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THRU: Henry Jacoby, Chief *Henry Jacoby*  
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Attached, please find the EFGWB review of...

Reg./File # : 114402

Common Name : Sodium 5-[(2-chloro-4-trifluoromethyl)-Phenoxy]-2-Nitrobenzoic Acid

Product Name : Blazer®, Tackle® Acifluorfen-sodium

Company Name : BASF, (Rhône-Poulenc)

Purpose : Review of final report for small-scale retrospective ground-water monitoring studies.

Type Product : Herbicide

Action Code : 627 EFGWB #(s): 92-0428 Total Review Time = 13 days

EFGWB Guideline/MRID/Status Summary Table: The review in this package contains...

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Y = Acceptable (Study satisfied the Guideline)/Concur P = Partial (Study partially satisfied the Guideline, but additional information is still needed)  
 S = Supplemental (Study provided useful information, but Guideline was not satisfied) N = Unacceptable (Study was rejected)/Non-Concur

1. CHEMICAL:

Chemical Name: Sodium 5-[2-chloro-4-(trifluoromethyl)-  
Phenoxy]-2-Nitrobenzoic Acid  
Common Name: Acifluorfen-Sodium salt  
Trade Name: Blazer, Tackle, Galaxy, Storm  
Structure: Not applicable

Physical/Chemical Properties:

Molecular Formula	C <sub>14</sub> H <sub>7</sub> ClF <sub>3</sub> NNaO <sub>5</sub> (sodium salt) C <sub>14</sub> H <sub>7</sub> ClF <sub>3</sub> NO <sub>5</sub> (acid)
Water Solubility	2.5 x 10 <sup>-5</sup> mg/L @ 20 °C
K <sub>d</sub>	1.0 ml/g silt loam
K <sub>oc</sub>	
logK <sub>ow</sub>	-4.85 (acid) (calculated)
pK <sub>a</sub>	2.5

2. TEST MATERIAL

Not Applicable.

3. STUDY/ACTION TYPE:

Review of final Small-Scale Retrospective Ground-Water Monitoring Studies for acifluorfen-sodium (Blazer® and Tackle®) in Tennessee, Indiana, North Dakota, and North Carolina, and Virginia.

4. STUDY IDENTIFICATION:

Title: A small scale retrospective and limited prospective ground-water monitoring study with acifluorfen-sodium, the active ingredient of Tackle® and Blazer® Herbicide: Final Report BASF Registration Document No. 91/5206. 415 pages.

Authors: Andrew M. Hiscock and Sandra C. Cooper

Submission By: BASF Corporation  
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Action: 627 Generic Data Submission  
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Submission: S409882  
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5. REVIEWED BY:

James K. Wolf  
Soil Scientist

Signature: James K. Wolf

OPP/EFGWB/Ground Water Section Date: January 14, 1993

6. APPROVED BY:

Elizabeth Behl  
Section Head

Signature: E. Behl

OPP/EFGWB/Ground Water Section Date: January 15, 1993

7. CONCLUSIONS:

The objective of this review is to assess the final report of the small-scale retrospective ground-water monitoring studies and limited prospective studies at five sites for acifluorfen-sodium (referred to as acifluorfen in this review) and make recommendations based upon these results. Many of the deficiencies and limitations identified in earlier reviews were still present in the final report. Efforts were made by the registrant to address some of these deficiencies and limitations. However, because the studies were initiated (and completed) prior to EFGWB approval of the study sites and a final protocol, a number of the deficiencies could not be overcome. Protocol modifications were also implement without Agency approval. Deficiencies or limitations included; limited history of previous use, over-emphasis on subsoil layers, larger than desirable soil-sampling increments, and remote weather stations.

The study was conducted by the registrant(s) to evaluate the rate of acifluorfen dissipation in soil, the extent of residue mobility in soil, and the potential for acifluorfen to leach to ground water in representative use areas. The study incorporated aspects of two ground-water study types: 1) the small-scale retrospective, and 2) small-scale prospective ground-water monitoring study types. The retrospective nature of the study was to monitor for residual acifluorfen in soils and in ground water from prior acifluorfen use. The limited prospective study was conducted within the retrospective study to monitor the dissipation and vertical movement in soil of a current acifluorfen application and the potential to contaminate

ground water. Study results were only able to partially address each these issues.

Acifluorfen is mobile in soils with permeable soils (i.e., sands, loamy sands, sandy loams), low in clay and low organic carbon contents. The persistence appears to be quite different between locations and years. The application of irrigation on these types of soils will also enhance the likelihood of ground-water contamination. Overall, results obtained in this study and the earlier prospective study indicate that acifluorfen residues (even when at levels lower than detection limits in soil samples) are able to leach through the soil profile and under certain conditions be detected in ground water.

The registrant conducted small-scale retrospective ground-water monitoring studies at locations in five states; North Carolina, North Dakota, Indiana, Tennessee, and Virginia. Studies were implemented at two of the sites (North Dakota and Tennessee) prior to EFGWB approval, and the Indiana site only had tentative approval. Agency approval has already been given to discontinue and decommission the Tennessee and Virginia study sites.

#### Study Site Selection

**Site Vulnerability:** Five small-scale retrospective ground-water monitoring studies were conducted in five states which are representative of the soil and hydrogeologic conditions in soybean growing areas in the United States. The registrant ranked the sites vulnerability to ground water contamination (most vulnerable to least vulnerable) as North Carolina, Virginia, North Dakota, Indiana, and Tennessee. EFGWB did not entirely agree with the registrant as to each sites vulnerability to ground water contamination or ranking of vulnerability and site selection. Although depth to ground water was acceptable at all sites, several sites (i.e., Tennessee and a lesser degree Virginia and Indiana) had too much silt and clay sized particles in the soil profile to be considered truly vulnerable by the Branch. Although, EFGWB does not entirely agree with the relative ranking of the sensitivity of these sites to ground water contamination, they span the range of use sites from vulnerable sorted sands to Mississippi delta sand and clay deposits.

**Prior Acifluorfen Use History:** Several of the sites were also found not to possess the necessary acifluorfen use history normally required for retrospective ground-water monitoring studies. The registrant partially alleviated this limitation by conducting the study for a second year by adding a second application of acifluorfen. The acifluorfen use history prior to 1989 at the five study sites were  
Indiana - 1 Year; North Carolina - 4 Years; North Dakota -  
1 Year; Tennessee 3 Years; And Virginia - 2 Years.

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**Depth to Water Table:** Water table depths varied both between sites and seasonally within sites. Depths ranged from less than a foot at the North Carolina site to more than 15 feet at the Tennessee site. Depth to water table was acceptable for the five sites.

**Soil Criteria:** Soil textures generally were sand or loamy sand in the subsoil, but contained a higher amount of clay and silt in the surface one to three foot zone than is generally acceptable to EFGWB.

**Climatic Data:** Climatological data was not measured at the study sites. NOAA weather stations were located as near as 8 miles and as far as 36 miles from the study sites. Because climatological data were collected at the NOAA weather stations, and not at the study site, precipitation at the study site may differ significantly from where it was measured. This variability may have influenced the fate and transport of pesticide residues monitored at each site. Also, none of the five sites were irrigated. The lack of irrigation and the pattern of precipitation events at each site or high evaporative demands may have limited the leaching observed at the sites. The amount of water available for leaching is influenced by precipitation (amount, rate, and temporal distribution) and evapotranspirative demands, plus the soil water content and soil water retention properties.

#### Environmental Fate

**Persistence in Soils:** Acifluorfen residue levels in the soil were greatest immediately after application, and generally decreased with time. However, acifluorfen residues appear to be very persistent in soil under certain conditions. Acifluorfen tended to be most persistent at the ND study site and least persistent at the NC site. Results from the Indiana site were inconsistent, as during 1989 the disappearance appeared to be rapid (< 1 month) and in 1990 quite persistent (detectable 12 months after application).

Residues were detectable in surface (0 - 12 inches) samples, prior to the 1989 application, at both the Tennessee and North Dakota sites. Although acifluorfen residues were present at the Tennessee from a 1988 (previous) application, there were no detectable levels of acifluorfen found one month after the 1989 application, at this site. There were also no detections at the Indiana, North Carolina and Virginia sites in the surface sampling increment one month after the 1989 application, with a detection limit of 0.010 µg/g. Acifluorfen residues were still detected in surface soil samples at 10 months after the 1989 application at the North Dakota site.

Acifluorfen residues were detected in surface (0 - 6 inches) soil samples prior to the 1990 application (approximately 1 year after the 1989 application) at both the Indiana and North Dakota sites. Although no residues were detected in samples collected 1 month after the 1989 application at the Indiana site, acifluorfen (0.013  $\mu\text{g/g}$ ) was detected in one of four samples collected prior to the 1990 application.

Acifluorfen appears to be more persistent at the North Dakota site for both years of the study as residues were detected in surface soil samples collected 10 months after the 1989 application and 13 months after the second year's. Residues also continued to be detected in the surface soil samples 12 months after the second year's application at Indiana site.

It is not entirely clear as to why acifluorfen was more persistent at the North Dakota and the Indiana site. The annual application rate may influenced the persistence in soil. The typical application rate reported for acifluorfen ranged between 0.21 to 0.26 lb-ai/ac, with the exception of North Dakota and Tennessee. At the ND site acifluorfen was applied at the rate of 1.13 lb-ai/ac (0.50 + 0.63 lb-ai/ac) in 1988 (prior use) and 0.43 lb-ai/ac in 1989. In 1990 only 0.25 lb-ai/ac was applied. The application rate for Tennessee during 1987 was 0.31 lb-ai/ac, and 0.23 lb-ai/ac for 1988 and 1989. Relationship between application rate and persistence does not hold for Indiana as 0.21 lb-ai/ac was applied in 1989 and 0.25 lb-ai/ac in 1990.

The amount and temporal distribution of precipitation also may be a factor, i.e., less rain less leaching or when it rained. Precipitation reported for the ND (13.6, 22.1 inches) site was less than half the rainfall reported at the other (42.8 - 61.2 inches) sites. Less precipitation was also reported for Indiana during 1990 which corresponded to the more persistent residues. Information concerning the distribution of precipitation with time was not provided and precipitation data was not collected at the study sites. Thus it is not possible to thoroughly evaluate the relationship between precipitation and dissipation. Other climatological factors such as temperature and evaporation may also be a factor.

Additionally, the sampling intervals for the soil samples may not have been frequent enough to adequately estimate the field dissipation rates. The shortest interval between sampling times was two weeks, i.e., two weeks after application, after this sampling intervals were 30 days or longer. Sampling should have been conducted with a greater intensity, such as daily or bi-daily for the first 10 to 14

days after application, as half life estimates ranged as low as 5.15 days. The sampling frequency was not adequate to adequately characterize the behavior of the chemical in the early part of the studies when the chemical activity was the greatest.

**Leaching and Mobility:** Acifluorfen residues were detected in the 12 to 24 inch (subsurface) soil samples 2-weeks after application at the North Dakota site indicating a downward movement of the residues. Acifluorfen residues were also detected in some 6 to 12 inch sampling increments up to 9 and 12 months after application at the Indiana and North Dakota sites, respectively. This demonstrates the movement and persistence of acifluorfen residues in soil.

A greater number of acifluorfen detections probably would have occurred had the detection limit be lowered or if suction lysimeters (used in prospective studies) were utilized to collect soil-pore water. It is also probable that had suction lysimeters been installed at the sites, and soil water samples collected with a lower detection limit, acifluorfen residues would have been detected in deeper sampling increments. This would have allowed for a more thorough evaluation of the leaching pattern of acifluorfen in the vadose zone. Observations obtained during the prospective study support this conclusion as there were no detections of acifluorfen residues were detected below 0.3 m (12 inches), but residues were detected in suction lysimeters at depths up to 3 meters and later in ground-water samples.

The limited number of samples and high soil detection limit (10 ng/g) may also result in an inaccurate assessment of acifluorfen residues present in soil over time. The inability of the registrant to detect acifluorfen residues in soil samples or ground water did not mean that residues were not present. Additionally, residues may have been present (at detectable and less than detectable levels) at soil depths deeper than sampled by the registrant.

**Ground-Water Detections:** There were no detections of acifluorfen residues in any of the five small-scale retrospective ground-water monitoring studies. Two detections reported at the North Carolina site were later classified by the registrant as "false positive" detections.

Results of an earlier prospective monitoring study indicate that acifluorfen residues can reach ground water under typical transport mechanisms. Results of the five retrospective studies reviewed here indicate that acifluorfen is quite persistent, and can be detected in soils for more than a year after application. Residue

mobility was also apparent at several of the study sites. Because of problems in site selection, deviations from protocol, and analytical difficulties it is difficult to make firm conclusions based on the results of these studies. Clearly an attempt was made to evaluate the leaching potential along a spectrum of use environments with different vulnerabilities.

The Branch will obtain additional insight concerning the fate and transport of acifluorfen residues at these sites through computer simulations using the model PRZM (Carsel et al., 1984).

8. RECOMMENDATIONS:

1) As a result of the information derived from these monitoring studies, we draw the conclusion that a label advisory should be developed indicating that a potential exists for ground-water contamination. The label advisory should state:

"Residues of acifluorfen have been found in ground water as a result of agricultural use. Use of this product in areas where soils are permeable and water tables are shallow could result in contamination of ground water. The utilization of irrigation water in these areas will increase the likelihood of contamination."

2) Because acifluorfen is a B2 carcinogen and the prospective study demonstrated that it can leach to ground water in certain vulnerable environments, EFGWB also recommends that use restrictions be placed upon acifluorfen. Use should be prohibited on soils which are highly permeable, such as sand and loamy sand textures, where depth to ground water is shallow, and irrigation is used.

3) The distances from the NOAA weather station to the study site were quite substantial for several of the sites. The registrant should provide any site specific information available for any of the study areas. This information can be used to determine if the precipitation frequency, intensity, and occurrences at the study sites correlated at all with the weather station data, and influenced the fate and transport of the acifluorfen residues.

4) The registrant showed on Figure 24, page 151 of 415 (May 9, 1990), that the direction of ground water flow was towards the east at the Indiana study site. Was the direction of flow always to the east? Did the ground water's direction of flow show any seasonal variation during the study? Specifically, is ground water flow controlled by

Black Creek which is closer to the site, or by the White River which is somewhat further from the site?

5) Acifluorfen recoveries for the soil stability ranged from 86 to 137 percent. An apparent discrepancy exists as page 60 of 415 states a maximum recovery of 104 percent, whereas Table XXVI, page 126 indicates a maximum of 137 percent recovery. This discrepancy should be clarified. It also appears that soil residue recovery may decrease after being frozen more than four weeks. Recoveries from water samples ranged from 65 to 198 percent, which we believe is poor for water.

6) It was unclear whether the well and ground surface elevations were surveyed or simply estimated. Because water table levels between wells usually show little variability, accurate water levels are required. Were the well elevations and ground surface elevations surveyed? This should be addressed. If well elevations were not surveyed, this should be done prior to well decommissioning.

9. BACKGROUND:

Acifluorfen is an active ingredient (a.i.) in Blazer herbicide, marketed by BASF. Blazer® is a selective pre- and post-emergence herbicide to control weeds and grasses in large seeded legumes, such as peanuts and soybeans (USEPA, 1989a). Application rates are between 0.25 and 0.75 lb a.i./acre (USEPA, 1990a). Rhone-Poulenc previously marketed the post-emergent herbicide Tackle® with acifluorfen as the active ingredient.

Acifluorfen has been designated a class B2 carcinogen. The Drinking Water Equivalent Level (DWEL) for acifluorfen has been established by the EPA at 0.4 mg/L (400 µg/L); however, no Health Advisory Level (HAL's) have been established.

The EPA issued a Data Call-In (DCI) Notice for ground-water monitoring data to Rhone-Poulenc Ag Company and BASF Corporation in September of 1987. The two companies agreed to jointly conduct several small-scale retrospective ground-water monitoring studies for herbicides with the active ingredient acifluorfen-sodium (Tackle® and Blazer®).

The registrants also previously conducted a small-scale prospective ground-water monitoring study in Wisconsin (Norris, 1988, 1989; USEPA, 1989b).

Rhone-Poulenc no longer sells Tackle®, thus the only source of acifluorfen is BASF. BASF assumed the responsibility associated with the studies in April 1990.

Blasland and Bouck Engineers were contracted by BASF to take over and complete the retrospective studies. These studies were originally started by Rhone-Poulenc's Special Environmental Programs for Rhone-Poulenc and BASF.

#### Environmental Fate

Chemistry and fate data indicates that acifluorfen is both persistent and mobile. In addition to the parent compound acifluorfen-sodium (salt-LS-80-1213), there are also several degradates. These include acifluorfen (free acid-LS-82-5276); LS-82-5281 the primary degradate; a secondary metabolite LS-82-5283; the amino metabolite LS-82-5282; and acifluorfen-methyl LS-81-5875. The metabolites have been found in the laboratory to be less mobile than the parent herbicide. The metabolites have only been detected at low levels. Only acifluorfen in the acid or sodium-salt form would be expected in ground water, and therefore required for analysis (Tinsworth, 1989).

Acifluorfen-sodium is a soluble salt that is stable to hydrolysis; no degradation was observed at pH 3, 6, or 9 within a 28 day period (USEPA, 1989a), and at pH 5.0, 7.0, and 9.0 stable for >56 days (USEPA, 1992b). It was also stable when varying temperatures from 18° to 40° C.

Aerobic soil metabolism studies showed that the dissipation rate of acifluorfen increased with increased soil water content. Reported aerobic soil metabolism half-lives range from 6 days to 180 days. Acifluorfen metabolizes rapidly under flooded anaerobic conditions, a half-life of 30 days has been reported. The primary degradate of acifluorfen under aerobic and anaerobic conditions is LS-82-5281, the product after reduction of the nitro group to an amino group.

For an irrigated Wisconsin sandy soil, the field dissipation half-life was found to be 15 days (Norris, 1989). After two months, residue levels were near detection levels. The decarboxy derivative of acifluorfen was the primary degradate found in solution. Anaerobic degradation is rapid, a half-life of about 30 days has been reported. The parent compound and bound materials were the dominant residue compounds after 6 months of aerobic incubation. The acetamide of amino-acifluorfen was the major degradate extracted from the soil after 60 days of anaerobic conditions.

The dissipation half-life for acifluorfen in a silt loam in Mississippi was about 59 days. The leaching of the parent below 3 inches was negligible during a 179 day study. Slower dissipation half-lives of 101 to 235 days were found in two silt loam soils in Illinois (USEPA, 1989a).

High rates of acifluorfen applied to soil columns were found to be very mobile. Seventy-nine to ninety-three (79 - 93%) percent of acifluorfen applied to soil columns could be found in the leachate, after 10 inches of water were added. Aerobic aging of residues in the columns reduced the mobility. The pesticide movement is influenced by soil CEC; decreasing with increasing CEC. Soil TLC measurements indicated that unaged residues have an intermediate to mobile mobility.

Acifluorfen has been sampled for in 1185 wells from five states (USEPA, 1992c). Detections of between 0.003 and 0.025  $\mu\text{g}/\text{L}$  were reported in three wells in Virginia and one well in Mississippi (0.017  $\mu\text{g}/\text{L}$ ). Detections have also been reported in Wisconsin (Norris, 1988, 1989; USEPA, 1989b) and North Carolina.

A comparison of chemical and physical properties of acifluorfen-sodium relative to the EPA leaching criteria are summarized in Table 1.

**Previous Recommendations:** The registrant requested, under a separate submittal (response EFGWB # 91-0807, 1992a) to discontinue monitoring and commence with the decommissioning of the Indiana, North Carolina, and North Dakota sites. We recommended that the request for decommissioning be approved with the following recommendations.

1). Prior to decommissioning, 0 to 6 inch soil samples should be collected at the Indiana and North Dakota sites, and monitoring well water samples should be collected (at the same time) at the Indiana, North Carolina, and North Dakota sites. The registrant should follow sampling and analytical protocol previously used, and continue to follow QA/QC practices.

2) The analytical results should be submitted to the Agency within 3 months of the decommissioning activities.

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<sup>1</sup> The detections in North Carolina were later defined as "false positive" detections by the registrant.

Table 1. Physical and Chemical Characteristics<sup>1</sup> of Acifluorfen - Sodium Relative to EPA Leaching Criteria<sup>2</sup>.

CHARACTERISTIC	LEACHING CRITERIA	ACIFLUORFEN PARAMETERS
Water Solubility	> 30 mg/L	2.5 x 10 <sup>5</sup>
Henry's Law Constant	<10 <sup>-2</sup> atm-m <sup>3</sup> /mol	1.51 x 10 <sup>-13</sup> (calculated)
Hydrolysis half-life	> 25 weeks	pH3 >28 days @40°C pH 5,7,9 >56 days
Photolysis half-life	> 1 week (water)	96 hrs, continuous exposure to UV @ 40-45°C
Soil adsorption: K <sub>d</sub>	< 5 (usually <1-2)	1 ml/g - silt loam
Soil adsorption: K <sub>oc</sub>	<300-500	113 (estimated)
Aerobic soil metabolism half-life	> 2-3 weeks	6 days in NJ; 30 days in sandy loam; 2-6 months in loam; 59 days
Field dissipation half-life	> 2-3 weeks	7 to 60 days
Depth of leaching in field dissipation study	> 75-90 cm	residues reported as deep as 5 meters

<sup>1</sup> USEPA One-liner Database.

<sup>2</sup> Cohen et al., 1984.

Shaded area indicates that chemical parameter exceeds trigger.

## 10. DISCUSSION:

### Study Background

The review and comments herein were generally directed toward the evaluation of how well the study answered the objectives of the study. Several general comments concerning the submitted studies should be made. First, the studies were conducted without a final and EFGWB approved protocol. Second, midway through the studies BASF became the sole registrant, which resulted in a change of the individuals conducting the studies. And finally, the registrant continually modified the protocol, in some instances without EFGWB concurrence.

Several exceptions to certification of Good Laboratory Practices (GLC) for the field phase were noted on page 3 and 4 of 415. The exceptions noted in the final report did not appear significant, and did not hinder the evaluation of the report.

Small-scale retrospective and limited prospective groundwater monitoring studies for the herbicide acifluorfen-sodium were conducted at five locations; Tennessee<sup>3</sup>, Indiana, North Carolina, North Dakota, and Virginia. The five study sites selected were located in representative use areas within major sales areas of herbicides containing the active ingredient acifluorfen-sodium. The Tennessee and Virginia sites have previously received EPA approval for decommissioning and have been decommissioned.

Confusion resulted because earlier submittals (Progress Reports) reported that one of the study sites was located in Arkansas, whereas later submittals reported that the site was in Tennessee. The issue was clarified, by this report (page 26 of 415) and Figure 7 (page 134 of 415).

The registrant stated that the five study sites met or exceeded EPA vulnerability criteria. The availability of selected soil properties used in site selection and characterization, site vulnerability rating, and application rates and use history are summarized in Table 2. Additional site characteristic information was obtained from a 1990 Progress Report (Norris, 1990). As previously noted (USEPA, 1990a), the only site with an adequate use history for a retrospective study was the North Carolina site, which had four acifluorfen applications prior to 1989 (1985 to 1988). The registrant identifies this limitation (page 26), and justifies it, because of crop rotation practices, soybeans are rarely grown in successive seasons in the same field. Therefore, locating fields with a consecutive acifluorfen-sodium use was difficult. Sites were selected where acifluorfen-sodium was used the season prior

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<sup>3</sup> Same as Arkansas site.

to the first study season, rather than two out of the last three or three out of the last five seasons. The limited use history may have influenced (i.e., lack of time to move from point of application to monitoring well) the presence of acifluorfen residues in ground-water samples.

EFGWB as noted in previous reviews (USEPA, 1990a), does not concur with focusing on the texture of the subsoil (sandy). The Branch believes that the soil texture and organic matter content of the surface layers are also important, as these layers represent the most biologically and chemically active portion of the soil (page 27 of 415). Thus EFGWB did not concur with the vulnerability at all the sites. The clay and silt contents in the soil profile at the Tennessee site were too high for the site to be considered vulnerable. Additionally, Indiana and Virginia contained greater amounts of clay and silt size particles normally considered desirable, thus reducing vulnerability.

Sites were further evaluated against SCS descriptions to confirm soil types. DRASTIC varscores were also derived to determine a sites relative vulnerability.

Table 2. Summary of Soil Properties for Site Characterization for Acifluorfen Studies and previous Acifluorfen use.

Soil Property	State				
	Tennessee	Indiana	North Carolina	North Dakota	Virginia
Segment Depth (m)	Y <sup>1</sup>	Y	Y	Y	Y
Number of Cores	4	2	2	4	1
Texture	Y	Y	Y	Y	Y
Sand (%)	Y	Y	Y	Y	Y
Silt (%)	Y	Y	Y	Y	Y
Clay (%)	Y	Y	Y	Y	Y
Organic Matter (%)	Y	Y	Y	Y	Y
CEC	Y	Y	Y <sup>2</sup>	Y	Y
Bulk Density	Y	Y	N <sup>2</sup>	Y	N
Field Capacity	N	Y	N	Y	N
Wilting Point	N	Y	N	Y	N
Number of Cores <sup>3</sup>	4	2	2	4 <sup>4</sup>	1
Years treatment <sup>3</sup>	3	1	4	1 <sup>4</sup>	2
1989 application <sup>5</sup>	0.23	0.21	0.23	0.43	0.26
1990 application <sup>5</sup>	-	0.25	-	0.25	-
vulnerability <sup>6</sup>	V	HV	UV	EV	EV
EPA assessment <sup>7</sup>	N	SL	SM	Y	Y
EPA vulnerability <sup>8</sup>	1	2	5	4	3

- 1 Data was available.
- 2 Data was not available.
- 3 Number of years with prior acifluorfen use history.
- 4 Two applications in one year, 1988.
- 5 pounds active ingredient per acre (lb ai/ac)
- 6 The registrants "Vulnerability Assessment" based on their interpretation (low to high) of EPA site selection criteria, V = vulnerable, HV = highly vulnerable, EV = extremely vulnerable, and UV = ultra vulnerable.
- 7 EFGWB evaluation of registrants rating Y = agree, N = disagree, SL = less vulnerable, and MR = more vulnerable.
- 8 EFGWB vulnerability rating (low to high) 1 = low vulnerability, 2 = less vulnerable, 3 = vulnerable, 4 = more vulnerable, 5 = most vulnerable. Note vulnerability is based on soil properties only. The North Dakota site is possibly the least vulnerable because it receives the least precipitation.

Two clusters of monitoring wells were initially installed at each site prior to herbicide application in 1989. Each well cluster consisted of three 1.5-inch-diameter PVC cased monitoring wells with a 0.6-foot long section of slotted PVC screen. The screened intervals were placed at approximately 1, 5, and 10 feet below the water table on the day of installation. A third well cluster was installed at each site, per EFGWB reviews (USEPA, 1990a), 5 to 6 months after the 1989 acifluorfen applications (except North Dakota which was 10 months later). Ground-water samples were, generally, sampled and analyzed for acifluorfen residues at monthly intervals for twelve months after each acifluorfen application.

The five study plots were divided into four subplots. Soil samples were collected from each of the subplots and analyzed for acifluorfen residues. All soil samples analyzed, with the exception of the 1989 pre-application soil samples, were conducted on four soil cores from each of the four subplots composited by equal depth increment. Pre-application (1989) soil samples were collected to a depth of 6 feet in North Carolina, North Dakota and Virginia sites, and to a depth 8 feet at the Indiana and Tennessee sites. The upper 2 feet were divided into 12 inch increments and the remaining four or eight feet were divided into 24 inch increment. Soil sampling locations were not delineated on any maps.

Immediately following the 1989 applications of acifluorfen-sodium, soil samples were collected to a maximum depth of 6 inches for all sites, except Tennessee where samples were collected to a maximum of 8 inches. Soil samples were collected to a maximum of 2 feet (4 feet in TN) in 1 foot increments approximately two weeks after the 1989 application.

Following the two week 1989 post-application sampling interval, soil samples were collected and analyzed, at monthly intervals (after application), in 12-inch increments to a depth of 24 inches, and then a 24-inch increment to a depth of 48 inches.

These soil samples were to collected and analyzed until the residue levels were non-detectable (Detection limit  $<0.010$  ppm; 10 ng/g) in all depth increments analyzed. It was not stated, but assumed that the 0.010 ppm is based upon dry soil weight, and is equivalent to 0.010  $\mu\text{g}$  acifluorfen/g dry soil or 10 ng acifluorfen/g dry soil. Soil sampling was conducted through one month after application the 1989 for the Indiana, Tennessee, and Virginia sites, and through two months after application at the North Carolina site. Soil samples were collected at 1, 2, 4, and 10-months after the 1989 application at the North Dakota site. Ground-water samples were generally collected monthly after the 1989 application of acifluorfen.

Soil and ground-water samples were collected prior to the 1990 acifluorfen applications at the Indiana and North Dakota sites. Pre-application soil samples were taken in 6-inch increments to a depth of 18 inches. Soil samples were taken to a depth of 6 inches immediately following application. Soil samples were then collected in 6-inch increments to a depth of 24 inches at two weeks, 1, 5, 9, 13-months, and in 6-inch increments to 18-inches at 2, 3, 4, 10, 11, and 12-months, after the 1990 application. Soil samples were not collected due to weather, at the Indiana site for months 6, 7, and 8 post application, and at North Dakota for months 6, 7, 8, 9 after application.

Ground-water samples were collected monthly after the 2-week sampling for 12 months after application the 1990 for the Indiana site, and 13 months after 1990 application for North Dakota. Water samples were not collected at the North Dakota site for the 7th month after application.

#### Precipitation Data

The distances from the NOAA weather station to the study site is quite substantial for several of the sites. The registrant should provide any site specific information available for any of the study areas. This might help to determine if the precipitation frequency, intensity, and occurrences at the study sites correlated at all with the weather station data.

#### Soil and Ground-Water Residue Analysis

Soil and ground-water residue analysis were conducted by Rhone-Poulenc and BASF. Soils were analyzed by Rhone-Poulenc Method 1002 and Method 1002 with modifications, and water samples were analyzed by Rhone-Poulenc Method 1001 and Method 1001 with modifications. The registrant reports that the detection limit for acifluorfen residues in soil was 0.010  $\mu\text{g/g}$  (10 ng/g) and in water 1.0  $\mu\text{g/L}$  (1.0 ppb).

Storage stability studies of frozen soil and water samples and procedural recovery samples were conducted. Acifluorfen recoveries for the soil stability ranged from 86 to 137 percent. An apparent discrepancy exists as page 60 of 415 states a maximum recovery of 104 percent, whereas Table XXVI, page 126 indicates a maximum of 137 percent recovery. This discrepancy should be clarified. It also appears that soil residue recovery may decrease after being frozen more than four weeks. Recoveries from water samples ranged from 65 to 198 percent, which we believe is poor for water.

Soil samples with acifluorfen detections are summarize in Table 3 (Table XXIV, pages 115 to 121 of 415 from the report). Soil acifluorfen values ranged from less than the detection limit ( $<0.010 \mu\text{g/g}$ ) to  $0.287 \mu\text{g/g}$  for a 0 - 6 inch sample collected after the 1990 application at the North Dakota site.

## SMALL-SCALE RETROSPECTIVE STUDIES

Virginia The 9.9 acre study plot was located on the Delmarva Peninsula in Accomack County, Virginia. The site had an average water table depth of 3.7 feet (range 0.9 to 10.5 feet). The soil was mapped as the Munden sandy loam. The registrant defined this site to be "extremely vulnerable". Two soil cores were used for site characterization, one 6-foot core with 1-foot increments down to 6 feet, plus a single 1.5 foot core. The upper three depth increments (3 feet) were classified sandy loam to loamy sand textures (clay + silt ranged from 18 to 30 percent). Thus the upper three depth increments exceeded the maximum clay and silt content typically allowed by the Ground Water Section for ground water studies. EFGWB would have classified this site with a lower vulnerability than did the registrant. Thus with registrants rating scheme we would have considered it "vulnerable" or "highly vulnerable", rather than "extremely vulnerable". Below three feet the predominate soil texture was sand (96%). Organic matter was 1.8 percent in the upper 1 foot and decrease to 0.1 below 2 feet.

Precipitation at the weather station (6 miles from the site) recorded 51.36 inches of rain, or 122% of the historical mean of 42.11 inches, for 1989 after application. The 8.08 inches of precipitation during the month of application (July 1989) application exceeded the historical monthly mean of 4.31 inches by 3.77 (87%).

This site had two year previous use history of acifluorfen prior to the July 6, 1989 application. Soil samples collected in 12 inch increments to 24 inches, and 24 inch increments to 72 inches were analyzed for acifluorfen residues prior to the 1989 acifluorfen application. There were no pre-application detections of acifluorfen residues in the soil samples (Table 3).

Acifluorfen was applied at a rate of 0.26 lb ai/acre (0.29 kg ai/ha) for 1989. The mean acifluorfen residues detected in the 0 to 6 inch layer immediately after application was 0.038  $\mu\text{g/g}$  (0.028 to 0.059  $\mu\text{g/g}$  or 17 to 35% of applied), with a theoretical application concentration of 0.166  $\mu\text{g/g}$  ). A single detection of 0.012  $\mu\text{g/g}$  two weeks after application occurred in the 0 to 12 inch sampling increment. The acifluorfen residue data are summarized in Table 3. The half-life of acifluorfen at the Virginia site was reported to be between 14 to 16 days (Table 4). No acifluorfen residues were detected in the ground-water samples collected at the site. This site was approved for decommissioning on July 26 1990, and abandoned on August 10 1990.

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SODIUM ACIFLUROFEN REVIEW

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Pages 19 through 25 are not included.

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Table 4. First Order Kinetic Rate for decay equation<sup>1</sup> by state and year from the interim 1989 (Norris, 1990) and 1990 final (Hiscock and Cooper, 1991) reports.

	TN	IN	NC	ND	VA
	1989				
<u>Model 1<sup>2</sup></u>					
Intercept (A <sub>0</sub> )	0.141	0.294	0.120	0.292	0.087
Slope (k)	-0.0417	-0.0929	-0.100	-0.0124	-0.0438
Correlation Coeff.	-0.807	-0.943	-0.977	-0.875	-0.991
Half-life ( days)	16.7	7.46	6.91	55.99	15.84
<u>Model 2<sup>3</sup></u>					
Intercept (A <sub>0</sub> )	0.327	0.345	0.281	0.247	0.225
Slope (k)	-0.0696	-0.1006	-0.134	-0.0105	-0.0859
Correlation Coeff.	-0.972	-0.968	-0.999	-0.894	-0.947
Half-life (days)	9.96	6.89	5.15	66.16	8.08
	1990 <sup>4</sup>				
<u>Model 3<sup>5</sup></u>					
Intercept (A <sub>0</sub> )	0.021	0.0719	0.021	0.129	0.0195
Slope (k)	-0.318	-0.0182	-0.047	-0.0116	-0.0491
Correlation Coeff.	0.799	0.996	0.998	0.969	0.996
Half-life ( days)	21.8	38.11	6.91	59.73	14.1

<sup>1</sup> For 1989:  $A = A_0 e^{(kt)}$ , A<sub>0</sub> initial concentration in kg ai/ha, A is concentration in kg ai/ha at time t, k is the slope in days<sup>-1</sup>, and t is time in days.

For 1990:  $A = A_0 e^{(kt)}$ , A<sub>0</sub> initial concentration in μg/g, A is concentration in μg/g at time t, k is the slope in days<sup>-1</sup>, and t is time in days.

<sup>2</sup> Model 1 used the analytically determined applied rate for A<sub>0</sub> in the 1989 interim report.

<sup>3</sup> Model 2 used the theoretically applied rate for A<sub>0</sub> in the 1989 interim report.

<sup>4</sup> Half life determinations for North Dakota and Indiana are for 1990, TN, NC, and VA are for 1989 data re-determined in the 1990 final report.

<sup>5</sup> Model 3 used the analytically determined applied rate for A<sub>0</sub> in the Final report 1990 for ND and IN and 1989 data for TN, NC, and VA.

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Tennessee The 3.5 acre site in Tennessee was located on the Armstrong Bar (inside the levee along the Mississippi River) in Shelby County. This site was defined by the registrant to be "vulnerable", the least vulnerable of the five study sites. The water table depth ranged between 8.1 and 15.6 feet, with a mean of 11.5 feet. Four cores with 1 foot sampling increments were collected to 2 feet, two foot increments to 8 feet, and a one foot increment to a depth of nine feet for soil characterization. The soil at the site was mapped as Robinsonville fine sandy loam. The upper two depth increments contained between 12 to 20 percent clay and 38 to 54 percent silt. Below 2 feet, the sand content was generally greater than 90 percent. Organic matter content decreased with depth, but did vary from 0.1 to 0.5 percent below 2 feet. The registrant considered this site to be the least vulnerable to the five sites evaluated. This site was not approved in advance of the initiation of monitoring (USEPA, 1990a) and would not have been considered vulnerable by EFGWB. The Ground Water Section indicated that although the clay content was higher than normally approved for this type of study, useful information could be obtained from the study (USEPA, 1990a).

Precipitation, reported at the NOAA site, (10 miles from the study site) after application (1989) was 61.62 inches, which was approximately 122 percent higher than the historical mean of 50.5 inches.

Acifluorfen was applied to soybeans three years prior (1986, 1987, 1988) to the initiation of the study in 1989. Acifluorfen residue at the 0.016  $\mu\text{g/g}$  level was found in one of the 0 to 12 inch samples, during the pre-application acifluorfen assessment (Table 3). Acifluorfen was applied at a rate of 0.23 lb ai/acre (0.26 kg ai/ha) for 1989. Immediately after sampling acifluorfen residues averaged 0.033  $\mu\text{g/g}$  (0.033 to 0.034  $\mu\text{g/g}$ , or approximately 30% of applied) in the upper 8 inches, with a theoretical application concentration of 0.11  $\mu\text{g/g}$ .

Acifluorfen residues were identified in the 0 to 12 inch increment in three of the four cores (Table 3) collected 20 days after application (2 week sampling). The mean residue level of the three sampling increments with levels greater than the detection limit (0.010  $\mu\text{g/g}$ ) was 0.021  $\mu\text{g/g}$ , and ranged between 0.015 to 0.028  $\mu\text{g/g}$ . There were no soil residues detected after this sampling. Soil half-lives were found to be between 10 and 22 days at the site (Table 4). Acifluorfen was not detected in any ground water samples collected, up to 12 months after application. Site decommissioning was approved effective July 26, 1990, and completed on August 13, 1990.

The registrant failed to sample the standing water at the Tennessee site as agreed EFGWB # 90-002, page 10, Tennessee scenario #3. (USEPA, 1990a).

North Carolina The North Carolina site was located on the Atlantic coastal plain in Columbus County. The site was defined by the registrant to be "ultra vulnerable", the most vulnerable of the five sites evaluated during the study. The soil series at the 4.4 acres site was reported to be the Echaw loamy sand. The average water table depth was 2.28 feet and ranged between 0.38 to 4.68 feet. Two soil cores for site characterization showed that the sand content increased with depth, and was generally greater than 85 percent sand and less than 10 percent clay (highest 13%). The organic matter content was moderately high (1.8%, 2.3%) in the surface layer (0 to 1 foot) for both cores. However, in one of the two cores the organic matter content increased from 0.4 at 3 to 4 feet to 3.0 and 3.4 % at the 5 to 6 and 6 to 7 foot increments. EFGWB would concur with the registrants selection that overall this site does exhibit soil characteristics of a site vulnerable to ground water contamination.

Precipitation measured at the NOAA weather station, 19 miles from the study area, was 42.82 inches (84% of normal of 50.79 inches; September data were not available).

Acifluorfen was applied to soybeans four years (1985, 1986, 1987, and 1988), prior to the initiation of the monitoring study in 1989. Acifluorfen soil residue values for the study site are summarized in Table 3. Pre-application acifluorfen residues were not detected in any of the soil cores. During 1989, acifluorfen was applied at a rate of 0.23 lb ai/acre (0.26 kg ai/ha) with a theoretical soil concentration of 0.15  $\mu\text{g/g}$ . Immediately after application, residues were detected in four 0-6 inch soil cores. The values ranged from 0.019 to 0.052  $\mu\text{g/g}$  (13 - 35% of applied), with a mean of 0.041  $\mu\text{g/g}$  of acifluorfen. Two weeks after application, residue levels at 0.010  $\mu\text{g/g}$  were detected in the two out of four 0 to 12 inch cores. The two remaining 0 to 12 inch cores, and four 12 to 24 inch from the 2 week sampling, and soil cores for the one month after application sampling were all less than the reported detection limit of 0.010  $\mu\text{g/g}$ . Soil dissipation half-lives for the North Carolina site were found to be between 5 and 15 days (Table 4). There were no acifluorfen detections in any of the monthly ground water samples collected for up to 12 months after application.

Indiana The 9.9 acre Indiana site was located in the central glaciated region of Knox County. Soils at the site were mapped as the Lomax loam soil series, with an average water table depth of 8.0 feet (range 4.0 to 10.9 feet). The site was defined

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<sup>4</sup> Detections of acifluorfen residues (1 and 2  $\mu\text{g/L}$ ) were detected in two samples collected during the 7 month sampling. These detections were later classified as "false positive" (MRID 414485-00 and 414485-01).

by the registrant as "highly vulnerable". Clay and silt contents in two soil cores were greater than the lower depths, especially in the upper two feet (15 to 21% clay, 17 to 25% silt). Sand contents ranged from a low of 56 percent to a high of 92 percent. The clay and silt contents present in the upper two feet in one core and upper four feet is higher than what the Ground Water Section normally considers suitable for ground-water monitoring studies and would have rated this site with a lower vulnerability rating. Organic matter content decreased with depth and was 0.2% or less below 2 feet.

The study site reportedly was flooded, during June 1990 for the first time in 30 years, by Black Creek. The registrant failed to sample and analyze the standing water, due to flooding, at the Indiana in keeping with the spirit of the request to sample standing water at the Tennessee site (as agreed EFGWB # 90-002, page 10, Tennessee scenario #3; USEPA, 1990a). Black Creek is approximately 2000 feet northwest of the study site, and the White River is about 1.5 miles southeast of the study area. The study site is protected from flooding by the White River by the Neal Levee.

The registrant shows on Figure 24, page 151 of 415 (May 9, 1990) that the direction of ground water flow was towards the east. Was the direction of flow always to the east? Did the ground water's direction of flow show any season variation during the study? Specifically, is ground water flow controlled by Black Creek which is closer to the site, or by the White River which is somewhat farther from the site?

Precipitation and temperature data were obtained from the a NOAA weather station about 8 miles from the site. Evaporation pan data were obtained from a station approximately 50 miles from the site. Precipitation following the June 30, 1989 application was 8.8, or 189 percent the historical mean of 4.7 inches for the area. The precipitation for the year following the 1989 application was 53.9 inches (120% of average) of the historical average (45.0 inches). Rainfall following the July 7, 1990 application was 4.1 inches, or 87 percent of the historical mean of 4.7 inches. Precipitation for the year following the 1990 application was 43.4 inches, which is only slightly less than the normal average (45.0 inches) for the period.

This site had one year prior history of acifluorfen use prior to the initiation of the study in June 1989. Acifluorfen was also applied in July 1990. Acifluorfen concentrations in the soil samples for the Indiana study are given in Table 3. All soil samples analyzed for acifluorfen residues prior to the 1989 application were less than detection limit of 0.010  $\mu\text{g/g}$ . The acifluorfen application rate in 1989 was 0.21 lb ai/acre (0.24 kg ai/ha). The mean acifluorfen residues in the 0 to 6 inch soil increment immediately following the 1989 application was 0.096

$\mu\text{g/g}$  (ranging from 0.090 to 0.101  $\mu\text{g/g}$ , or 69 - 78% of applied), with a theoretical application concentration of 0.13  $\mu\text{g/g}$ . Residues ranging between 0.020 to 0.031  $\mu\text{g/g}$  (mean 0.023  $\mu\text{g/g}$ ) were detected in the upper 0 to 12 inch soil increment 2 weeks after application. There were no acifluorfen residues detected at 12 to 24 inches at two weeks, and 0 to 12, 12 to 24, and 24 to 48 inches at one month after application. Soils were not sampled after the one month sampling after the 1989 sampling.

Prior to the 1990 application, acifluorfen residues were found at 0.013  $\mu\text{g/g}$  in one of four soil cores from 0 to 6 inches, but not at the 6 to 12 and 12 to 18 inch sampling increments. Acifluorfen was applied at a rate of 0.25 lb ai/acre (0.28 kg/ha) for 1990, with a theoretical application concentration of 0.16  $\mu\text{g/g}$ . Immediately after the 1990 acifluorfen application, multiple soil samples were collected to a depth of 6 inches. Acifluorfen residues levels ranged from less than the detection limit (0.010  $\mu\text{g/g}$ ) to 0.160  $\mu\text{g/g}$ , with a mean of about 0.078  $\mu\text{g/g}$  (Tables 3 and 5). Residues were collected by 6-inch increments to a depth of 24 inches two weeks after application, and then by monthly time increments. Mean and ranges of residues for each sampling time for the 0 to 6 and 6 to 12 inch sampling increments are summarized in Table 5. The residue levels in the 0 to 6 inch increment generally decrease with time. The detection of acifluorfen residues at 6 to 12 inches indicates residue mobility. Residue levels were less than the detection limit of 0.010  $\mu\text{g/g}$  for the 12 to 18 and 18 to 24 sampling increments. Soil dissipation half-live values reported ranged from about 7 days to more than 38 days (Table 4). Samples were not collected during several months because of inclement weather conditions.

Acifluorfen residues appear to be somewhat persistent at the Indiana site, as residue values were detected prior to the 1990 (0.013  $\mu\text{g/g}$ ) acifluorfen application.

Ground-water monitoring wells were sampled prior to and monthly after acifluorfen application. Flooding at the site apparently prevented the collection of an 11 month sampling. There were no detections of acifluorfen in the ground-water samples collected at the Indiana site with a detection limit of 1.0  $\mu\text{g/L}$ .

Table 5. Acifluorfen residues levels in  $\mu\text{g/g}$  for the 0 to 6 inch and 6 to 12 inch sampling increments by time after the 1990 application for the Indiana small scale retrospective and limited prospective ground-water monitoring study site.

Sampling Interval	Mean <sup>2</sup> Concentration		Mean <sup>2</sup> Concentration	
	Range		Range	
	$\mu\text{g/g}$		$\mu\text{g/g}$	
	0 to 6 Inches		6 to 12 Inches	
0 DAT <sup>3</sup>	0.078	(<0.010 to 0.160)	not sampled	
2 Weeks	0.051	( 0.039 to 0.065)	0.010	(<0.010 to 0.011)
1 Month	0.038	( 0.031 to 0.052)	0.010	(<0.010 to 0.011)
2 Months	0.025	( 0.018 to 0.037)	<0.010	(<0.010)
3 Months	0.015	( 0.010 to 0.025)	<0.010	(<0.010)
4 Months	0.014	( 0.011 to 0.022)	<0.010	(<0.010)
5 Months	0.024	( 0.011 to 0.041)	0.035 <sup>3</sup>	(<0.010 to 0.035)
9 Months	0.027	( 0.020 to 0.042)	0.021 <sup>5</sup>	(<0.010 to 0.021)
10 Months	0.024	( 0.012 to 0.034)	<0.010	
11 Months	0.019	( 0.010 to 0.027)	<0.010	
12 Months	0.018	(<0.010 to 0.030)	<0.010	

<sup>1</sup> Time after acifluorfen application.

<sup>2</sup> Value maybe the average of replicate analysis.

<sup>3</sup> Sampled on day of application.

<sup>4</sup> Three of four <0.010  $\mu\text{g/g}$ ; average of replicated values = 0.035  $\mu\text{g/g}$ .

<sup>5</sup> Three of four <0.010  $\mu\text{g/g}$ ; one of four = 0.021  $\mu\text{g/g}$ .

North Dakota The 3.5 acre North Dakota study area was located in the north central glaciated region of the Central Plains in Ransom County. The site was defined as "extremely vulnerable" by the registrant. The site was situated about two miles southwest of a wetland area, seven miles south of the Maple River, and 7 miles north of the Sheyenne River. The soil mapping unit indicated that the dominant soils were the Ulen-Hecla sandy loam/loamy sand. Four cores were collected to characterize the study site. Clay contents ranged from 7% to 23% in the upper two feet. The soil particle size below two feet were 87 percent or more sand, and 9 percent or less clay. Organic matter content in the surface 1 foot range from 2.1 to 4.7 percent. The water table fluctuated about 4.8 feet over the period of the study. Shallowest depth was 1.6 feet below the land surface (May 1989) and the deepest was about 6.4 feet below the land surface (November 1989). Ground-water flow was reportedly to the south. Acifluorfen was applied twice (0.50 and 0.63 lb ai/acre) to the site in 1988, one year prior to the initiation of study. The Branch would concur with the registrants vulnerability assessment based upon soil characteristics and depth to ground water.

Precipitation and temperature were measured at a NOAA weather station approximately 36 miles to the northeast (Fargo) of the study site, and pan evaporation was measured at a NOAA weather station approximately 160 miles to the northwest (Mandan). Precipitation following the 1989 application was 22.1 inches, which is approximately 114 percent of the normal mean (19.5 inches). Precipitation for the year after the 1990 acifluorfen application was 13.6 inches, or about 81 percent of the historical mean (19.5).

Acifluorfen appears to be relatively persistent at the North Dakota study site. Residues ranging from  $<0.010 \mu\text{g/g}$  to  $0.057 \mu\text{g/g}$  (mean =  $0.027 \mu\text{g/g}$ ) were detected in the 0 to 12 inch depth increment of soil samples collected, prior to the 1989 application of the test chemical (Tables 3 and 6). This suggests that residues at detectable levels remained in the soil from the previous year's two applications (0.50 and 0.63 lb ai/acre). Residues were not detected in soil samples collected from 12 to 72 inches in three 24-inch increments for the pre-application sampling. Soil sampling increments may have been too large in the early portions of the study, as previously noted in other reviews.

Acifluorfen residues in 6 inch soil samples collected immediately after application ranged between  $0.155$  and  $0.204 \mu\text{g/g}$  (or 55-73% of applied), with a mean of  $0.173 \mu\text{g/g}$  and a theoretical application concentration of  $0.28 \mu\text{g/g}$ . Residues were detected in all 0 to 12 inch soil samples collected 2-weeks, 1, 2, 4, and 10- months, and in the 12 to 24 inch sampling increment 2-weeks after the 1989 acifluorfen application (Tables 3 and 6). Values ranged between  $0.010$  and  $0.057 \mu\text{g/g}$  in the

surface increments, and between <0.010 to 0.026  $\mu\text{g/g}$  in the lower increment (Tables 3 and 6).

Soil samples, were collected in three 6-inch increments to a depth of 18-inches, prior to the 1990 acifluorfen-sodium application. Residues were detected in the upper 6-inch increment ranged between 0.029 to 0.052  $\mu\text{g/g}$  (mean = 0.039  $\mu\text{g/g}$ ) (Table 3 and 6). Acifluorfen residues in 0 to 6 inches soil samples collected immediately after application (0.25 lb ai/ac) ranged from 0.041 to 0.287  $\mu\text{g/g}$  (26-180% of applied), with a theoretical application concentration of 0.16  $\mu\text{g/g}$ . Thus, residue concentration levels were greater than the theoretical concentration levels, indicating possible residue accumulation. Residues were detected in the 0 to 6 inch and the 6 to 12 inch sampling increments after the 1990 application and are summarized in Table 3. Acifluorfen residue detections at 6 to 12 inch increment suggest a downward movement of acifluorfen residues.

The data suggest that acifluorfen residues are quite persistent at the North Dakota site, as residues are still present at detectable concentrations one year following application. An interesting trend (Figure 1) is that while acifluorfen application rates decreased from 1988 through 1990, the residue concentration remaining in the surface sampling (0 to 6 inches) increment is greater 13 months after the 1990 application than one year after the 1988 application (pre-1989 application). The mean acifluorfen value and range of detections for the North Dakota listed in Table 6.

The leaching of acifluorfen residues from the surface sampling increment to deeper sampling increments is also apparent, as acifluorfen residues were detected in some of the deeper soil sampling increments (Tables 3 and 6). It is also suspected that had shorter sampling increments been used, or soil pore water collected with suction lysimeters additional detections of acifluorfen residues with depth would have occurred. Because detection limits for soil samples are 10 (10 ng/g, or 10 ppb) times greater than for water samples (1  $\mu\text{g/L}$ , or 1 ppb).

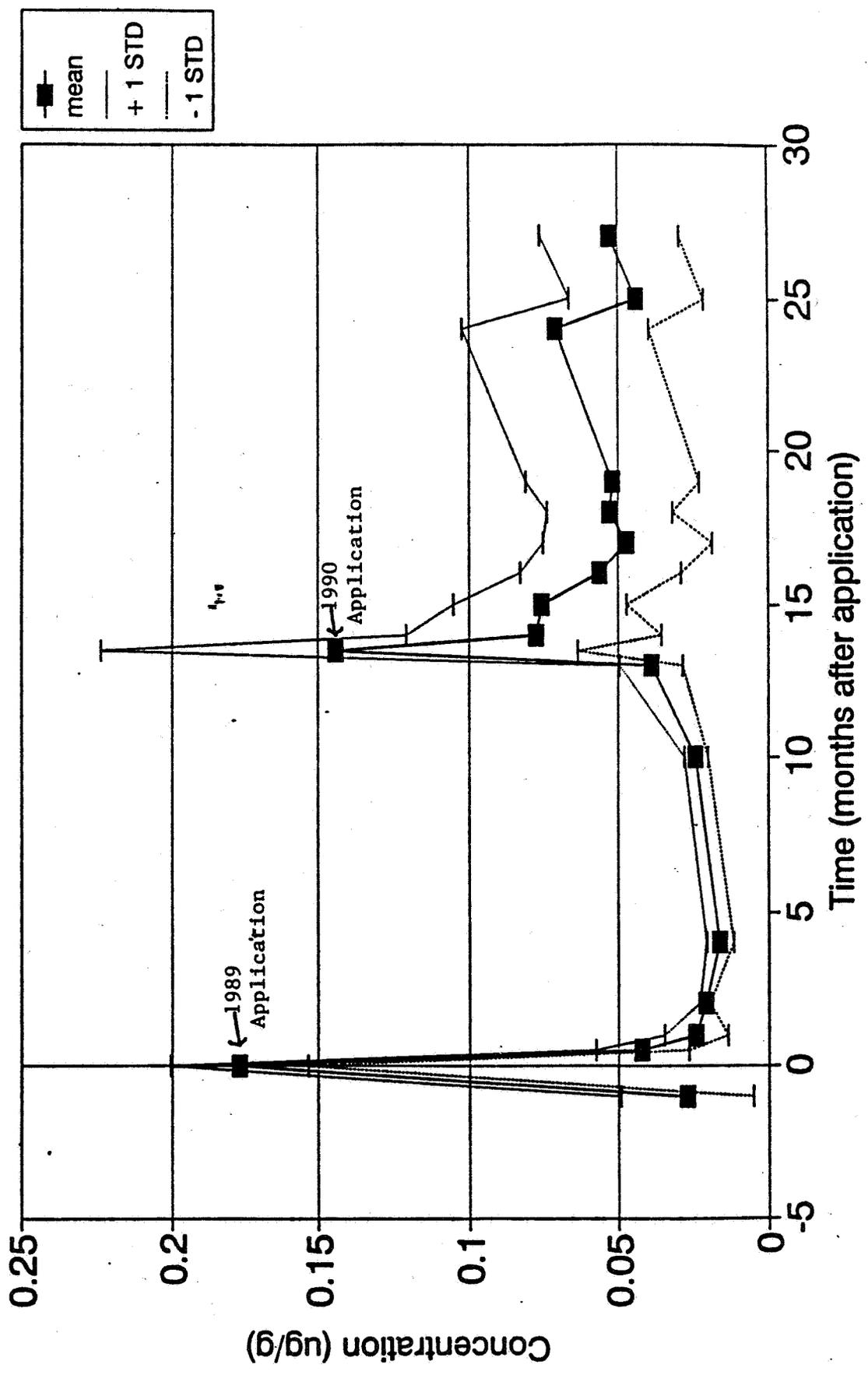
There were no detections of acifluorfen residues in any of the ground-water samples collected at the North Dakota site. Ground-water samples were generally collected monthly, except during the winter months.

Differences in amounts, frequency, and duration of precipitation between years at the site may have influenced the fate and transport acifluorfen residues. Resulting in higher soil concentrations remaining in the surface soil layer during 1990 compared to 1989. Approximately two more inches of precipitation was reported at the NOAA weather station for the year following the June 30, 1989 pesticide application (7/1/89

through 6/30/90) than for the same period following the June 23, 1990 application (7/1/90 through 6/30/91), based upon monthly averages. For the period July 1 through October 31, 4.4 more inches of rainfall occurred during 1989 compared to 1990. The maximum and minimum monthly temperatures did not appear to be highly different. However, because site specific meteorological data are not available this cannot be fully evaluated.

Figure 1. Acifluorfen residues in the surface (0-6;0-12 inch) layer over time.

### Acifluorfen Residues North Dakota Surface Layer



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Table 6. Mean acifluorfen residues for two sampling increments by time for the North Dakota small scale retrospective and limited prospective ground-water monitoring study site. Means were calculated from samples where the acifluorfen values were 0.010 µg/g or greater.

Sampling Interval	Mean <sup>1</sup> Concentration		Range	Mean <sup>1</sup> Concentration		Range
	----- (µg/g) -----			-----		
	<u>0 to 12 inches</u>			<u>12 to 24 inches</u>		
Pre-1989 <sup>2</sup>	0.027	(<0.010 to 0.057) <sup>3</sup>		<0.010 <sup>4</sup>		
0 DAT <sup>5</sup>	0.177	(0.155 to 0.204) <sup>6</sup>		not sampled <sup>7</sup>		
	<u>0 to 12 inches</u>			<u>12 to 24 inches</u>		
2 Weeks	0.042	(0.025 to 0.057)		0.018	(<0.010 to 0.026)	
1 Month	0.024	(0.010 to 0.033)		<0.010	(<0.010) <sup>8</sup>	
2 Months	0.021	(0.018 to 0.022)		<0.010	(<0.010) <sup>8</sup>	
3 Months	not sampled			not sampled		
4 Months	0.016	(0.013 to 0.022)		<0.010	(<0.010) <sup>8</sup>	
5 Months	not sampled			not sampled		
6 Months	"	"		"	"	
7 Months	"	"		"	"	
8 Months	"	"		"	"	
9 Months	"	"		"	"	
10 Months	0.024	(0.019 to 0.028)		<0.010	(<0.010) <sup>8</sup>	
11 Months	not sampled			not sampled		
12 Months	"	"		"	"	
	<u>0 to 6 inches</u>			<u>6 to 12 inches</u>		
Pre-1990 <sup>9</sup>	0.039	(0.029 to 0.059)		not sampled		
0 DAT <sup>2</sup>	0.144	(0.041 to 0.287)		"	"	
2 Weeks	0.078	(0.035 to 0.136)		0.027	(0.014 to 0.038) <sup>10</sup>	
1 Month	0.076	(0.039 to 0.103)		0.019	(0.011 to 0.032) <sup>10</sup>	
2 Months	0.056	(0.026 to 0.089)		<0.010	(<0.010) <sup>11</sup>	
3 Months	0.047	(0.022 to 0.088)		<0.010 <sup>11</sup>		
4 Months	0.053	(0.034 to 0.076)		<0.010	(<0.010) <sup>11</sup>	
5 Months	0.052	(0.029 to 0.94)		0.015	(<0.010 to 0.015) <sup>10</sup>	
6 Months	not sampled			not sampled		
7 Months	"	"		"	"	
8 Months	"	"		"	"	
9 Months	"	"		"	"	
10 Months	0.071	(0.030 to 0.101)		<0.010 <sup>11</sup>		
11 Months	0.044	(0.015 to 0.063)		<0.010 <sup>11</sup>		
12 Months	not sampled			not sampled		
13 Months	0.053	(0.019 to 0.073)		0.016	(<0.010 to 0.016) <sup>10</sup>	

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Table 6 (Continued)

- 1 Value maybe the mean of replicated analysis.
- 2 Sampling prior to the 1989 application.
- 3 Sampling increment of 0 to 12 inches.
- 4 Sampling increments of 12 to 24, 24 to 48, and 48 to 72 inches. All values were less than the detection limit of 0.010  $\mu\text{g/g}$ .
- 5 Sampled on day of application.
- 6 Sampling increment of 0 to 6 inches.
- 7 not sampled - no samples collected.
- 8 Sampling increments of 12 to 24 inches and 24 to 48 inches. All increments were less than 0.010  $\mu\text{g/g}$ .
- 9 Sampling prior to the 1990 application.
- 10 Sampling increments: 6 to 12, 12 to 18, and 18 to 24 inches. Increments 12 to 18 and 18 to 24 inches were  $<0.010 \mu\text{g/g}$ .
- 11 Sampling increments: 6 to 12 and 12 to 18 inches. The increment 12 to 18 inches were  $<0.010 \mu\text{g/g}$ .

## SUMMARY

Five small-scale retrospective ground-water monitoring studies were conducted in five states which are representative of the soil and hydrogeologic conditions in soybean growing areas in the United States. The acifluorfen use history prior to 1989 at the five study sites were Indiana - 1 year; North Carolina - 4 years; North Dakota - 1<sup>5</sup> year; Tennessee - 3 years; and Virginia - 2 years. There were no<sup>5</sup> detections of acifluorfen residues in ground water in any of the five small-scale retrospective ground-water monitoring studies. Previously, a small-scale prospective acifluorfen study has also been conducted by the registrant in central Wisconsin. Acifluorfen residues up to 23 µg/L were found in the ground water at the Wisconsin site.

The registrant ranked the sites vulnerability to ground-water contamination (most vulnerable to least vulnerable) as North Carolina, Virginia, North Dakota, Indiana, and Tennessee. Several of the sites were found not to possess the necessary acifluorfen use history normally required for retrospective ground-water monitoring studies. The registrant partially alleviated this limitation by conducting the study for a second year by adding a second application of acifluorfen. Water table depths were suitable, ranging from less than one foot at the North Carolina site to more than 15 feet at the Tennessee site. Thus, depth to water table was acceptable for the five sites.

EFGWB, as noted in previous reviews does not concur with the registrant focusing on the texture of the subsoil (sandy). Also, EFGWB does not entirely agree with the specific ranking of the sensitivity of these sites to ground water contamination, we believe that they span the range of use sites from vulnerable sorted sands to non-vulnerable Mississippi delta sand and clay deposits.

Soil sampling increments were also too large (Recommendation 4; USEPA, 1990a). Confusion continued to exist concerning the number of cores collected, as this varies from one to four, and was therefore, not in agreement with the Protocol.

The registrant failed to sample the standing water at the Tennessee site as agreed EFGWB # 90-002, page 10, Tennessee scenario #3 (USEPA, 1990a). Additionally, in keeping with the spirit of the request to sample standing water at the Tennessee site, the standing water present at the Indiana site, due to flooding should also have been sampled and analyzed.

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<sup>5</sup> Acifluorfen residues were detected at the North Carolina site, but were determined by the registrant to be "false positive" detections.

The studies were conducted using protocol that did not have EFGWB approval. Protocol modifications were also implemented without Agency approval. The registrant has already received Agency approval to discontinue and decommission the Tennessee and Virginia study sites. Two of the sites (North Dakota and Tennessee) were also implemented without EFGWB approval, and the Indiana site only had tentative approval.

Soil and ground-water samples were collected prior to the 1989 acifluorfen application at all study sites. Acifluorfen residues were detected in one pre-1989 application soil sample from the Tennessee site (0 to 12 inches, 0.016  $\mu\text{g/g}$ ) and three samples from the North Dakota (0 to 12 inches, 0.011 to 0.057  $\mu\text{g/g}$ ). There were no pre-application acifluorfen detections in ground-water at the five sites.

Post-application soil samples were collected immediately after 1989 application, two weeks after application, and then monthly at each site until residue levels were not detectable (detection limit for soil was 0.010  $\mu\text{g/g}$ ) in all depth increments analyzed. Soil samples were collected through month 1 at Indiana, Tennessee, and Virginia and through month 2 at the North Carolina site. Samples were also collected during the 4th and 10th month after the 1989 acifluorfen application at the North Dakota site. Residues were greatest in the surface 6-inch<sup>6</sup> soil sampling increment collected immediately after the 1989 application ranged between 0.019 and 0.204  $\mu\text{g/g}$ . Residues were detected in soil samples collected (0 to 12 inches) two weeks after application in one sample (0.012  $\mu\text{g/g}$ ) at the Virginia site, two (0.010  $\mu\text{g/g}$ ) at the North Carolina site, three (0.015 to 0.028  $\mu\text{g/g}$ ) at the Tennessee site, four (0.020 to 0.031  $\mu\text{g/g}$ ) at the Indiana site and (0.025 to 0.057  $\mu\text{g/g}$ ) at the North Dakota site. There were no acifluorfen residues in soil one month after the 1989 application at any of the sites, with the exception of North Dakota. Residues ranging between 0.010 to 0.057  $\mu\text{g/g}$  were detected in the 0 to 12 inch sampling increment at the North Dakota site for all sampling intervals.

Soil samples were collected at the Indiana and North Dakota sites prior to the 1990 application of acifluorfen. One pre-application 0 to 6 inch core at the Indiana site had a detectable level of 0.013  $\mu\text{g/g}$  of acifluorfen. All four of the 6-inch surface increment at the North Dakota site had detectable levels (0.029 to 0.052  $\mu\text{g/g}$ ) of acifluorfen residues.

Acifluorfen-sodium was applied for a second year at the Indiana and North Dakota study sites. Detectable ( $\geq 0.010$   $\mu\text{g/g}$ )

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<sup>6</sup> The surface sampling increment at Tennessee was 8-inches for the soil increment collected immediately after the 1989 application, rather than 6 inches.

to 0.287  $\mu\text{g/g}$ ) levels of acifluorfen residues were measured in nearly all of the post-application 0 to 6 inch sampling increments for the North Dakota (up to 388 days after application) and Indiana (up to 373 after application) sites. Downward movement of acifluorfen residues were noted at both sites. Residues were identified in the 6 to 12 inch increment for the 2-week (12 days), 1-month (26 days), 5-month (150 days) and 13-month samplings for North Dakota, and 2-week (14 days), 1-month (28 days), 5-month (148 days) and 9-month samplings at Indiana. A greater number of acifluorfen detections would probably have occurred had the detection limit be lowered. It is also probable that had suction lysimeters been installed at the sites, and soil water samples collected with a lower detection limit, acifluorfen residues would have been detected in deeper sampling increments.

There were no acifluorfen residues detected ( $1.0 \mu\text{g/L}$ ) in ground water at the Indiana, North Carolina, North Dakota, Tennessee, Virginia sites.

Additionally, the sampling intervals for the soil samples may not have been frequent enough to adequately estimate the field dissipation rates. The shortest interval between sampling times was two weeks, i.e., two weeks after application, after this sampling intervals were 30 days or longer. Sampling should have been conducted with a greater intensity, such as daily or bi-daily for the first 10 to 14 days after application, as half life estimates ranged as low as 5.15 days. The sampling frequency was not adequate to adequately characterize the behavior of the chemical in the early part of the studies when the chemical activity was the greatest.

The Branch will obtain additional insight concerning the fate and transport of acifluorfen residues at these sites through computer simulations using the model PRZM (Carsel et al., 1984).

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<sup>7</sup> Acifluorfen residues were detected in two wells 7 months after application, registrant determined that these were "false positive" results.

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