobic Aquatic Metabolism

Cloransulam-methyl transformed under anaerobic aquatic conditions with a half-life of approximately 16 days. Parent concentrations were below detection limits by 120 days. The transformation product *cloransulam* increased to 29-36% at 65 days before declining with a half-life of 45 days. *5-OH-cloransulam* plateaued at 14-22% between 65 and 273 days, then declined with an estimated half-life of 60 days. *Cloransulam-methyl fluorethenyl [N-(2-carboxyphenyl-6-chloro)-[1-methyl-5-(2-fluoroethenyl)-1,2,4-triazolo-3-sulfonamide]]*, comprised <5% of the applied radioactivity through 28 days before increasing steadily to 52-66% after 365 days (MRID 437154-03). Cloransulam-methyl fluorethenyl appears to be a persistent product under anaerobic conditions.

The study is only marginally acceptable because the sediments were not completely characterized (pH and CEC were omitted). While the pH was measured at the sampling times, it is unclear whether the measurements were made for the water, sediments or the mix (all of which are likely to differ). Because of these gaps in data, relationships with sediment properties cannot be determined and applicability of the results of this study to broader conditions is limited.

162-4 Aerobic Aquatic Metabolism

This study is not normally required for terrestrial uses.

C. Mobility

163-1 Leaching and Adsorption/Desorption

In standard batch equilibrium studies, *cloransulam-methyl* was very mobile (Freundlich K_{ads} values 0.15 to 0.46 ml/g) in four soils and mobile (K_{ads} 1.49 ml/g) in a fifth. Single desorption K_{des} values ranged from 0.27 to 1.25 ml/g. *Cloransulam* was mobile in the same five soils (K_{ads} of 1.1 to 2.3 ml/g; K_{des} of 1.6 to 2.8 ml/g). Freundlich n values were close to unity for both chemicals. Mobility generally decreased with increasing cation exchange capacity (CEC) but showed no discernible correlation with pH or organic carbon content (MRIDs 430034-35 and 432166-02).

A second part of the study used non-standard methodology to determine aged desorption in six different soils incubated for up to 3 months under aerobic conditions with 0.2 ppm cloransulam-methyl (approximately 10 times the maximum field concentration at application). At various sample periods, the aged samples were equilibrated overnight with 0.01 M $CaCl_2$ and simple (non-Freundlich) desorption coefficients (apparent K_ds) were calculated from the ratio of extractable material and

material associated with soil pore water. The parent and its transformation products *cloransulam*, *cloransulam-methyl acetic acid*, *5-OH-cloransulam methyl*, and *5-OH-cloransulam* all had low desorption coefficients. Median apparent K_ds for the parent ranged from 0.2 ml/g initially to 1.8 ml/g after 3 months. Initial median K_ds for the four products ranged from 0.2 to 0.7 ml/g; three-month median K_ds ranged from 0.4 to 1.2 ml/g. The K_d values were correlated with pH (increasing with decreasing pH) but not organic carbon content, clay content, or CEC. In general, sorption increased with time; in some soils the apparent increase was substantial. The sorptivities of the degradates were comparable to the parent (MRIDs 430034-35 and 432166-02).

Another aged desorption study on 16 soils, including 6 from the previous study, found low desorption coefficients for cloransulam-methyl and its major transformation products. The respective median non-Freundlich sorption K_ds and K_{oc}s (ranges in parentheses) were 0.43 (0.19-4.9) and 43 (12-260) for cloransulam-methyl, 0.41 (0.25-3.4) and 42 (9-130) for cloransulam, 0.36 (0.18-4.8) and 38 (13-200) for 5-OH-cloransulam-methyl, and 0.21 (0.13-0.49) and 14 (12-44) for 5-OH-cloransulam. A slight, but not categorical, trend for increased sorption over time (through the 55-day study) was noted (MRIDs 430034-34 and 432166-01).

163-2 Volatility -- Laboratory

Because of the low reported vapor pressure (3×10^{-16} mm Hg), cloransulam-methyl is not expected to be volatile.

D. Field Dissipation

164-1 Terrestrial Field Dissipation

Radiolabeled cloransulam-methyl dissipated relatively rapidly from the upper 15 cm of bare-ground plots in Greenfield, IN, and Wayside, MS. The DT_{50} (the time within which 50% of the 0-day concentration dissipated from the upper 15 cm) was less than 5 days at Greenfield, IN, and less than 8 days at Wayside, MS. The DT_{90} was less than 45 days at both sites. The rate of dissipation did not follow first-order kinetics. Based on a nonlinear 2-compartment model, the half-life for cloransulam- methyl ranged from 3.5 days (IN) to 5 days (MS). Five degradates detected in the study reached maximum concentrations of 8-11% within 21-28 days before declining to $\leq$ 3% after 10 months. Four degradates -- cloransulam, 5-OH-cloransulam-methyl, 5-OH-cloransulam, and sulfonamide (ASTP) -- were detected in aerobic and/or anaerobic metabolism studies while sulfonic acid (TPSA) was a photolysis-specific degradate. The degradates identified in the study indicate that metabolism and photolysis are likely to be major routes of degradation for cloransulam methyl in the field. The timing of rainfall and/or irrigation in relation to dissipation at each site and the chemical's known mobility and low affinity for adsorption to soil suggest that leaching through the profile may also play an important role in the dissipation of cloransulam methyl from the surface layer (MRID 437160-02). The results of the field dissipation study are considered supplemental

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because the samples were apparently stored frozen for an unspecified period of time with no storage stability data provided (a previous study -- MRID 430034-34 -- indicated that cloransulam methyl residues decreased in extractability with time in frozen storage).

164-2 Aquatic Field Dissipation

This study is not normally required for terrestrial uses.

E. Accumulation

165-4 Accumulation in Fish

Cloransulam methyl's low reported octanol/water coefficients (log K_{ow} ranges from 1.12 at pH 5.0 to -1.24 at pH 8.5) and its solubility in polar solvents (properties summarized in 436689-33) suggest a low potential for bioaccumulation in fish. Provided that no other evidence of bioaccumulation is found, this data may be waived.

STATUS OF DATA REQUIREMENTS

All of the environmental fate data requirements for the use of cloransulam-methyl as a broad-leaf herbicide on soybeans have been satisfied through acceptable studies or data waivers, with the following exception:

The terrestrial field dissipation study (164-1; MRID 437160-02) is considered supplemental because the samples were apparently stored frozen for an unspecified period of time with no storage stability data provided (a previous study -- MRID 430034-34 -- indicated that cloransulam methyl residues decreased in extractability with time in frozen storage). The registrant can upgrade this study to acceptable by submitting the appropriate storage stability data and, if dictated by the results of this study, make any adjustments as needed in the terrestrial field dissipation results.

Due to concerns about the mobility and the potential persistence of cloransulam-methyl and its structurally-similar, biologically active transformation products in the subsurface and ground water, EFED is requesting that the registrant conduct a prospective ground water monitoring study (166-1).

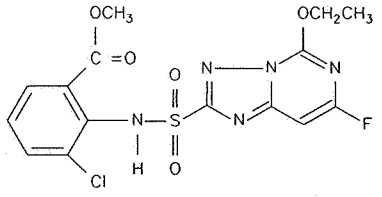
REFERENCES

MRID	CITATION
430034-32	Zabik, S.E. 1993. Hydrolysis of XDE-565 in three water systems: buffered at pH 5, 7, and 9, natural water, and soil slurry. Laboratory Study ID ENV91086. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.
430034-33	Wolt, J.D., J.K. Smith, and G.K. Sims. 1993. Aerobic metabolism of ^{14}C-(phenyl)- and -(pyrimidine)-XDE-565 in two soils. Laboratory Study ID ENV91095. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.
430034-34	Smith, J.K., J.D. Wolt, and G.K. Sims. 1993. A kinetic study of XDE-565 sorption and degradation on sixteen soils. Laboratory Study ID ENV91095.01. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.
430034-35	Cleveland, C.B., J.A. Ostrander, and J.R. Miller. 1993. Laboratory mobility assessments of XDE-565 and metabolites. Laboratory Study IDs ENV92042 and ENV93086. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.
432166-01	Smith et al. 1993. Raw data for a kinetic study of XDE-565 sorption and degradation on sixteen soils. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.
432166-02	Cleveland et al. 1994. Raw data for laboratory mobility assessments of XDE-565 and metabolites. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.
436689-33	Cleveland, C.B. 1995. Environmental fate summary for cloransulam-methyl (DE-565). Laboratory Study ID GH-C 3629. Unpublished study summary submitted by DowElanco, Indianapolis, IN.
437154-02	Cook, W.L., and D.G. Saunders. 1995. Aqueous photolysis of XDE-565. Laboratory Study ID ENV92002. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.
437154-03	Erhardt-Zabik, S., P.L. Havens, and K.F. Hawes. 1995. The anaerobic aqueous metabolism of XDE-565. Laboratory Study ID ENV91110. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.
437160-02	Zabik, J.M., J.R. Miller, J.A. Ostrander, D.W. Roberts, and G.W. Thompson. 1995. Amended report for terrestrial field dissipation of cloransulam-methyl. Laboratory Study ID ENV93031. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.

437600-01 D.A. Merritt, and W.L. Cook. 1995. Photodegradation of DE-565 (cloransulam-methyl) on soil. Laboratory Study ID ENV92003. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.

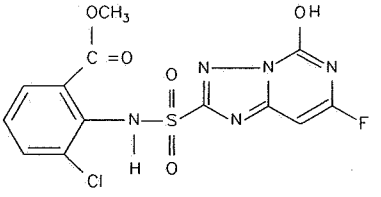
Sposito, G. 1989. The chemistry of soils. Oxford University Press (New York; Oxford).

APPENDIX A
Cloransulam Methyl and Its Structurally-Similar Transformation Products



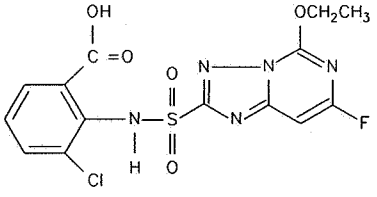
cloransulam methyl

Parent



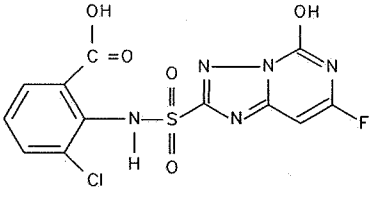
5-hydroxy-cloransulam

Major transformation product in metabolism studies



cloransulam

Major transformation product in metabolism studies



5-hydroxy-cloransulam

Major transformation product in metabolism studies

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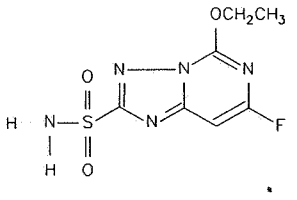
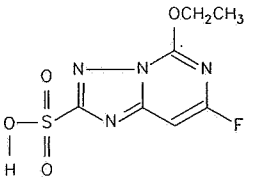
Additional Transformation Products of Cloransulam Methyl



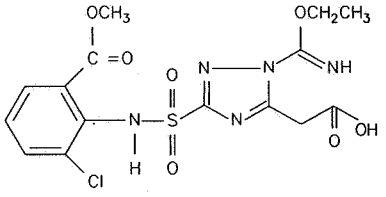
sulfonamide (ASTP)
(aminosulfonyltriazolopyrimidine)

Found in anaerobic metabolism study.



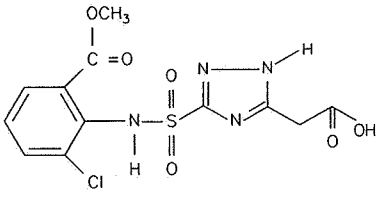
sulfonic acid (TPSA)
(triazolopyrimidine sulfonic acid)

Found in photolysis studies.



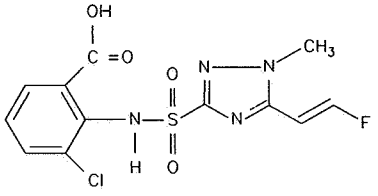
cloransulam methyl imidate

Found in hydrolysis study.



cloransulam methyl acetic acid

Found in hydrolysis study.



cloransulam methyl, fluoroethenyl

Found in anaerobic aquatic metabolism study.

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APPENDIX B

New Data Evaluation Reports For Supporting Environmental Fate Studies

Additional Analyses of Supplemental Study on Aerobic Soil Metabolism and Desorption
MRIDs 430034-35 and 432166-02

ID	Series	Text.	pH	%OC	CEC	Kd	Koc	Aerobic Metab. $t_{1/2}$, days: Parent Chemical	Aerobic Metab. $t_{1/2}$, days: Structurally Similar Prod.
M345	Hoytville	c	7.0	1.23	14.4	0.82	67	15	27
M354	Barnes	cl	7.8	2.52	20.1	0.40	16	15	38
M355	Cecil	sl	7.1	0.31	2.8	0.49	158	15	35
M356	Appling	scl	6.6	0.60	3.0	1.45	242	18	41
M369	Folin	cl	7.4	1.94	17.3	0.32	16	22	32
M373	Sharkey	sic	7.4	1.06	19.9	0.21	20	21	29
M378	?	l	5.7	2.96	18.1	4.89	157	21	51
M388	Hanford	l	7.0	0.48	11.5	0.29	60	13	25
M393	Catlin	sil	6.5	1.96	13.5	1.06	54	30	61
M395	Tama	sil	6.8	2.52	11.4	0.45	18	15	32
M396	Cecil	ls	6.3	0.37	1.9	0.97	262	17	47
M398	Mahoon	cl	7.2	1.02	19.0	0.29	28	17	39
M400	Barnes	l	7.9	2.70	22.2	0.33	12	18	26
M403	Hanford	sl	7.5	0.56	6.9	0.19	34	19	36
M404	Catlin	sil	6.9	2.08	12.3	1.06	51	20	50
M405	Commerce	sil	7.7	0.94	9.7	0.25	27	19	34

Statistical Analyses:

No correlation was found between K_d and %OC [$r^2 = 0.16$ with a p of 0.13]. Any appearance of linearity was primarily due to the M378 sample, with a pH of 5.7 and the highest K_d of 4.89. When that sample is dropped, the resulting plot shows no linearity [$r^2 = 0.004$ with a p of 0.83].

A linear correlation exists between K_d and pH [$r^2 = 0.60$; negative slope; $p < 0.01$]. If M378 is dropped as a potential outlier, the correlation has a lower r^2 (0.56) and a shallower slope. A linear correlation also exists between K_{oc} and pH [$r^2 = 0.45$; negative slope; $p < 0.01$]. Three possible "outliers" (the three highest K_{oc} values) may have been the result of soil samples with low OC contents (<0.6%). The relationships suggest that pH is the dominant factor affecting the adsorption of cloransulam-methyl, with adsorption increasing as the pH decreases.

No correlation exists between the transformation half-life of cloransulam-methyl and pH. However, a linear correlation [$r^2 = 0.40$ with a negative slope] was found between pH and the degradation half-life of the combined cloransulam-methyl and similar transformation products (with potential herbicidal activity). This suggests that persistence of cloransulam-methyl transformation products may be greater at lower pHs.

A more detailed review can be found in the EFGWB review of the EUP application for cloransulam-methyl; 12/23/95 memorandum from A. Clem to R. Taylor and E. Allen.

DATA EVALUATION RECORD

STUDY 1

CHEM 129116 **Cloransulam-Methyl** §161-2
(XDE-565)
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 437154-02
Cook, W.L., and D.G. Saunders. 1995. Aqueous photolysis of XDE-565. Laboratory Study ID ENV92002. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.

REVIEWED BY: Nelson Thurman
TITLE: Environmental Engineer
ORG: EFGWB/EFED/OPP
TEL: 703-308-0465

Nelson Thurman DATE: 07/09/96

CONCLUSIONS:

Degradation - Photolysis in Water

1. This study is acceptable and fulfills EPA data requirements for registering pesticides by providing information on the photolysis of cloransulam-methyl in a sterile pH 7 aqueous buffer solution. No additional information is needed on the aqueous photolysis of cloransulam-methyl at this time.

2. Cloransulam-methyl (XDE-565), applied at a concentration of 1 ug/ml in pH 7 buffer solution, photodegraded rapidly when exposed to natural sunlight near noon on a clear summer day in Indianapolis, IN. XDE-565 concentrations declined from 93 to 96% of the applied radioactivity initially to 40` to 43% after 20 minutes and 9 to 11% after 60 minutes. XDE-565 did not degrade in the dark during that time period. The first-order degradation rate constant was 56.25 da^{-1} and the half-life was 18 minutes (22 minutes for an "average" summer day at 40°N Latitude).

   The sulfinic acid of XDE-565 [5-ethoxy-7-fluoro(1,2,4)tirazolo(1,5c)pyrimidine-2-sulfinic acid], was the major degradate, increasing to a maximum of 23.1% after 60 minutes. The sulfinic acid was formed by the cleavage of the sulfonamide bridge and the loss of the phenyl ring, and would be expected to oxidize readily to the sulfonic acid (TPSA) in natural waters. Six other photodegradates did not exceed 10% of initial concentrations. Four of these were characterized and were believed to form by Cl loss, ester hydrolysis, and loss of SO_2 (cleavage of the sulfonamide bridge and recombination of the phenyl and triazolopyrimidine rings).

METHODS:

Study Design: Phenyl ring radiolabeled (AN XDE-565; 29.3 mCi/mMole; 97.5% pure) or triazolopyrimidine ring radiolabeled (TP XDE-565; 26.9 mCi/mMole; 96.9% pure) cloransulam-methyl (XDE 565) was added to sterile pH 7 buffered solution at a nominal concentration of 1.0 ppm (no co-solvent was used since this concentration is less than the reported solubility of 184 ppm at pH 7). The samples were placed in a constant temperature (25 ± 1°C) water bath and exposed to natural summer sunlight in Indianapolis, IN (39.9° N latitude). Exposure began at 11:20 am, 7/20/93 (no

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cloud cover during test). Duplicates of each radiolabeled sample were removed after 0, 5, 10, 20, 40, and 60 min of exposure, stored in the dark, and refrigerated for up to 16 days prior to HPLC analysis. Replicates of each label were taken at 0 and 60 minutes to serve as dark controls.

Sunlight intensity was determined using PNA/pyridine chemical actinometry. PNA photodegradation data was used to correct for variations in light intensity. Absorbance spectra (290-800 nm range) of the pyrex test tubes, buffer solution, and XDE-565 in water were determined by spectrophotometry.

Analysis: The parent XDE-565 was separated from its photoproducts with reverse phase HPLC using an acidified (1% acetic acid) acetonitrile:water mobile gradient. Method validation using known concentrations showed recovery rates of 80 to 118% for 0.003 ppm and from 75 to 97% for 0.01 ppm of XDE-565. Radioactivity detected by LSC. Photoproducts were identified from higher concentration samples (10 ug/mL of XDE-565 dissolved with 1% acetonitrile co-solvent), which were irradiated with a xenon lamp. HPLC analyses indicated that the photoproduct profile was similar to that found in samples exposed to natural sunlight. Solution aliquots were analyzed by LC/MS directly and after ethyl acetate extraction. GC/MS was used to confirm XDE-565 in 1.0 ug/mL solutions and to identify some photoproducts.

DATA SUMMARY:

Cloransulam-methyl (XDE-565) absorbs light strongly at wavelengths below 280 nm and continues with an absorbance tail extending to 340 nm (Figure 7). The buffer absorbs little light above 290 nm while the Pyrex sample tubes absorb some radiation between 290-340 nm, which could reduce the photolysis rate of the test substance. The first-order degradation rate constant for PNA during the study was 19.04 da^{-1}, slightly faster than the calculated constant of 15.14 da^{-1} for an average summer day at 40°N latitude (Comment 1).

XDE-545 photodegraded rapidly, with a rate constant of 56.25 da^{-1} and a half-life of 18 minutes (Table VII). The plot of the natural log of XDE-565 concentration vs time was approximately linear, reflective of first-order degradation. An analysis of the 0 and 60 minute dark control samples showed no differences in the XDE-565 concentration (Table on p. 23 of study results), suggesting that degradation did not occur in the dark (Comment 2). The authors "normalized" the rate constant for an average summer day at 40°N latitude using the PNA results to come up with a rate constant of 44.73 da^{-1} and a half live of 22 minutes.

Total radioactivity recovered by HPLC compared to stock solution concentration prior to exposure, was 91 to 98% for the AN label and 98 to 101% for the TP label. Little radioactivity was lost to volatiles and few degradates were retained on the HPLC column after elution (Comment 3).

The following photoproducts were identified (Table XI; Figures 19, 23):

> U2 [the sulfinic acid of XDE-565; 5-ethoxy-7-fluoro(1,2,4)tirazolo(1,5c)pyrimidine-2-sulfinic acid], identified in the TP study, increased to a maximum of 23.1% after 60 minutes. The sulfinic acid was formed by the cleavage of the sulfonamide bridge and the loss of the phenyl ring (Comment 4).
> U6, identified in both studies increasing to just over 5% after 60 minutes, resulted from the loss of a methanol group and the replacement of Cl with a proton.
> U7, which increased to a maximum of 7.8% after 60 minutes in both studies, resulted from the loss of the sulfonamide bridge (cleavage and recombination of the phenyl and triazolopyrimidine rings) and replacement of Cl with a proton.

> U5, increasing to a maximum of 6% after 60 minutes in both studies, could be the hydrolysis product of U7 (the methyl ester is hydrolyzed to carboxylic acid).
> U1, which reached a maximum just less than 10% in the AN study, appears to be a mix of degradates. Neither U3 nor U4, found only in the TP study, exceeded 6.7%; the structures of these degradates were not identified.

REVIEWER'S COMMENTS:

1. According to the study authors, the measured rate constant for PNA was greater because the study was conducted near noon, during peak sunlight intensity, while the given rate constant applies to an average day. The correlation coefficient for the plot of the natural log of PNA concentration vs. time was 0.996, indicating that sunlight intensity varied little during the study.

2. Cloransulam-methyl is relatively stable to hydrolysis at pH 7, with only 18% of the parent hydrolyzing after 30 days (registrant estimated half-lives ranging from 118 to 231 days; MRID 430034-32).

3. The study authors referred to the total radioactivity recovered by HPLC compared to stock solution concentration prior to exposure as the material balance. The amount of recovered radioactivity not accounted for by the parent (in Table VII) and the seven degradates (Table XI) increases to as much as 55% by the end of the study as the peaks spread out and other minor peaks form. This method is not a good method for quantifying parent and degradate concentrations.

4. Attempts by the authors to isolate U2 and confirm the structure by other methods identified the sulfonic acid of XDE-565 (TPSA). They noted that the sulfinic acid is easily oxidized to sulfonic acid and that U2 may oxidize to TPSA in natural waters.

STUDY AUTHORS' RESULTS AND CONCLUSIONS

INCLUDING PERTINENT TABLES AND FIGURES

RIN 1455-99

Page _____ is not included in this copy.

Pages 28 through 33 are not included in this copy.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of quality control procedures.

_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

_____ A draft product label.

_____ The product confidential statement of formula.

_____ Information about a pending registration action.

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DATA EVALUATION RECORD

STUDY 2

CHEM 129116 **Cloransulam-Methyl** §161-3
(XDE-565)
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 437600-01
D.A. Merritt, and W.L. Cook. 1995. Photodegradation of DE-565 (cloransulam-methyl) on soil. Laboratory Study ID ENV92003. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.

REVIEWED BY: Nelson Thurman Nelson Thurman DATE: 07/11/96
TITLE: Environmental Engineer
ORG: EFGWB/EFED/OPP
TEL: 703-308-0465

CONCLUSIONS:

Degradation - Photolysis on Soil

1. This study is acceptable and fulfills EPA data requirements for registering pesticides by providing information on the photolysis of cloransulam-methyl on soil irradiated with a xenon lamp. No additional information is needed on the photolysis of cloransulam methyl on soil at this time.

2. Triazolopyrimidine- (TP) and aniline- (AN) labeled cloransulam methyl, applied to soil and exposed to simulated sunlight, degraded with respective half-lives of 13 and 28 days on irradiated samples and 16 to 67 days on dark control samples. The resulting half-lives, corrected for aerobic metabolism and adjusting to "sunlight equivalent" days at 40°N Latitude, were 70 and 30 days. Differences between the two label studies may be partly due to the lower light intensity and lack replications in the 0-8 day samples of the AN label study.

   The amount of parent (DE-565) declined from an initial concentration of 90-96% of the applied radioactivity to 43-60% after 15 days, and 15-45% after 30 days of irradiation. In contrast, parent concentrations declined more slowly in the dark, especially in the AN-labeled study. The amount of CO_2 increased to a maximum of 8-9% after 30 days of irradiation, compared to <3% in dark controls. Only one degradate -- TSPA (SCE-565 sulfonic acid) in the TP study -- occurred only in the irradiated samples, increasing to a maximum of 14 to 18% after 22 days before declining to 5-10% after 30 days. Three additional degradates -- ASTP (XDE-565 sulfonamide), XDE-565 acid, and 5-OH XDE-565 -- occurred in similar or greater concentrations in the dark controls than in the irradiated samples.

3. Cloransulam methyl degraded more rapidly in a separate aqueous photolysis study (MRID 437154-02) while the results here suggest that soil binding may act to reduce the impact of photolysis. The major degradate of the aqueous photolysis study -- the sulfinic acid of cloransulam methyl -- is expected to oxidize readily to TSPA, the major photodegradate in this study, in natural waters.

METHODS:

Study Design: Samples of a Hanford sandy loam (pH 7.4, 8.8% clay, 60% sand, 0.99% organic C, CEC 5.15 meg/100 g), sieved to <2 mm and adjusted to 75% of 1/3-bar water-holding capacity, were placed in the bottom of a quartz flask. Phenyl ring radiolabeled (AN XDE-565; 29.3 mCi/mMole; 95.3% pure) or triazolopyrimidine ring radiolabeled (TP XDE-565; 26.9 mCi/mMole; 98.0% pure) cloransulam-methyl (XDE 565) was added to the soil surface at rates of 1.70 µg/g (equivalent to 48 g/ha or 0.26 lb/A) for all AN samples, 1.51 µg/g (43 g/ha; 0.23 lb/A) for the 0 and 8 day TP samples, and 1.76 µg/g (50 g/ha; 0.27 lb/A) for the remaining TP samples. The flasks were connected to a trapping system that contained activated charcoal and Mallcosorb or Ascarite (CO_2 traps) and maintained at 25°C (Comment 1).

Samples were irradiated on a 14- hr light and 10-hr dark cycle with a xenon lamp equipped with a filter to absorb wavelengths below 290 nm . Light output was monitored using *p*-nitroacetophenone (PNAP) actinometry and compared to "average" summer conditions at 40°N latitude (Comment 2). Duplicate irradiated TP samples were taken at 1, 2, 4, 8, 15, 22, and 30 days. Single AN samples were taken at 1, 2, and 4 days; duplicates at 8 and 15 days; and triplicates at 30 days. Duplicate dark control samples were also taken at each sample time, except for single AN samples at 1, 2, and 4 days.

Analysis: Soil samples were extracted 3 times with 90:10 acetone:1N HCl using sonication at 40°C and shaking (Comment 3). The extracts analyzed by reverse-phase HPLC using an acidified (1% acetic acid) acetonitrile :water mobile phase. A second HPLC method used water with 0.005 M Pic A reagent as an eluent to characterize the zone of polar material near solvent front. The 30-day samples were analyzed by TLC to confirm identified chemicals. The extracted soil, activated charcoal, and Mallcosorb sorbents were combusted. Total radioactivity of the combusted samples, soil extracts, and Ascarite layers were assayed by LSC. $^{14}CO_2$ absorbed by the Ascarite was confirmed with $BaCl_2$ precipitation.

DATA SUMMARY:

Light intensity measured by PNAP actinometry approximated 101% of the average sunlight intensity at 40°N for the 15 to 30 day TP samples and 72% intensity for the AN samples and 0 to 8 da TP samples. Except for fluctuations (15-35°C) at the onset of light/dark cycles, the temperatures were maintained at 25°C. Material balances ranged from 91 to 104% for samples except for the 15 and 30 day AN irradiated samples, which were 87 to <90% (Table IV, V).

The amount of radioactivity detected in the CO_2 traps increased in the irradiated samples to a maximum at the end of 30 days of 9.0% of the applied in the TP-label study and 7.7% in the AN-label study (Table IV, V). In contrast, the amount of radioactivity recovered in the CO_2 traps in the dark controls was <3% in the TP-label study and <1% in the AN-label study. The amount of unextracted radioactivity (labeled "Bound to Soil") increased over the course of the study, to approximately 10% in both irradiated and dark control samples in the TP-label study, 11-14% in the irradiated AN-labeled samples, and <5% in the dark AN-label samples.

In the AN-label study, the amount of parent (DE-565) declined from an initial concentration of 90-96% of the applied radioactivity to approximately 60% after 15 days and 35-45% after 30 days of irradiation (Table VI; Comment 4). In contrast, parent concentrations declined more slowly in the dark, with 69-70% remaining after 15 days and 61-72% after 30 days. The two major degradates identified in the AN-label study occurred in similar concentrations in both the irradiated and dark

control samples. XDE-565 acid (cloransulam) increased to a maximum of 9% after 30 days while 5-OH XDE-565 increased to a maximum of 13% after 15 to 30 days.

In the TP-label study, the amount of parent declined from an initial concentration of 95-96% of the applied radioactivity to 43 to 51% after 15 days and 15% after 30 days of irradiation (Table VII). In the dark controls, parent concentrations declined to 44% after 15 days and 26-31% after 30 days. Three major degradates identified in the TP-label study -- ASTP (XDE-565 sulfonamide), XDE-565 acid, and 5-OH XDE-565 -- occurred in greater concentrations in the dark controls than in the irradiated samples. Only one degradate -- TSPA (SCE-565 sulfonic acid) -- occurred only in the irradiated samples, increasing to a maximum of 14 to 17.5% after 22 days before declining to 5-10% after 30 days.

The degradation half-lives, assuming first-order kinetics, were 13 days for the irradiated TP-label samples and 16 days for the dark control samples (Table VIII). Correcting for aerobic metabolism (degradation in the dark) and adjusting to "sunlight equivalent" days at 40°N Latitude, the photolysis half-life for the TP-label was 70 days. Calculated half-lives for the AN-label study were 28 days (irradiated), 67 days (dark), and 30 days (adjusted for metabolism) (Comment 5). Results of the AN-label study may be less reliable because of the lower light intensity and lack replications in the 0-8 day samples (see Comment 4).

REVIEWER'S COMMENTS:

1. Because the radioactivity was unextractable from the Mallcosorb traps in the 15 to 30 day TP samples, Ascarite was used for the 1 to 8 day TP samples and all AN samples.

2. The authors reference Leifer, 1988 (*The Kinetics of Environmental Aquatic Photochemistry*; ACS Professional Reference Book) for the PNAP-pyridine actinometry procedure. A similar procedure was used for the aqueous photolysis study (MRID 437154-02).

3. The original study protocol (Appendix A) stated that the analytical method for XDE-565 on soil would be developed and validated as a part of the study:
   "The method will be validated by analysis of duplicate samples fortified with at least two different initial concentrations on three separate days. Analysis of the samples maintained in the dark should also be indicative of the method precision."
   This protocol was later amended by the study director to use irradiated samples analyzed between 16 and 30 days. No discussion of method validation is presented in the study results.

   EFGWB is concerned that the amended protocol does not include spiked matrix samples as a part of the method validation. The registrant should be aware that a Data Reporting Guideline (DRG) published in the Federal Register on April 19, 1995 requires independent laboratory validation (ILV) of environmental chemistry methods for new chemicals.

   The impact of the fairly rigorous extraction procedure, which included sonication and heating to 40°C, on the parent molecule is of concern. In an earlier aerobic soil metabolism study (MRID 430034-33), a similar extraction method was used on soil samples because of decreasing extraction efficiency with acetone (90%) acidified with glacial acetic acid (Organic Acid extract) While the more rigorous acetone:1N HCl (Mineral Acid extract) method recovered more radioactivity than the Organic Acid extract, the quantity of the parent XDE-565 did not differ significantly between the two methods. In addition, XDE-565 comprised all of the radioactivity recovered from the soil extracts in the 0-day samples, indicating that the extraction procedure did not affect the parent molecule.

4. The AN-label study suffered from a lack of sufficient replications and poor experimental control. Only one sample was taken on each of the 1, 2, 4, and 8 day periods. Because of mixing errors, the 2-day sample was discarded and no additional samples were available for this time frame. In addition, the study authors reported that the rate of degradation decreased after 8 days (in relation to the TP-label study), probably due to a decrease in soil moisture associated with absorption by the Ascarite traps. Mallcosorb, used in the 15 to 30 day TP-label samples, did not draw water from the soil samples.

5. In comparison to the results of this soil photolysis study, cloransulam methyl photodegraded more rapidly in water (MRID 437154-02). Soil binding may act to reduce the impact of photolysis on the degradation of cloransulam-methyl. In the aqueous photolysis study, the sulfinic acid of cloransulam methyl was the major degradate identified. The authors of that study hypothesized that this degradate would oxidize readily to TSPA in natural waters. In the soil photolysis study, TSPA was indeed the major photodegradate.

STUDY AUTHORS' RESULTS AND CONCLUSIONS

INCLUDING PERTINENT TABLES AND FIGURES

RIN 1455-99

Page _____ is not included in this copy.

Pages 39 through 44 are not included in this copy.

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_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

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_____ The product confidential statement of formula.

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DATA EVALUATION RECORD

STUDY 3

CHEM 129116 **Cloransulam-Methyl** §162-3
(XDE-565)
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 437154-03
Erhardt-Zabik, S., P.L. Havens, and K.F. Hawes. 1995. The anaerobic aqueous metabolism of XDE-565. Laboratory Study ID ENV91110. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.

REVIEWED BY: Nelson Thurman Nelson Thurman DATE: 7/11/96
TITLE: Environmental Engineer
ORG: EFGWB/EFED/OPP
TEL: 703-308-0465

CONCLUSIONS:

1. This study is marginally acceptable, fulfilling the minimum EPA data requirements for registering pesticides by providing information on the metabolism of cloransulam-methyl under anaerobic aquatic conditions.

2. Cloransulam-methyl (XDE 565) degraded under anaerobic aquatic conditions with a half-life of approximately 16 days at 25°C. The parent declined below detection limits by 120 days. The XDE-565 acid metabolite increased to a peak of 29-36% at 65 days before declining with a half-life of 45 days. The 5-hydroxy acid metabolite plateaued at 14-22% of the applied from 65 to 273 days and declined with an estimated half-life of 60 days. Another metabolite, N-(2-carboxyphenyl-6-chloro)-[1-methyl-5-(2-fluoroethenyl)-1,2,4-triazolo-3-sulfonamide], comprised <5% of the applied radioactivity through 28 days before increasing steadily to 52-66% after 365 days.

3. The study is deemed marginal because the sediments were not completely characterized (pH and CEC were omitted). While the pH was measured at the sampling times, it is unclear whether the measurements were made for the water, sediments or the mix (all of which are likely to differ). Because of these gaps in data, relationships with sediment properties cannot be determined and applicability of the results of this study to broader conditions is limited.

METHODS:

Test Substance and Medium: Experiments were conducted using both phenyl (aniline) ring labeled (AN) XDE-565 (29.9 mCi/mMole; ≥96% pure) and triazolopyrimidine ring labeled (TP) XDE-565 (27.8 mCi/mMole; ≥96% pure). The sediment (8.2% organic matter; 23% clay, 22% sand; silt loam; see Comment 1) and water (pH 7.3; total suspended solids 1010 mg/L) were collected from a lake in an agricultural watershed in Washington Co, MS.

Experimental Design: Biometer flasks containing 2:1 water: sediment, spiked with finely-ground alfalfa (Comment 2), were connected to 0.2N NaOH trapping solution, flushed with O_2-free nitrogen,

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and incubated in dark at 25°C or 5°C for 40 days. XDE-565 applied at 0.055 ppm (AN label, 25°C), 0.059 ppm (TP label, 25°C), or 0.063 ppm (TP, 5°C). 10X samples were prepared for product isolation. Samples were taken at 0, 3, 7, 15, 28, 65, 120, 273, and 365 days for the 25°C samples and at 0, 20, 35, 70, and 140 days for the 5°C samples. Eh and pH were measured at several sample intervals.

Extraction and Analysis: Water and sediment were separated by centrifugation. Sediment samples were extracted with acetone/ethyl acetate/1N HCl (85:10:5). Non-extractable residues determined by combustion and trapping of $^{14}CO_2$. Bound residues for 273 and 365 da TP-label samples and the 377 da exaggerated rate samples were extracted by citrate buffer digestion and NaOH for characterization. The NaOH trapping solutions were removed and assayed for dissolved $^{14}CO_2$. Radioactivity was determined using LSC. Sample extracts were analyzed by reverse phase HPLC with an acidified (1% acetic acid) acetonitrile:water mobile phase. Minimum detectable level for both labels was 0.3% (59 ppb) of the applied radioactivity. Confirmation of chemical identity was made by either reverse or normal phase TLC. Unknown degradates were analyzed by LC/MS.

DATA SUMMARY:

25°C Anaerobic Aquatic System: The test system appeared to remain anaerobic throughout the study (Comment 3). The material balance ranged from 91 to 112%. The results of the AN-label and TP-label studies were similar, indicating that the two ring structures were not separated during the study. The majority of the radioactivity was associated with the water fraction throughout the first 28 days (Table V). From 65 to 120 days, the water fraction contained approximately half of the applied radioactivity; from 273 to 365 days, the majority of the radioactivity was found in the sediment fraction (combined total of extracted and nonextracted fractions). The decline in radioactivity in the water fraction coincided with the decline and disappearance of the parent cloransulam methyl (XDE 565) (Tables VI and VII). The amount of unextracted residues (labeled "Combustion" in Table V) increased throughout the study to a maximum of 20-32% after 365 days.

Cloransulam methyl declined in concentration from an initial 87-94% of the applied to 54-65% after 28 days (combined water and sediment fractions) and below limits of detection at 120 days. The rate of metabolism followed apparent first-order kinetics, with a calculated half-life of 15.8 days. The parent remained predominantly within the water fraction. The acid metabolite increased to a peak of 29-36% at 65 days before declining to <2% after 365 days. The 5-hydroxy acid metabolite plateaued at 14-22% of the applied from 65 to 273 days, declining to 2-6% at 365 days. The estimated half-lives, assuming first-order rates for both the parent and degradates, were 45 days for the acid and 60 days for the 5-hydroxy acid metabolites. "Unknown 1," identified as N-(2-carboxyphenyl-6-chloro)-[1-methyl-5-(2-fluoroethenyl)-1,2,4-triazolo-3-sulfonamide], comprised <5% of the applied radioactivity through 28 days before increasing steadily to 52-66% after 365 days. Substantial portions of the metabolite residues remained in the water fraction, although the metabolites demonstrated a higher affinity for the sediments than did the parent (Table VIII). A proposed metabolic pathway is illustrated in Figure 15.

5°C Anaerobic Aquatic System: As would be expected, metabolism proceeded at a slower rate in the 5°C samples. The calculated half-life for cloransulam methyl was 237 days. The XDE-565 acid was the major metabolite, increasing to approximately 10% of the applied after 140 days. The 5-hydroxy acid and "Unknown 1" were detected at $\leq$1% at 140 days.

REVIEWER'S COMMENTS:

1. The sediment used in the experiment was not completely characterized because of limited sample size. The reviewer believes that better prioritization of data needs could have been employed. While pH and CEC, two important properties useful in understanding adsorption and metabolism dynamics, were not determined, bulk density, a meaningless parameter in a lab bench study on metabolism, was analyzed. The study authors state that pH was measured at the sampling times, but are unclear as to whether the measurements were made for the water or sediments or the mix (all of which are likely to differ). Because of these gaps in data, relationships with sediment properties cannot be determined and applicability of the results of this study to broader conditions is limited.

2. The finely-ground alfalfa was added as an organic matter source. While the amount added (equivalent to 1% by weight) was low, the organic matter content of the sediment (8.2%) was adequate for the microbial activity in the study.

3. The pH and redox potential were not measured every time (Table IVa,b). Where both measurements are made (28, 65, 273 da), the Eh-pH is within the anaerobic range. For the 0 and 3 day samples, no measurements were taken to confirm anaerobicity. For the remaining samples, anaerobic conditions can be inferred assuming that the pH did not vary. In all likelihood, anaerobic conditions existed during the study as long as no leaks occurred in the system.

STUDY AUTHORS' RESULTS AND CONCLUSIONS

INCLUDING PERTINENT TABLES AND FIGURES

RIN 1455-99

Page _____ is not included in this copy.

Pages 49 through 55 are not included in this copy.

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_____ Identity of product inert ingredients.

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DATA EVALUATION RECORD

STUDY 4

CHEM 129116 **Cloransulam-Methyl** §164-1
(XDE-565)
FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 437160-02
Zabik, J.M., J.R. Miller, J.A. Ostrander, D.W. Roberts, and G.W. Thompson. 1995. Amended report for terrestrial field dissipation of cloransulam-methyl. Laboratory Study ID ENV93031. Unpublished study performed and submitted by DowElanco, Indianapolis, IN.

REVIEWED BY: Nelson Thurman Nelson Thurman DATE: 8/11/96
TITLE: Environmental Engineer
ORG: EFGWB/EFED/OPP
TEL: 703-308-0465

CONCLUSIONS:

1. This study provides supplemental data that may be used toward fulfillment of Subdivision N environmental fate data requirements on the dissipation of cloransulam methyl from bare-ground plots in two use areas (IN and MS). This study may be upgraded by providing information on length of frozen storage and storage stability data for cloransulam methyl and its degradates.

2. Radiolabeled cloransulam methyl dissipated relatively rapidly from the upper 15 cm of bare-ground plots in Greenfield, IN, and Wayside, MS. The DT_{50} (the time within which 50% of the 0-day concentration dissipated from the upper 15 cm) was less than 5 days at Greenfield, IN, and less than 8 days at Wayside, MS. The DT_{90} was less than 45 days at both sites. The rate of dissipation did not follow first-order kinetics. Based on a nonlinear 2-compartment model, the half-life for cloransulam methyl ranged from 3.5 days (IN) to 5 days (MS).

   Five degradates detected in the study reached maximum concentrations of 8-11% within 21-28 days before declining to $\leq$ 3% after 10 months. Four degradates -- cloransulam, 5-OH cloransulam methyl, 5-OH cloransulam, and sulfonamide (ASTP) -- were detected in aerobic soil and/or anaerobic aquatic metabolism studies. Sulfonic acid (TPSA) was the only photolysis-specific degradate identified. The degradates identified in the study indicate that metabolism and photolysis are likely to be major routes of degradation for cloransulam methyl in the field. The timing of rainfall or irrigation in relation to dissipation at each site and the chemical's known mobility and low affinity for adsorption to soil suggest that leaching through the profile may also play an important role in the dissipation of cloransulam methyl from the surface layer.

METHODS:

Test Substance and Plot Information: Phenyl-labeled (AN) and triazolopyrimidine-labeled (TP) cloransulam methyl (XDE-565) were applied by pressurized hand boom sprayer at a target rate of 50 g a.i./ha (approx. 0.27 lb/A) to bare-ground plots in Greenfield, IN, and Wayside, MS

(Comment 1). Filter paper disks (55 mm diameter) placed on the plots were used to evaluate the uniformity of the application. The sites included a separate 122 x 520 cm (4 x 17 ft) plot for each label, with 91 x 244 cm (3 x 8 ft) control plots located upwind from the treatments. A wood containment wall was built around each plot, with a runoff collection system installed at the downslope end. Rainfall, air and soil temperatures, and solar radiance were measured on-site while pan evaporation data was obtained from nearby NOAA stations. Precipitation was supplemented with irrigation in order to achieve 125% of the 30-year monthly average. The soils at each site were characterized to 90 cm (Tables X and XI; Comment 2). No plot history is provided. The infiltration rate for each plot was measured using a constant head infiltrometer.

XDE-565 was applied to the plots on June 9, 1993, in MS and on July 8, 1993, in IN, coinciding with the end of the soybean planting season. The final field sample was taken on September 9, 1994 (453 DAT) in MS, and on October 11, 1994 (458 DAT) in IN. No dates for analysis or length of time in storage are provided. The study was completed on June 9, 1995 (Comment 3).

Sampling: The plots were divided along the slope gradient into 3 sections and a core sample to 90 cm was taken from each section (3 per plot) at each sample interval. The top 15 cm was sampled as a 5.7- (MS) or 11.4- (IN) cm diameter core; lower depths were sampled with a 3.2- (MS) or 2.2- (IN) cm diameter core. The samples were frozen and transported to the laboratory for analysis (Comment 3). The cores were analyzed separately rather than composited in order to provide information on core-to-core variability (Comment 4). Aliquots of runoff water were collected periodically during the first 10 months of the study.

Analysis: The filter paper disks used to evaluate the rate and distribution of application were extracted with acidified acetone (10% 1N HCl) and the extracts were analyzed by LSC. Total radioactivity retained by the soil was determined by combustion and LSC analysis. Soil samples were extracted with acidified acetone (10% 1N HCl), concentrated, filtered, and analyzed by HPLC. The parent and degradates cloransulam, 5-OH cloransulam-methyl, and 5-OH cloransulam were confirmed using LC-MS/MS. The sulfonamide and sulfonic acid degradates were confirmed using TLC and LC-MS. The extracted soil was combusted and analyzed by LSC for non-extracted residues. The runoff water was analyzed for total radioactivity by LSC. Sediment in the water was combusted and the amount of $^{14}CO_2$ collected was determined by LSC.

DATA SUMMARY:

The average rate of application detected by filter paper disks for the AN- and TP-label studies was, respectively, 117% (range of 70-152% with a standard deviation of 28% for 9 samples) and 98% (75-132%; sd 22%) on the MS plots, and 109% (65-151%; sd 28%) and 106% (46-158%; sd 32%) on the IN plots. Except for the AN-plot in MS, the rate of application estimated from the 0-15 cm soil cores was lower: 60% (sd 16%) for the TP plot in MS, 91% (sd 16%) for the AN plot and 70% (sd 24%) for the TP plot in IN (Comment 5). The majority of the radioactivity in the TP travel spikes remained intact as cloransulam methyl (86-88%), with 9-13% as unextracted residues. No radiolabeled materials were observed in the control samples. The concentrations of the parent and the degradates were similar for both label studies and, except where noted, the results represent a combined range of the two labels.

Greenfield, IN. The combined rainfall and irrigation exceeded the 30-year average in each of the first five months of the study, and exceeded the pan-evaporation rate in 3 of the first 4 months (Table VIII; Comment 6). The warm, sunny weather and moist soil at the time of application

favored photolysis and metabolism. The concentration of cloransulam-methyl in the surface 15 cm declined from an initial level of 64-70% of the 0-day recovered radioactivity (equivalent to 19.4-26.4 ng/g or 34.8-43.7 g/ha) to 27-35% (10.2-10.6 ng/g; 15.4-19.8 g/ha) after 4 days and $\leq$ 6% (0.3-1.2 ng/g; 0.2-2.9 g/ha) from 21 to 300 days (Tables XV-XVI). Sulfonic acid (TPSA) reached a maximum of 11% at 21 days while cloransulam (acid), 5-OH cloransulam methyl (5-OH), 5-OH cloransulam (5-OH acid), and sulfonamide (ASTP) reached maximums of $\leq$ 8% within 27 days; all were $\leq$ 3% after 300 days (Comment 7). Unextractable residues varied between 6-25% throughout the study and 11% was lost by runoff. The total amount of recovered radioactivity declined throughout the study to 21-29% after 300 days (Comment 8).

Wayside, MS. The combined rainfall and irrigation exceeded the 30-year average in each of the first 8 months of the study but was less than the pan-evaporation rate during the first 5 months (Table IX; Comment 6). Although the soil and air temperatures at the time of application were warmer than at the IN site, solar radiation was lower (3,164 vs 25,069 W/m^2). As a result, the parent made up a greater percentage of the 0-day recovered radioactivity in this study. The concentration of cloransulam-methyl in the surface 15 cm declined from an initial level of 84-87% of the 0-day recovered radioactivity (16.7-35.9 ng/g; 29.8-58.5 g/ha) to 33-35% (6.6-14.4 ng/g; 11.3-26.0 g/ha) after 8 days and $\leq$ 6% (0.4-1.8 ng/g; 0.2-3.6 g/ha) from 42 to 299 days (Tables XIX-XX). Cloransulam (acid) reached a maximum of 7% at 28 days before declining to 1% after 299 days and sulfonamide (ASTP) reached a maximum of 14-16% between 3 and 42 days before declining to 4-6% after 92 days (Comment 7). Unextractable residues varied between 3-21% throughout the study and 2% was lost by runoff. After 299 days, the total amount of recovered radioactivity declined to 15% in the AN-label and 54% in the TP-label (Comment 8).

Dissipation Rates: Cloransulam methyl dissipated relatively rapidly from the upper 15 cm at both sites. The DT_{50} (the time within which 50% of the 0-day concentration dissipated from the upper 15 cm) was less than 5 days at Greenfield, IN, and less than 8 days at Wayside, MS. The DT_{90} was less than 45 days at both sites. The rate of dissipation did not appear to follow first-order kinetics (Comment 9). Using a nonlinear 2-compartment model, the study authors calculated a half-life for cloransulam methyl of 3.5 days at Greenfield, IN (with 84% of the variability explained) and 4.8 days at Wayside, MS (with 91% of the variability explained).

Dissipation Pathways: Based on the degradates detected in the study, metabolism (aerobic and anaerobic) and photolysis appear to be major pathways of degradation for cloransulam methyl in both field studies (Figure 22). The differences in dissipation rates between the IN and MS sites illuminate potential pathways of dissipation. On the day of application, the solar radiation was much greater at the IN site (25,069 vs. 3,164 W/m^2). As a result, degradation of the parent was evident even in the day 0 samples (the parent comprised 64-70% of the radioactivity recovered on day 0 at IN compared to 84-87% at MS). On subsequent days within the first week, the amount of solar radiation reaching the sites was similar (Appendix F). Since the dissipation rates were calculated based on day-0 concentrations of the parent, the initial photolysis does not completely account for the differences in dissipation rates between the two sites. The daily weather data indicate that soil temperatures were higher at the MS site. However, the organic matter content was higher in the IN soils and, based on the authors' results and discussion, the IN soils were moist at the time of application so that conditions for metabolism may have been more favorable. Although the study authors did not discuss leaching as a mode of dissipation, the timing of rainfall or irrigation and the known mobility of cloransulam methyl suggest that leaching may also play a role in dissipation from the surface layer (Comments 8 and 10).

REVIEWER'S COMMENTS:

1. Phenyl ring labeled XDE-565 had a specific activity of 29.3 mCi/mMole and was >99% pure. Triazolopyrimidine ring labeled XDE-565 had a specific activity of 26.9 mCi/mMole and was >91% pure for the IN site and >99% for the MS site. The test substance was prepared in a 50:50 acetonitrile:water mix rather than the usual 100% water solvent to "insure that the test substance was completely re-solubilized after transport to the field site." Such a mix might result in differences in mobility or persistence in the field that would not normally be encountered with the 100% water mix to be used for actual applications.

2. The soil mapping units identified both sites suggest that the soils are seasonally wet. Crosby (Greenfield, IN) is classified as a fine, mixed, mesic Aeric Ochraaqualf; Commerce (Wayside, MS) is a fine-silty, mixed, nonacid thermic Aeric Fluvaquent. The authors report that the depth to seasonal high water table is 1 to 3 feet at Greenfield, IN, and 2 feet at Wayside, MS. The IN site was tile-drained; the MS site was not. In drained soils, movement of mobile pesticides, such as cloransulam methyl and its degradates, off the site in the drainage water should be evaluated as a route of dissipation. This was not done in this study.

   No analytical methods or references are provided for the soil characterization data. While the soils were analyzed in 15-cm intervals to coincide with sampling intervals, differences in soil properties with depth are reflected in natural horizons of variable thickness. Such differences may be obscured if the 15-cm intervals encompass portions of more than one soil horizon.

3. The length of storage is not provided in the study. An examination of the sampling dates (Table VII in the study report) and HPLC-MS/MS figures provided by the authors (Figures 27a through e in the study report) suggest that the 27 DAT Greenfield, IN, sample was sampled on 8/4/93 and analyzed by HPLC between 5/12/94 and 7/6/94. Storage stability is a concern since the extractability of XDE-565 residues decreased as a result of frozen storage prior to extraction in an earlier study (MRID 430034-34). The 27-day AN and TP samples and 155-day TP samples from the IN site were re-analyzed after "approximately 3 months of storage." No discernable pattern of decline was evident. However, it is unclear if frozen soil samples were extracted and analyzed or if the original extracts were re-analyzed. In addition to the sampling date, the author needs to provide information on (1) the length of time the samples were held in storage and the storage conditions, (2) the date of extraction, (3) the date of analysis, and (4) the necessary data to demonstrate that the samples were stable in storage.

4. The EPA reviewer commends the study designers for analyzing the core samples separately rather than compositing them. As the data in this study indicates, the distribution of the applied pesticide across the site is not uniform and compositing would mask the differences. Although the data may appear "messy" from a summary point of view, it allows for a better assessment of variability of the results. The small core diameters likely contributed to the variability of the data since these samples were likely too small to include a true representative elemental sample volume (REV). The study authors noted that fewer cores (3 rather than 5) were taken because of the small plot size in order to avoid a "swiss cheese" effect. While a larger core (sufficient to encompass the REV) may have contributed to the hole effect, it may also have reduced the variability between samples.

5. The study authors attribute discrepancies between the filter paper and soil results to degradation of cloransulam methyl in the soil at the beginning of the study and to the loss of up to 12% of the radioactivity in clean-up or extraction. Other factors may also include differences in sample

coverage between the two methods (nine 5.5-cm disks were placed on the field compared to three 5.7-cm or 11.4- cm soil cores), differences in the media (paper vs. soil), and the possibility that the extractability of cloransulam methyl residues decreases during frozen storage (see Comment 3).

6. Although no conservative tracer was used, the weather data suggest that the potential for leaching existed for at least part of the study, particularly at the Greenfield, IN, site. During the critical beginning of the study, 1 inch of rain fell before the day 4 sample, an additional 2.2 inches before the day 12 sample, and 2.1 inches before the 21 day sample at the Greenfield, IN site. At Wayside, MS, 2.4 inches of rain/irrigation were added before the day 8 sample and an additional 1.8 inches occurred before the 14 day sample.

7. Cloransulam (acid), 5-OH cloransulam methyl (5-OH), and 5-OH cloransulam (5-OH acid) were major degradates identified in an aerobic soil metabolism study (MRID 430034-33). Sulfonic acid (TPSA) was the only photolysis-specific degradate identified in a soil photolysis study (MRID 437600-01). Sulfonamide (ASTP), cloransulam, and 5-OH cloransulam occurred in equal concentrations in both the light and dark controls in the photolysis study and were also the major degradates in an anaerobic aquatic metabolism study (MRID 437154-03).

8. The study authors attribute the declining material balance over the course of the study to the production of $^{14}CO_2$. However, they provide no evidence to support this conclusion. Losses due to leaching should also be considered a major route of dissipation. Laboratory studies (MRIDs 430034-35 and 432166-02) show that cloransulam-methyl has little affinity to adsorb to the soil (K_{ads} values <0.5 in four soils, <1.5 in a fifth). Although sorption increased with time (MRIDs 430034-34 and 432166-01), aged cloransulam methyl was still mobile (non-Freundlich K_d value of 1.8 after 3 months). If the chemical is leached from the surface with little affinity for adsorption, a portion of it may be carried through the soil profile and not show up in the soil cores. This potential could have been evaluated by analyzing for the presence of cloransulam methyl (radioactivity) in the tile-drainage water at the IN site.

9. In the aerobic soil metabolism study (MRID 430034-33), the rate of metabolism for cloransulam methyl did not follow first-order kinetics either. The authors used a similar nonlinear, 2-compartment model to estimate dissipation rates for the metabolism study (MRID 436689-33).

10. The first potential leaching rain (1.05 inches) in IN fell on day 3, prior to the 4-day sampling period. The first potential leaching period in MS occurred on days 5-6, when 0.99 inches of irrigation was followed by 1.33 inches of rain. The differences in timing could potentially account for differences in dissipation. Data presented by the authors indicate that radioactivity was detected primarily within the upper 45 cm at the IN site (with occasional detects at 60 cm and one at 90 cm) and within the upper 30 cm at the MS site (Figures 28-29). As noted in Comment 8, cloransulam-methyl has little affinity to adsorb to soil, the analyses of the soil samples may underestimate the actual amount of radioactivity that moved through the soil by leaching. In addition, dilution of the chemical with depth may result in concentrations below the detection limit.

STUDY AUTHORS' CONCLUSIONS

INCLUDING PERTINENT TABLES AND FIGURES

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