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**DYNAMAC**  
CORPORATION

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**ENVIRONMENTAL FATE AND EXPOSURE  
ASSESSMENT OF ACIFLUORFEN**

**REVIEW AND EVALUATION OF DATA  
SUBMITTED SUBSEQUENT TO THE  
INITIAL REVIEW**

Contract No. 68-01-6679

Final Report

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**SUBMITTED TO:**

Environmental Protection Agency  
Arlington, Virginia 22202

**SUBMITTED BY:**

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## Environmental Fate and Exposure Assessment of Acifluorfen

The following is a reassessment of the environmental fate and exposure data submitted by Rhone-Poulenc Inc. for the registration of acifluorfen as a herbicide to control broadleaf weeds in soybeans (Accession No. 071323-071327). The reassessment is based on additional data and comments submitted by Rhone-Poulenc (Accession No. 250467, May 27, 1983) in response to the initial review of these data (Dynamac Corp., March 10, 1983). The initial review contains a complete description of the procedures and results from each study and that information is not fully repeated here. New data submitted by Rhone-Poulenc subsequent to the initial review are included if pertinent. In this review, all studies have been reevaluated in light of the additional data submitted. Also included are responses to Rhone-Poulenc comments regarding the initial review of these studies. In some instances Rhone-Poulenc comments were concerned with points of clarification that had no effect on the validity or interpretation of data. Such comments were either briefly noted or not mentioned in this report. In studies that have been reevaluated to meet data requirements, a complete description of the data is included. In studies that do not satisfy current guideline requirements, a description of the studies' deficiencies is listed.

#### 4.1 STUDY 1

Norris, F.A., and A.E. Hassell. November, 1980. Hydrolytic stability of MC-10978 in buffered aqueous solutions. Mobil Chemical Company. Technical Memorandum TME-80.17. Acc. No. 071323.

Additional information submitted by the registrant is adequate to characterize the test substance. In response to the observation noted in the initial review (Dynamac Corp., March 10, 1983) that the report did not state that the study was conducted in the dark, the registrant has reiterated that the samples were held in an incubator or a styrofoam box. If these containers shielded the samples from light this should be stated. Additional data submitted indicate that acifluorfen was not hydrolyzed over a 28-day period. Variation in acifluorfen levels between the 92- and 120-day samples at pH 3 and 6 in the 1-ppm samples is high. However, these data appear to reflect variations inherent in the analytical methodology rather than changes in the acifluorfen concentration. It is obvious from the 25-ppm samples that acifluorfen is stable in water. The experiment was conducted at 20 and 40°C. Although these temperatures meet the 1978 guidelines the variation at the lower temperature was too high (18-25°C) to meet data requirements. Variation in temperature for the 40°C samples was not specified. However, the data adequately demonstrate that the stability of the test substance in aqueous solution is not influenced by temperature in the 18-40°C range.

Acifluorfen (analytical grade, 99.8% pure) is stable over a 28-day incubation in buffered aqueous solutions (pH 3, 6, and 9) at 18-25°C and 40°C. Data requirements are fulfilled. No further data are required.

#### 4.2 STUDY 2

Somma, N., F.A. Norris, and A. Guardigli. September, 1982. Photodegradation of Tackle in aqueous solution. Rhone-Poulenc Inc., Monmouth Junction, New Jersey. ASD Report No. 82/048. Acc. No. 071323.

The registrant has supplied additional data to fully characterize the test substance and standards used. All compounds were >99% chemically pure. Labeled materials were >98% radiochemically pure. In light of the 1978 proposed Guidelines for Pesticide Registration and the low pKa of acifluorfen, the requirements in the 1983 Guidelines for buffer controlled pH are waived. Additional information submitted indicated that the study was conducted at 40-45°C and the microbial activity in test solutions was sufficiently low so as to have a negligible affect on the rate of acifluorfen disappearance. The hydrolytic stability study (Mobil Technical Memorandum TME-80.17) provides data to serve as a control in this study. In the initial review (Dynamac Corp., March 10, 1983) Table 1 in Appendix 9.9 of the submitted data was partially misinterpreted by Dynamac. The question concerning excessive evaporation during the study study has been clarified by the registrant. Essentially no evaporation occurred. Unaccounted for <sup>14</sup>C activity was equivalent to ~10% of the total <sup>14</sup>C initially added. The total <sup>14</sup>C trapped as volatiles was only 3.7% of the total. However, substantial volumes of the test solution were removed for analysis during the experiment. Volatiles collected

subsequent to aliquot removal only reflect losses of the solution remaining. Therefore, the volatile losses occurring in the later phases of the experiment are underestimated. As illustrated in Table 1, the loss of  $^{14}\text{C}$  activity from solution accelerated with increased length of exposure to light. An estimated 36.6% of the  $^{14}\text{C}$  activity was removed from solution within 216 hours either by volatilization, adsorption, precipitation or a combination of these mechanisms. Because of the potentially high losses of  $^{14}\text{C}$  as volatiles, the quantitative data for the individual amounts of 2-chloro-4-trifluoromethyl phenol and 4-[2-chloro-4-(trifluoromethyl)phenoxy]-1-nitrobenzene recovered from the volatile traps should be submitted. Additional data to quantify the losses of  $^{14}\text{C}$  from solution are required. It is suggested that  $^{14}\text{C}$ -labeled glyphosate solution be irradiated as in the original study for 216 hours. Gross  $^{14}\text{C}$  activity in the solution and in the volatile trap should be determined. If a significant portion of the  $^{14}\text{C}$  is not recovered, the reaction vessel should be exhaustively extracted to determine if insoluble or adsorbed photodegradation products are present.

In the initial review of these data the half-life of acifluorfen was incorrectly printed as 92 days in the Conclusions section. The estimated half-life is 92 hours, as was correctly stated in the Results section of the initial review.

This study demonstrates that acifluorfen in aqueous solution is rapidly degraded on exposure to light. The estimated half-life is 92 hours of continuous exposure; this is roughly equivalent to 8 days of natural exposure (11-12 hours/day of sunlight). Major degradates in solution and volatilized from solution have been identified. Because of the sampling procedure the  $^{14}\text{C}$  activity either volatilized from the solution or otherwise lost from the solution (unaccounted for  $^{14}\text{C}$  activity) was underestimated. Additional data are required to provide a more accurate materials balance. Data to identify additional degradates or to further quantify degradates may also be necessary. The need for these data is dependant upon the results from the material balance study.

Table 1. <sup>14</sup>C Activity not recovered in the solution irradiated with artificial light.

Time (hours)	Volume <sup>a</sup> (ml)	Calculated <sup>14</sup> C activity (DPM) <sup>b</sup>	Measured <sup>14</sup> C activity (DPM) <sup>c</sup>	<sup>14</sup> C lost <sup>d</sup> (%)
0	500	9.580X10 <sup>7</sup>	9.580X10 <sup>7</sup>	-- --
24	497	9.523X10 <sup>7</sup>	8.981X10 <sup>7</sup>	5.7
72	347	6.523X10 <sup>7</sup>	5.882X10 <sup>7</sup>	6.2
96	197	6.270X10 <sup>7</sup>	3.038X10 <sup>7</sup>	9.0
216	70	3.339X10 <sup>7</sup>	9.100X10 <sup>6</sup>	15.7

<sup>a</sup>Volume of acifluorfen solution before the sampling aliquot was removed during a given sampling time.

<sup>b</sup>Calculated <sup>14</sup>C activity based upon previous sampling.

<sup>c</sup><sup>14</sup>C activity based upon DPM/ml measured in sampling aliquot.

<sup>d</sup>(Calculated <sup>14</sup>C activity - measured <sup>14</sup>C activity)/calculated <sup>14</sup>C activity.

#### 4.3 STUDY 3

Gerecke, D.R., and J.P. Wargo. August, 1982. Photodegradation of Tackle (MC-10109) on a soil surface. Rhone-Poulenc Inc., Monmouth Junction, New Jersey. ASD Report No. 82/045. Acc. No. 071323.

All the information that was requested in the initial review (Dynamac Corp, March 10, 1983) has been submitted by the registrant. The temperature at which the study was conducted was 42 ± 1°C. The actual recoveries of acifluorfen were provided and are given in Table 2. Recovery of the parent decreased from 95.0% at time 0 to 75.7% after 30 days of continuous exposure to light. The half-life estimate is extremely poor because the data do not conform well to first first order kinetics (r<sup>2</sup>=0.6182) and the predicted half-life (140 days) is well beyond observed data points (30 days). All data requirements are met. No further data are required.

Table 2. Recovery of [<sup>14</sup>C]acifluorfen from soil TLC plates after exposure to artificial sunlight.

Time of exposure (hrs)	[ <sup>14</sup> C] Acifluorfen <sup>a</sup> recovered (%)
0	95.0
1	93.6
2	87.0
4	84.2
8	84.5
24	86.3
48	90.2
72	82.8
168	80.3
336	82.0
672	77.7
720	75.7

<sup>a</sup>Recovery from dark controls was 93.0-99.6%

#### 4.4 STUDY 4

Wargo, J.P. July, 1982. Metabolism of carbon-14 labeled MC-10978 in Kansas, Virginia, Georgia, and New Jersey soils under aerobic and anaerobic conditions. Rhone-Poulenc Inc., Monmouth Junction, New Jersey. ASD Report No. 82/040. Acc. No. 071324.

The effectiveness of the extraction procedure was questioned in the initial review of these data (Dynamac, March 10, 1983) because sizeable quantities of <sup>14</sup>C not removed by the three initial extractions were solubilized in the hot 2% HCl in methanol extract (3.2-15.9%). TLC autoradiographs revealed that the parent and metabolites found in the extracts at ambient temperatures were also in the hot acidified methanol extracts. The registrant has indicated that only minimal quantities of the parent were present in the hot extracts, but quantification of identifiable <sup>14</sup>C components in these extracts has not been submitted. Therefore, an evaluation of the significance of the residues in these extracts cannot be completed. In addition, it is not known if additional metabolites or parent remained in the soil after the fourth and final extraction.

The registrant has pointed out that the three initial extractions (collectively) were effective in extracting all residues at time 0. However, it is apparent from the data in this study and from Study 8 that the extractability of acifluorfen residue decreases with time. The registrant has provided no data with which the efficiency of the extraction procedures used on aged residues can be evaluated.

The registrant has stated that the results from the anaerobic incubations in this study should be considered supplementary data. Therefore no additional data concerning anaerobic metabolism in this study will be requested. The  $^{14}\text{C}$  reported as "bound residue" in the soil incubated aerobically accounted for  $\leq 10.2\%$  of the total radioactivity in three of the four soils. Presumably portions of the reported values reflect  $^{14}\text{C}$  incorporated into soil organic matter. Therefore, any parent or primary metabolite not extracted in these studies must be relatively low, and possible errors resulting from poor extraction efficiency must be relatively low. Therefore, no additional data on extraction efficiency are required.

A single autoradiograph of the residues in the flood water from the anaerobic study was included in the initial submission of these data. It was evident from this autoradiograph that substantial quantities of  $^{14}\text{C}$  degradation were in the time 0 sample. The registrant has responded to this observation by stating that this autoradiograph represented the only sample in which degradation had apparently occurred during storage. No TLC data on other time 0 samples were submitted. No additional data are requested because the anaerobic soil metabolism data in this study were submitted as supplementary information not intended to fulfill data requirements.

In the initial review of this study the TLC systems used were judged to be inadequate to clearly separate acifluorfen metabolites. This judgement was based upon the sample autoradiographs included in the petition. The registrant has responded by submitting  $R_f$  values for the suspected metabolites and parent in two solvent systems. (Table 3). Metabolites MC-10074 and MC-10108 are obviously not separated by the TLC analysis. Separation of MC-10879 and MC-14621 is minimal when chromatographing standards. Separation of these compounds when chromatographing uncleaned soil extracts does not appear to be adequate based on the information available for review. The registrant has not provided sufficient data to substantiate the claim that the TLC analyses are adequate. The information submitted is only a summary of results, including a few sample autoradiographs. It is obvious from these autoradiographs that difficulties arose in separating all the metabolites. The registrant has stated that when poor separations were encountered, additional TLC separations were performed to obtain reliable data. In addition to the TLC separations, HPLC and MS analyses were employed to identify metabolites and verify TLC analyses. The data from these analyses have not been submitted. As a result insufficient information is available to determine what analyses were performed on any given sample, and whether these analyses, taken collectively, are adequate to provide reliable data. Summaries of all of the TLC, HPLC, and MS data are required.

Characterization of soil organic matter is not required for data registration. These data were submitted and are considered supplementary information. In the initial review of these data it was observed that the organic matter extraction (0.5N NaOH) was short (1 minute) compared to commonly used procedures which extract the soil for 12 hours. This point was emphasized so that any interpretation of the data subsequent to the initial review would take this into account. No further data on organic matter characterization are requested.

In summary, the data on anaerobic metabolism are supplemental data and therefore, no additional information concerning anaerobic metabolism is



requested. The extraction procedures used are adequate for the aerobic studies. However, summaries of all the TLC HPLC, and MS data are required to evaluate aerobic soil metabolism.

Table 3. Thin-layer chromatographic R<sub>f</sub> values for acifluorfen and related compounds.

Compound	R <sub>f</sub> in solvent system	
	B	C
MC - 10879	0.75	0.37
MC - 14621	0.71	0.48
MC - 10108	0.98	0.95
MC - 10109	0.60	0.24
MC - 14620	0.89	0.87
MC - 10074	0.98	0.96

<sup>a</sup>Solvent System B = Toluene:tetrahydrofuran:acetic acid (45:30:1)  
Solvent System C = Toluene:methanol (3:1)

#### 4.5 STUDY 5

Piznik, M., and J.P. Wargo. September 1982. Abbreviated aerobic/anaerobic soil metabolism study with radiolabeled Tackle (MC-10978). Rhone-Poulenc Inc., Monmouth Junction, New Jersey. ASD Report No. 82/047. Acc. No. 071324.

In the initial review of this study (Dynamac Corp., March 10, 1983) insufficient data were available to validate the extraction and TLC methodology.

Subsequently the registrant has submitted additional data to verify that the extraction procedures used were adequate to recover residues aged up to 7 days (Table 4). The data also illustrate that aging over a 7-day interval substantially decreased the extractability of the residues. Harsher extractants were needed to solubilize the aged residues and recoveries decreased with aging. It cannot be determined if the extraction procedures were adequate for soil incubated longer than 7 days. However, the pattern of acifluorfen breakdown under aerobic conditions was established within 7 days.

The TLC methodology was the same as that used in Study 4. Therefore, additional TLC data for this study may be required pending the evaluation of additional data requested for Study 4. The registrant has submitted recovery of <sup>14</sup>C degradates from the aerobic study as determined by TLC (Table 5).

The total quantity of  $^{14}\text{C}$  accounted for decreased with time. This decrease was substantial (35% loss in aerobic soil, 33% in anaerobic soil) and was correlated to the reported decrease in acifluorfen recovery ( $r = 0.936$ ). At present, there is no demonstrative explanation for this loss. High  $^{14}\text{C}$  losses were also observed in Study 4 in soils that were treated with the nitrophenyl label and incubated anaerobically. The aerobic soil in this study (treated with nitrophenyl-labeled [ $^{14}\text{C}$ ]acifluorfen) was reportedly maintained at 60% of the moisture content at 1 atm (as opposed to the 30% of the moisture content at 1 atm maintained in Study 4 for aerobic samples). However, the rapid rate of degradation and the unaccounted for loss of the nitrophenyl  $^{14}\text{C}$ -label suggest that the soil intended to be anaerobically incubated in this study may have been partially anaerobic. The moisture content of the soil (loamy sand) was reported as 45% at 1 atm. This appears to be an excessively high quantity of water for a light textured soil to hold. A loamy sand soil would be expected to have a water content of 10-20% at field capacity, and the water content at 1 atm is somewhat lower than at field capacity (0.33 atm). In order to clarify the moisture conditions under which the soil was incubated, a description of the procedure used to measure the soil water content at 1 atm must be submitted.

The decline of acifluorfen was initially represented by a second order kinetics regression. This is generally not considered an appropriate model for soil metabolism studies because the half-life determined is based upon the initial concentration. As the initial concentration is increased this model predicts that the half-life will decrease. The first order model is more appropriate and fits the data almost as well as the second order model (second order  $r = 0.9932$ ; first order  $r = 0.9361$ ). In the initial review of this study it was incorrectly stated that the formula used to calculate the second order half-life was erroneous. All half-life calculations were correct.

The mass balance for the anaerobic portion of this study is inadequate. Unaccounted for  $^{14}\text{C}$  was 32-34% of the total radioactivity applied.

Table 4. Preliminary extraction tests of [ $^{14}\text{C}$ ]acifluorfen from aged soil.

Time (days)		Sequence of extraction (% recovery) <sup>a</sup>				Total
		A	B	C	D	
0	1	110.7	-	-	-	110.7
	2	104.1	-	-	-	104.1
2	2	77.0	2.3	15.9	-	95.5
	7	55.6	-	25.3	11.3	92.2

- <sup>a</sup> A Mechanically shaken for one hour with 1:1 methanol:methylene chloride  
 A<sub>2</sub>, B Refluxed for 1 hour with 1:1 methanol:methylene chloride  
 C Refluxed for 1 hour with 3:1 methanol:0.1 N HCl  
 D Refluxed for 1 hour with 98:2 methanol:HCl

Table 5. <sup>14</sup>C Metabolites extracted from aerobically incubated loamy sand soil treated with [<sup>14</sup>C]acifluorfen at 4.82 ppm.<sup>a</sup>

Metabolite	Time (days)							
	0	1	3	7	14	28	56	84
MC-14620	0.1	0.4	0.8	1.3	2.0	2.1	1.9	2.8
MC-10074								
MC-10108	0.3	0.7	1.2	1.8	2.7	2.7	1.6	2.1
MC-10879	0.1	0.9	1.1	1.6	1.1	2.5	3.2	--
MC-15598	1.8	2.3	2.5	2.8	2.9	3.1	1.8	1.9

<sup>a</sup>Expressed as percent of total <sup>14</sup>C.

#### 4.6 STUDY 6

Gemma, A.A., and J.P. Wargo. October, 1982. The metabolic fate of <sup>14</sup>C-MC-10978 in New Jersey loamy sand soil. Rhone-Poulenc Inc., Monmouth Junction, New Jersey. ASD Report No. 82/051. Acc. No. 071324.

In response to the initial review of this study (Dynamac Corp., March 10, 1983) the registrant has submitted rainfall, air temperature, relative humidity, and soil moisture data. No soil temperature data were obtained during the study.

Additional information submitted included the <sup>14</sup>C activity of the leachate from the columns. The volumes of leachate were not given, and therefore, actual quantities of <sup>14</sup>C lost through leaching could not be calculated. However, the low <sup>14</sup>C activity in the leachate suggests that losses in the leachate were probably low. The registrant indicated that the metabolites identified as MC-10879, MC-10074, MC-14620, or MC-10108 did not individually constitute >10% of the total residue. Data verifying the efficiency of the partitioning procedure used to clean the solvent extraction were also submitted.

No conclusions can be made from this study. The range of total <sup>14</sup>C recovered was unacceptably large. The absolute recovery of radioactivity ranged from 56 to 192%. The pesticide application was made over soybeans with 3-4 trifoliolate leaves/plant. According to newly submitted data from the registrant, soybeans this size planted in rows 3 feet apart (four plants/square foot) intercept 69% of the pesticide allowing 31% to reach the soil. If it is assumed that the soybeans in the present study (3.3-3.7 plants/square foot) also intercepted 69% of the pesticide, then recovery of the pesticide from the soil ranged from 181 to 619% of the theoretical amount applied. The registrant should submit a reasonable explanation for these data.

#### 4.7 STUDY 7

Gemma, A.A., and J.P. Wargo. October, 1982. Tackle soil metabolism: Metabolic fate of  $^{14}\text{C}$ -MC-10978 in Maryland silt loam soil. Rhone-Poulenc Inc., Monmouth Junction, New Jersey. ASD Report No. 82/053. Acc. No. 071324.

This study has been judged to be scientifically invalid (Dynamac Corp., March 10, 1983) and the newly submitted information from the registrant concerning analytical methodology does not alter the initial judgement. Samples from three of seven sampling intervals could have been stored improperly before being analyzed. Recovery of total  $^{14}\text{C}$  was highly erratic. The nitrophenyl  $^{14}\text{C}$  label initial recoveries were more than twice that applied. Radioactive residues in subsurface soil samples were sporadically high. The registrant's only response concerning these data is that bad sampling technique may be to blame. No confidence can be placed in these data.

#### 4.8 STUDY 8

Norris, F.A., and K.M. Miller. December, 1980. Mobility of MC 10978 in four soil types. Mobil Chemical Company. Technical Memorandum TME-80.24. Acc. No. 071325.

The registrant has submitted most of the additional data requested in the initial review of this study (Dynamac Corp., March 10, 1983). The chemical purity of the test substance was >98%; radiochemical purity was 98.4%. The columns were treated by adding 30 g of soil previously treated with an ether solution of [ $^{14}\text{C}$ ]acifluorfen at 5000  $\mu\text{g/g}$  of soil. Unnormalized data were submitted from each replicate along with the material balance. It is clear from this information that replication was generally good and normalization of the data did not distort its interpretation. Total  $^{14}\text{C}$  recovery (106.5-122.6% in unaged soil and 91.2-117.3% in aged soil) is acceptable. The solvent systems utilized in the two dimensional TLC analyses were toluene:tetrahydrofuran:acetic acid (90:60:2) and chloroform:acetic acid (90:10). This method of analysis is adequate to separate the parent from soil metabolites. The bulk density of the soil in the columns was not given. In light of high mobility of acifluorfen and the good agreement between replicate samples it is assumed that the columns were adequately packed. No further requests for bulk density data are necessary.

The pesticide loading in the columns was at an excessively high rate (682 lb ai/A). Radioactivity leached from the column (10 inches of water) immediately after pesticide treatment comprised 79-93% (normalized values) of the applied  $^{14}\text{C}$ . The rate of leaching is probably enhanced by the high treatment rate. The parent was the only  $^{14}\text{C}$  compound found in the leachate. A variable amount of the pesticide (<2-10%) appeared to resist leaching and remained in the top 5 cm of the column. No explanation was given for this adsorption in the top of the column. It is possible that the adsorption is an artifact of treating the soil with ether (used in pesticide application). Adsorption below the top 5 cm was minimal. The  $^{14}\text{C}$  distribution with depth suggests that most of the radioactivity in the

column below the top 5 cm is residue trailing behind the pesticide front and would be readily leached from the column with additional water.

Aging [ $^{14}\text{C}$ ]acifluorfen 30 days before leaching (@0.30 in/day for 45 days) substantially reduced the mobility of the residues. In the heavier textured soils (silt loam and clay loam) >97% of the radioactivity was retained in the column. However, in the sandy loam soils 38-77% of the  $^{14}\text{C}$  was leached from the column. As in the unaged study, the only  $^{14}\text{C}$ -compound in the leachate was the parent. Aside from a bulge in  $^{14}\text{C}$  activity (11-45% of the total  $^{14}\text{C}$ ) in the top 5 cm of all soils, the  $^{14}\text{C}$  distribution with depth varied with soil type. It is suspected that the metabolism of acifluorfen into less mobile compounds is partially the cause for reduced  $^{14}\text{C}$  mobility. However, identification of  $^{14}\text{C}$  compounds in the soil was not performed, and it is not possible to distinguish between acifluorfen breakdown and increased adsorption of the parent with aging. Correlation between the mobility of aged acifluorfen residues and easily measured soil properties does not appear to be feasible, but mobility can be expected to be generally greater in lighter textured soils. The treatment rate for the column leaching study is unrealistically high, leading to exaggerated mobilities and possibly masking soil effects on mobility. The column studies do provide data for a worst case situation of pesticide spills or dumping. These studies also demonstrate the decreased mobility of aged residues. The soil TLC studies (Refer to initial review, Dynamac Corp., March 10, 1983) provide valid data for estimating the mobility of unaged residues. Collectively these data fulfill data requirements. No further data are needed.

#### 4.9 STUDY 9

Norris, F.A., and A. Guardigli. May, 1982. Adsorption-desorption of acifluorfen sodium (LS-80-1213, MC-10978) from a silt loam soil. Rhone-Poulenc Inc., Monmouth Junction, New Jersey. PDD Report No. 82/030. Acc. No. 071325.

All data requirements for soil mobility studies have been met by Study 8 (Mobil Technical Memorandum TME-80-24). Therefore the data in this study will be considered supplementary information. For reasons stated in the initial review (Dynamac Corp., March 10, 1983), primarily that the experimental procedures were incorrect and that adsorption and desorption equilibration times were not determined, the data in this study are considered to be semiquantitative. The registrant has responded that following each adsorption and desorption cycle the solution that was removed was brought to a 50-ml volume to obtain a "reliable quantitation of the decantable solution." Instead of adjusting the volume it should have been measured to determine what volume of solution remained in the soil. The solution in the soil contributes soluble acifluorfen to the following desorption cycle. This soluble acifluorfen was not compensated for in the registrant's calculations. Although the volume of solution which was not removed from the soil was small the error associated with this procedure is disproportionately large because the test substance has a much greater affinity for water than for adsorption sites in the soil. When the test substance is determined in the supernatant which has been slightly diluted this results in a slight error in determining the concentration in solu-

tion, but a relatively large error in quantifying the adsorbed test substance. Data from the adsorption cycle for sample 462 are presented to illustrate the error involved.

Concentration in solution 0.04272 µg/ml (experimentally determined).

Assume that 2 ml of the solution remained in the soil. Therefore 2 ml of distilled water was added to the supernatant removed.

Corrected concentration in solution 0.0445 µg/ml.

	<u>Original data</u>	<u>Corrected data</u>
Total acifluorfen added to system	2.325 µg	2.325 µg
Concentration in equilibrium solution	0.04272 µg/ml	0.0445 µg/ml
Total in equilibrium solution	2.136 µg	2.225 µg
Total adsorbed	0.189 µg	0.100 µg
Concentration adsorbed	0.038 µg	0.020 µg

Coordinates plotted for Freundlich isotherm:

Original data

$$X = \log (2.136) = 0.7589$$

$$Y = \log (0.189) = -1.6660$$

Corrected data

$$X = \log (2.225) = 0.7998$$

$$Y = \log (0.020) = -3.3120$$

Carrying this error into the first adsorption cycle it would appear that 0.150 µg of test substance was desorbed. The correct quantity is estimated to be ~0.061 µg.

Despite these deficiencies the data clearly do indicate that acifluorfen is only slightly adsorbed and that the adsorption is reversible. These data support the findings from the column leaching and soil TLC studies.

#### 4.10 STUDY 10

Norris, F.A., and C.C. Ku. April, 1981. Field dissipation and Leaching studies. Mobil Chemical Company. Progress Memorandum PME-81.48. Acc. No. 071325.

The registrant has submitted additional information describing the test substance (1980 season Formulated Tackle, 2 lb ai/gal) and treatment of the test plots (2500- to 3000-square foot plots treated in early June, 1980 using backpack sprayers). Single analyses (in most cases) were performed on composite soil samples (like segments pooled from 10 core samples). In the original Mobil report, data from "A" and "B" samples from New Jersey and Kansas are given. The registrant has not indicated if these duplicate values are from subsampling within a single plot or single subsamples from duplicate plots. No data from control samples have been submitted.

The manner in which the data are reported has created some confusion. The registrant determined the concentration of the test substance on a

fresh weight basis. This was done to avoid pesticide losses via volatilization and irreversible adsorption that may occur during sample drying. In this type of study where field samples of soil are analyzed for pesticide residues, it is a common practice to take sufficiently large samples so that a portion of the sample can be dried to determine the moisture content and a second portion of the sample can be used for the residue quantification. Because the data were in this unusual form, in the initial review (Dynamac Corp., March 10, 1983) the total residues detected in each soil profile at time 0 were divided by the cross sectional area of a core sample to put the data in the form of lb/A. In these initial calculations it was assumed that only one core sample was taken for each analysis. As a result the pesticide present at time 0 was calculated to be 2-29.8 lb ai/A (Application rate was 1 lb ai/A). Information submitted subsequently stated that 10 core samples were pooled for each determination. Adjusting the calculations from the initial review, acifluorfen concentrations present in the soil at time 0 were equivalent to 0.2-2.98 lb/A. The registrant has indicated that time 0 concentrations were equivalent to 0.5-7 lb/A. A spot comparison of time 0 concentrations between those reported by the registrant and those calculated by the reviewer indicates that values differ by an even factor of either 4 or 2. This discrepancy cannot be resolved without information from the registrant showing the actual calculations used to convert ppm (fresh weight basis) to lb/A (area basis). A possible explanation is that 4 or 2 core samples were pooled for analysis, rather than the 10 core samples reported to be in each composite.

The results from these studies are highly variable and sample contamination is evident. Although application was a surface treatment, high levels of pesticide were found in subsurface samples at time 0. Initial levels of pesticide were variable (0.5-7 lb/A according to the registrant) and concentrations in the soil did not consistently decrease with time (Table 6). Assuming that the questions concerning how to determine the lb/A equivalent of acifluorfen in the soil are resolved, these studies are still scientifically invalid because the data are variable and inaccurate. All data to satisfy field dissipation requirements are needed.

Table 6. Total recovery of acifluorfen from 22.5 or 30-cm core samples<sup>a</sup>.

Time after application (days)	Georgia <sup>b</sup> sand	Virginia <sup>c</sup> loamy sand	New Jersey <sup>b</sup> silt loam	Kansas <sup>c</sup> silt loam
0	273	1270	320	78
1	370	748	250	52
3	154	307	265	116
7	62	89	105	25
14	78	140	102	68
28-31	124	79	21	21
84-90	21	--	46	ND <sup>d</sup>
109	--	ND	--	--

<sup>a</sup>Total µg of acifluorfen recovered from 22-mm (diameter) core.

<sup>b</sup>Core depth 30 cm.

<sup>c</sup>Core depth 22.5 cm.

<sup>d</sup>ND = nondetectable; limit of detection not given.

#### 4.11 STUDY 11

Ku, C.C., and K.M. Miller. November, 1980. Determination of Mobil 10978 and Mobil 10109 residues in soils - Mobil Chemical Method 157-80. Mobil Chemical Company. Acc. No. 071325.

Ku, C.C., and F.A. Norris. May, 1981. Validation of Mobil Chemical Method 157-81 "Determination of Mobil 10978 and Mobil 10109 residues in soil". Mobil Chemical Company. Progress Memorandum PME-81.57. Acc. No. 071325.

Additional information was submitted by the registrant as requested in the initial review (Dynamac Corp., March 10, 1983). The soil extracting solution is a 50:50 mixture of methanol:water. The detection limit was defined as 0.05 ppm. Method 157-81 is method 157-80 with the modifications specified in the Biospherics report of April 24, 1981.

#### 4.12 STUDY 12

Gemma, A.A., J.P. Wargo, Jr., and G. Heinzelmann. September, 1982. Tackle greenhouse rotational crop study: The potential uptake of <sup>14</sup>C MC 10978 in various crops from soil treated with <sup>14</sup>C MC 10978. Rhone-



Poulenc Inc., Monmouth Junction, New Jersey. ASD Report No. 82/046.  
Acc. No. 071326.

The registrant has submitted the results from a study that demonstrates that soybeans with three or four trifoliolate leaves planted in rows with 3 feet between rows intercept 69% of spray-applied acifluorfen. In light of these data the intended application rate of 0.16 lb ai/A in the rotational crops study is appropriate. The study was conducted in tubs (1x1x2 feet) filled with 10 inches of soil according to the registrant's initial report. It was assumed from this description that each plot (tub) had a surface area of 1 square foot. Given this assumption the application rate was double that intended or the purity of the test substance was ~50%. This was noted in the initial review of this study (Dynamac Corp., March 10, 1983). The registrant responded to this by supplying calculations to demonstrate that the actual treatment was 0.16 lb ai/A. However, in these calculations it was assumed that each plot had a surface area of 2 square feet. Either rate of application (0.16 or 0.35 lb ai/A) is acceptable for meeting data requirements, but the actual application rate must be verified to evaluate the data. The registrant must verify which plot size is correct and must also submit the purity of the test substance. No soil analyses are available to confirm the application rate. The registrant has indicated that the treated soil was not leached. Therefore, it is assumed that <sup>14</sup>C residues did not appreciably dissipate during the study and soil analyses will not be required.

Under the proposed label, rotational crops cannot be grown on acifluorfen-treated land for a 12-month period after application. Residues in food and feed commodities from wheat, beets, and spinach, which were planted 12 months after treatment, were <0.04 ppm. Although the <sup>14</sup>C metabolite distribution was only semiquantitative, these data are adequate in light of the low rate of uptake. Constituents of the residue included the parent, MC-10879, and MC-10074.

The MC-10108 and MC-14621 metabolites could have been in the residue, but insufficient information is available to confirm their presence.

#### 4.13 STUDY 13

Gemma, A.A., J.P. Wargo, and G. Heinzelmann. September, 1982. Tackle field rotational crop study: The potential uptake of <sup>14</sup>C-MC 10978 in various crops grown under field conditions in soil treated with <sup>14</sup>C-MC 10978. Rhone-Poulenc Inc., Monmouth Junction, New Jersey. ASD Report No. 82/042. Acc. No. 071326.

Spare, W.C., F. Dillon, and C. Hutchinson. October, 1982. Field metabolism studies with <sup>14</sup>C-MC 10978. Prepared for Rhone-Poulenc, Inc. by Biospherics, Inc., Rockville, Maryland. Report No. 349. Acc. No. 071326.

The registrant has submitted a summary of the weather conditions at the test plot and has given a reasonable explanation for not identifying the residues taken up by rotational crops. The registrant has also correctly noted that rotational crop studies need only be conducted at one site.

instead of the intended rate of 0.5 lb ai/A. Soil analyses were not performed at the required intervals. Therefore, this study does not fulfill data requirements for rotational crop studies. However, the data may be used as supplementary information on rotational crop uptake of acifluorfen keeping in mind that the treatment level was well below the minimum recommended rate (0.5 lb ai/A).

#### 4.14 STUDY 14

Thompson, C.M., and W. Cranor. January, 1981. Uptake, depuration and bioconcentration of  $^{14}\text{C}$ -MC 10978 by bluegill sunfish (Lepomis macrochirus). Submitted to Mobil Oil Corporation by Analytical BioChemistry Laboratories Inc., Columbia, Missouri. ABC Report No. 26610. Acc. No. 071327.

In the initial review of the study (Dynamac Corp., March 10, 1983) the data were accepted to partially fulfill data requirements for fish accumulation. The only deficiency noted was that  $^{14}\text{C}$  residues in the fish were not identified. The registrant has responded that metabolite identification was not pursued because of the low bioconcentration factor. If the highest residue levels obtained in fish (~5 ppm, whole fish; 1.2 ppm, fillet) are not a toxicological concern, the metabolite identification requirement can be waived. The decision on the importance of these residues is deferred to the Toxicology Branch. Other comments in the initial review were concerned with procedures that were judged to have relatively minor effects on the data. Therefore, further discussion of these points is not necessary.

#### 4.15 STUDY 15

Forbis, A.D., and P. Boudreau. March, 1981. Uptake, depuration, and bioconcentration of MC-10978 by channel catfish (Ictalurus punctatus) in a static system with soil. Submitted to Mobil Oil Company by Analytical BioChemistry Laboratories, Inc., Columbia, Missouri. ABC Report No. 26611. Acc. No. 071327.

Static fish accumulation studies are no longer required for pesticide registration. In the initial review of the study (Dynamac Corp., March 10, 1983) the data were judged to be scientifically valid and were used as ancillary information in support of the flow through fish accumulation study. The registrant, however, has issued a reply to the review to defend the data. The initial review did not state that the specific activity of the test was low. The rates of bioaccumulation and depuration could not be accurately determined because of low bioconcentration, not because of any experimental inadequacy. Characterization of metabolites was not requested nor was it implied that the data should have been provided. The registrant suggests that soil aging was in the dark rather than the 16-hour photoperiod that is described in the materials and methods of the report. The registrant raises the question but does not answer it. It would be useful to know how the soil was aged, since it has been demonstrated that acifluorfen is photolabile.

## EXECUTIVE SUMMARY

Only additions to or alterations of the conclusions in the initial review (Dynamac Corp., March 10, 1983) of the environmental fate and exposure assessment data on acifluorfen (Accession No. 071323 - 071327) are discussed here. Acifluorfen is stable to hydrolysis. No degradation in solutions at pH 3, 6, or 9 was observed within a 28-day interval. Varying temperatures (18-40°C) did not alter this stability. Sufficient information was submitted to verify the validity of the photodegradation in water study. The half-life of the parent is 92 hours under continuous exposure of light that approximates natural sunlight. Degradates have been identified; the decarboxy derivative of acifluorfen was the primary degradate found in solution. Additional data are needed to provide an adequate materials balance. It is suspected that a substantial percentage of the photodegraded parent is lost from solution (through volatilization or other mechanisms).

Acifluorfen applied to soil columns at excessive rates (682 lb ai/A) is very mobile. Acifluorfen leached from the columns with 10 inches of water accounted for 79-93% of that applied. Aerobic aging of the residues in the column substantially reduced the mobility and pesticide movement was inversely proportional to the soil CEC. These data simulate a worst case situation where the pesticide is spilled or dumped and as such may somewhat overestimate mobility. Results from soil TLC (unaged residues only) predict acifluorfen mobility to be intermediate to mobile. Supplementary data from a batch adsorption study indicate that unaged acifluorfen is weakly and reversibly adsorbed.

## RECOMMENDATIONS

Available data are insufficient to fully assess the environmental fate of acifluorfen as well as the potential for exposure of humans and nontarget organisms to acifluorfen. The submission of data to fulfill registration requirements (Subparts N and K) is summarized below:

Hydrolysis studies: One study (Norris and Hassell, November, 1980, Acc. No. 071323) was submitted and reviewed. The study was scientifically valid and satisfied all data requirements. No further data are required.

Photodegradation studies in water: One study (Somma, et al; September, 1982, Acc. No. 071324) was submitted and reviewed. The study is scientifically valid and partially meets data requirements by providing information on the rate of degradation, and on the metabolites formed. Additional data are required to provide an adequate mass balance.

Photodegradation studies on soil: One study (Gerecke and Wargo, August, 1982, Acc. No. 071323) was submitted and reviewed. The study is scientifically valid and is in compliance with data requirements. No further data are required.

Photodegradation studies in air: No studies were submitted; all data are required.

Aerobic soil metabolism studies: Four studies were submitted and reviewed. One study (Gemma and Wargo, October, 1982, ASD Report No. 82/053, Acc. No.

071324) is scientifically invalid because of improper sample storage and erratic recovery of soil residues. The second study (Gemma and Wargo, October, 1982, ASD Report No. 82/051, Acc. No. 071324) is scientifically invalid because total residue recoveries were inadequate. The validity of the other two studies (Piznik and Wargo, September, 1982, Acc. No. 071324 and Wargo, July, 1982, Acc. No. 071324) cannot be evaluated based on the data submitted. Summaries of all the TLC, HPLC, and MS data from Wargo, 1982 are required. The procedure used to determine the soil moisture content at 1 atm tension is required.

Anaerobic soil metabolism studies: Two studies were submitted and reviewed. One study (Wargo, July, 1982, Acc. No. 071324) was submitted as supplementary information, not intended to fulfill data requirements. The second study (Piznik and Wargo, September, 1982, Acc. No. 071324) was not scientifically valid because of the inadequate mass balance. In addition, the validity of the aerobic portion of this study has not been verified. All data are required.

Anaerobic aquatic metabolism studies: No data were submitted, but these studies are not required because acifluorfen does not have a forestry, aquatic, or aquatic impact use.

Aerobic aquatic metabolism studies: No data were submitted, but these studies are not required because acifluorfen does not have an aquatic or aquatic impact use.

Leaching and adsorption/desorption studies: Two studies were submitted. One study (Norris and Miller, December, 1980, Acc. No. 071325) is scientifically valid and fulfills all data requirements. The second study (Norris and Guardigli, May, 1982, Acc. No. 071325) supplies supplementary data. No further data are required.

Laboratory and field volatility studies: No data were submitted. Requirements for these data depend upon toxicity data, product chemistry data, soil adsorption data, and methods of application.

Terrestrial field dissipation studies: One study (Norris and Ku, April, 1981, Acc. No. 071325) was submitted and reviewed. The study is scientifically invalid because the samples appeared to be contaminated with acifluorfen. All data are required.

Aquatic field dissipation studies: No data were submitted, but no data are required because acifluorfen does not have an aquatic or an aquatic impact use.

Forestry dissipation studies: No data were submitted, but no data are required because acifluorfen does not have a forestry use.

Long-term field dissipation studies: No data were submitted. Requirements for these data depend upon the results from the terrestrial field dissipation data; however, it is anticipated that these data will not be required.

Confined accumulation studies on rotational crops: Two studies were submitted. Both were reviewed and found to be scientifically valid. One

study (Gemma et al., September, 1982, ASD Report No. 82/042, Acc. No. 071326 and Spare et al., October, 1982, Acc. No. 071326) does not fulfill data requirements because the rate of application was too low. The second study (Gemma et al., September, 1982, ASD Report No. 82/046, Acc. No. 071326) does not meet data requirements because the application rate could not be verified. Data to confirm the application rate and the purity of the test substance are required.

Field accumulation studies on rotational crops: No data were submitted. Data requirements are dependant upon confined accumulation studies on rotational crops.

Accumulation studies on irrigated crops: No data were submitted; however, data are not required because acifluorfen has no aquatic food crop or aquatic noncrop use, is not used in and around holding ponds used for irrigation purposes, and has no uses involving effluents or discharges to water used for crop irrigation.

Laboratory studies of accumulation in fish: One study (Thompson and Cranor, January, 1981, Acc. No. 071327) was submitted and reviewed. The study is scientifically valid and partially fulfills data requirements by providing data on the quantity of acifluorfen residues accumulated in fish. The required characterization of residues in fish may be waived if the levels of residues are sufficiently low to be of no toxicological concern. Judgement is deferred to the Toxicological Branch.

Field accumulation studies on nontarget organisms: No data were submitted; however requirements for these studies depend upon the results from laboratory studies of accumulation in fish and toxicological data.

Reentry studies: No data were submitted. All data are required.

Ancillary studies reviewed.

Static studies of accumulation in fish (Forbis and Boudreau, March, 1981, Acc. No. 071327).

Methods evaluation studies (Ku and Miller, November, 1980. Acc. No. 071325 and Ku and Norris, May, 1981, Acc. No. 071325).

## 7. REFERENCES

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