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MEMORANDUM:

SUBJECT: Alachlor Revised RED, EFGWB Science Chapter

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The attached document contains the Environmental Fate and Groundwater Branch (EFGWB) Science Chapter for the List A Reregistration Eligibility Document (RED) for Alachlor. The RED Science Chapter contains an Executive Summary, General Information, Use Patterns, Environmental Fate Assessment, Technical Summaries of Environmental Fate Studies, and Data Evaluation Records.

Alachlor is a herbicide registered for use on various crops, such as succulent and dry beans, corn crops, peanuts, grain sorghum, and soybeans. Alachlor is typically applied as a broadcast or band application on these crops, either preemergent or postemergent. At this time, the following data requirements for alachlor have not been satisfied:

- 163-1 Mobility/Leaching and Adsorption/Desorption: a Batch Equilibrium study for the Ethane Sulfonic Acid degradate of alachlor
- 201-1 Droplet Size Spectrum
- 202-2 Drift Field Evaluation

Drift from approved use sites for alachlor could affect nontarget plants, for which the chemical is highly toxic. Droplet Size Spectrum and Drift Field Evaluation studies are required because alachlor can be applied aerially. The registrant, Monsanto, belongs to the Spray Drift Task Force (SDTF). The data requirements is held in Reserve until the final report of the SDTF is evaluated.

EFGWB believes that although the additional information provided by these studies is not likely to change the overall qualitative environmental fate assessment of alachlor, the additional data will confirm the predicted behaviour of parent alachlor and its major degradates. The environmental fate data currently available for parent alachlor is sufficient to provide a fairly complete qualitative fate assessment of the parent compound.

Following review of acceptable, partially acceptable, and supplemental information on the environmental fate data base, alachlor appears to be moderately persistent and very mobile. Its degradates appear to be even more persistent and very mobile. Alachlor is stable to abiotic degradation processes (hydrolysis, photolysis in aqueous media, or photodegradation on soil). The major dissipation routes for alachlor appear to be microbially mediated degradation and leaching in the soils. Alachlor degrades at moderate rates ($t_{1/2}$ ~2-3 weeks) under aerobic conditions in soils, with four major degradates observed: DM-oxanilic acid, alachlor sulfinylacetic acid, alachlor sulfonic acid, and alachlor oxanilic acid. Since all four degradates have carboxylic or sulfonic acid functional groups, which render a negative (anionic) character to the molecules under normal environmental conditions, it is expected that the degradates would have a high mobility in soils. This has been confirmed by evaluation of the mobility of structurally similar degradates of propachlor. In the field, alachlor dissipates at moderate rates, with observed half-life of 11 days, which compares favorably with half-lives observed in the aerobic soil metabolism studies. Detections of alachlor were observed through 36- to 48-inch soil depth. The degradates alachlor sulfonic acid, and alachlor sulfinylacetic acid, were detected through 18- to 24-inch soil depth; alachlor oxanilic acid was detected through 36- to 48-inches; and alachlor DM-oxanilic acid was detected through 6- to 12-inches soil depth.

Ground water monitoring data collected, since 1991, by the USGS and the Acetochlor Registration Partnership (ARP) have found alachlor parent in two to eight percent ground-water wells sampled. Less than 1.5 percent (0.03-0.01%) of these wells were found to have alachlor residues above the MCL of 2.0 $\mu\text{g}/\text{L}$. These recent monitoring data are in agreement with earlier studies. The maximum and minimum alachlor concentrations were 15.89 $\mu\text{g}/\text{L}$ and 0.05 $\mu\text{g}/\text{L}$, respectively. Monitoring data collected by the USGS also indicates that in addition to alachlor, more than 40 percent of the wells sampled in midcontinental US were contaminated with alachlor ESA degradate and/or 16 percent were contaminated with the 2,6-diethylaniline degradate. There is no groundwater monitoring data on the other degradates. These results

agree with the environmental fate predictions, which indicate that these alachlor degradates are more mobile and persistent than the parent compound.

These recent studies reflect that current alachlor use may still result in ground water concentrations which exceed the LOC's for alachlor parent as detections have occurred which exceed the MCL of 2.0 $\mu\text{g}/\text{L}$. Since a much greater proportion of ground water wells are impacted by alachlor degradates, if an MCL or cancer risk level is established for alachlor-ESA at the same level as alachlor parent, levels of concern would be exceeded with greater frequency than for the parent compound only.

Alachlor can contaminate surface water at application via spray drift. Substantial fractions of applied alachlor could be available for runoff for several weeks post-application. Most of the alachlor runoff occurs via dissolution in runoff water (as opposed to adsorption to eroding soil). Studies show that alachlor concentrations generally peak in May to early June during the first runoff events following application and then decline rapidly to almost preapplication levels by July or August. The major degradates of alachlor may be available for runoff longer than alachlor and will probably runoff primarily by dissolution in runoff water. Alachlor ethane sulfonic acid (ESA) has frequently been detected in midwestern reservoirs and streams at concentrations much greater than alachlor. High concentrations of ESA in flowing water even in early Spring before alachlor application may reflect discharges from ground water.

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EXECUTIVE SUMMARY

Alachlor (2-chloro-2',6'-diethyl-N(methoxymethyl)acetanilide is a herbicide registered for use on succulent and dry beans; field, pop, and sweet corn; peanuts; grain sorghum; and soybeans. Alachlor is typically applied as a broadcast or band application on these crops either preemergent, or postemergent.

Following review of acceptable, partially acceptable, and supplemental information on the environmental fate data base, alachlor appears to be moderately persistent and very mobile. Its degradates appear to be even more persistent and mobile; however, more data is needed to confirm the fate of these degradates. Alachlor is stable to abiotic processes (hydrolysis, photolysis in aqueous media, or photodegradation on soil). The major dissipation routes for the chemical appear to be microbially mediated degradation and leaching into the soils. Alachlor is degraded at a moderate rate (t_{1/2} 2-3 weeks) in aerobic soils, with the following major degradates formed: DM-oxanilic acid, alachlor sulfinylacetic acid, alachlor sulfonic acid, and alachlor oxanilic acid. Since these degradates of alachlor have carboxylic or sulfonic acid functional groups, which render a negative (anionic) character to the molecule under normal environmental conditions, it is expected that the degradates have high mobility. This is confirmed by evaluation of data provided for structurally similar chemicals which are degradates of propachlor. The degradates alachlor sulfonic acid, and alachlor sulfinylacetic acid, were detected through 18- to 24-inch soil depth; alachlor oxanilic acid was detected through 36- to 48-inches; and alachlor DM-oxanilic acid was detected through 6- to 12-inches soil depths.

Based on column leaching studies, parent alachlor is mobile in a silt loam soil and very mobile in silt, sand, and loamy sand soils. Although there are no valid K_a constants for alachlor or any of its degradates, the available data indicate that the parent is very mobile and is not appreciably adsorbed to soils with low organic matter. In the field it also dissipates at a moderate rate, the observed half-life of 11 days compares favorably with the half-lives observed in various aerobic soil metabolism studies. In the field, alachlor was observed consistently at depths of 18- to 24- inches, with detections at up to 36- to 48-inch soil depth. The major route of degradation of alachlor is microbially mediated; therefore, as the chemical reaches deeper soil levels with decreased biological activity, the chemical becomes more persistent, increasing the likelihood of further leaching. It appears that the mobility of the chemical may increase as it reaches deeper soils which typically have lower organic matter content. The monitoring data supports the conclusion from laboratory studies that alachlor has a high potential for leaching into groundwater.

Ground-water monitoring data collected, since 1991, by the USGS and the Acetochlor Registration Partnership (ARP) have found alachlor parent in two to fifteen percent ground-water wells sampled. Less than 1.5 percent (0.03 to 1.1%) of these wells were found to have alachlor

residues above the MCL of 2.0 $\mu\text{g/L}$. These recent monitoring data are in agreement with earlier studies. The maximum and minimum alachlor concentrations were 15.89 $\mu\text{g/L}$ and 0.05 $\mu\text{g/L}$, respectively. Monitoring data collected by the USGS also indicates that in addition to alachlor, more than 40 percent of the wells sampled in midcontinental US were contaminated with alachlor-ESA degradate and/or 16 percent were contaminated with the 2,6-diethylalanine degradate. There is no ground water monitoring data on the other degradates. These results correspond with the fate data, which indicates that these alachlor degradates are more mobile and persistent than the parent compound.

These recent studies reflect that current alachlor use may still result in ground-water concentrations which exceed the LOCs for alachlor parent as detections have occurred which exceed the MCL of 2.0 $\mu\text{g/L}$. Since a much greater proportion of ground water wells are impacted by alachlor degradates, if an MCL or cancer risk level is established for alachlor-ESA at the same level as alachlor parent, levels-of-concern would be exceeded with greater frequency than for the parent compound only.

Alachlor can contaminate surface water at application via spray drift. Substantial fractions of applied alachlor could be available for runoff for several weeks post-application. Most of alachlor runoff will occur via dissolution in runoff water. Studies show that alachlor concentrations generally peak in May to early June during the first runoff events following application and then decline rapidly to almost preapplication levels by July or August. The major degradates of alachlor may be available for runoff longer than alachlor and will probably runoff primarily by dissolution in runoff water. ESA has frequently been detected in midwestern reservoirs and streams at concentrations much greater than alachlor. That indicates that it is mobile and probably much more persistent than alachlor in surface water. High concentrations of ESA in flowing water even in early Spring before alachlor application may reflect discharges from ground water.

GENERAL INFORMATION

Common Name

Alachlor

Chemical Name

2-chloro-2',6'-diethyl-N(methoxymethyl)acetanilide
2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide

CAS #

15972-60-8

Shaughnessi No

090501

Case Number

0063

Trade Names

Lasso, Ala-Sept, Microtech, Partner

Chemical Formula

C₁₄H₂₀NO₂Cl

Formulations

Emulsifiable Concentrate, Granular, Flowable Concentrate,
Microencapsulated, Water Dispersible Granules

Physical and Chemical Properties

Physical State: White or yellow crystalline solid

Melting Point: 40-41°C

Specific Gravity: 1.133

Solubility: 240 ppm in water @ 20°C

Soluble in ether, acetone, benzene, alcohol, and ethyl acetate.

Octanol/Water Partition Coefficient: 434¹

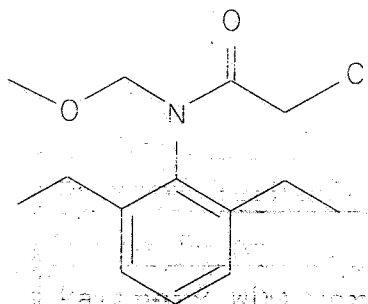
Molecular Weight: 269.77

Vapor Pressure: 2.2x10⁻⁵ mm Hg @24°C

MCL (Maximum Contaminant Level): 2 µg/L

-
1. One study (MRID# 00152209) reports partition coefficients of 33.0-37.1 in 20-120 ppm solutions.

Structure



USE PATTERN

Alachlor is herbicide registered for use on the following crops: succulent and dry beans; field, pop, and sweet corn; peanuts; grain sorghum; and soybeans. Alachlor is typically applied as a broadcast or band application on these crops, either preemergent, or postemergent.

The following is a table of end-use products:

Registrant: American Cyanamid Company

Product Name	EPA Reg. No.
Ala-Sept Herbicide	241-311
Ala-Sept® Herbicide	241-329

Registrant: Monsanto Company

Product Name	EPA Reg. No.
Lasso II Granular Herbicide	524-296
Lasso® Herbicide	524-314
Lariat®	524-329
Bronco® Herbicide	524-341
Micro-Tech®	524-344
Partner® WDG Herbicide	524-400
Partner® WDG Herbicide	524-403
MON-9850 Herbicide	524-408
Cannon Herbicide	524-412
Bullet® Herbicide	524-418
Freedom® Herbicide	524-422
Micro-Tech® C	524-458

The following table provides the maximum application rates of alachlor:

Crop	Maximum Application Rate (lb. ai/A)	Maximum Seasonal Rate (lb. ai/A)
beans, dry	3.0	3.0
beans, mung	2.0	2.0
beans, succulent (lima)	3.0	3.0
corn	6.0	6.0
peanuts	4.0	4.0
sorghum, grain	4.0	4.0
soybeans	3.0	3.0

ENVIRONMENTAL FATE ASSESSMENT FOR ALACHLOR

Based on both acceptable and supplemental studies, the following conclusions can be drawn:

Environmental Fate:

Alachlor is relatively stable to abiotic processes (hydrolysis, photolysis in aqueous media, or photodegradation on soil). The major dissipation routes for the chemical appear to be microbially mediated degradation and potential leaching. The degradation of alachlor is relatively moderate ($t_{1/2} \approx 2-3$ weeks) in aerobic soils, with several degradates observed, including DM-oxanilic acid, alachlor ethane sulfonic acid (ESA), alachlor oxanilic acid, and alachlor sulfinylacetic acid. Although there are no valid K_{ds} for alachlor or any of its degradates, the column-leaching study for the parent indicates that it is very mobile and is not appreciably adsorbed to soils with low organic matter. In the field, alachlor dissipated at moderate rates; the observed half-life of 11 days compares favorably with the half-lives observed in various aerobic soil metabolism studies. It appears that the persistence and mobility of the chemical may increase as it reaches deeper soil horizons which have lower organic matter content and decreased biological activity, thus increasing its potential to leach into groundwaters.

Alachlor was stable to hydrolysis in buffered solutions at pHs 3, 6, and 9. It was also relatively stable in natural lake water. The absorption spectrum of alachlor does not show any absorption at wavelengths above 290 nm and; therefore, it is not expected to undergo photolysis in water or on soil.

In soils, under aerobic soil metabolism conditions, alachlor appears to degrade at a moderate rate. Results of three different studies (one acceptable, and two supplemental), show that alachlor degrades with half-lives in the range of 6-18 days. The studies include use of different sites, different formulations, and different soil types. Several degradates were observed in the studies. The major degradates were DM-oxanilic acid, alachlor sulfonic acid (ESA), alachlor oxanilic acid, and alachlor sulfinylacetic acid. CO_2 is the ultimate degradate; it comprised 16.17-30.00% of the applied after 175 days in a valid study. Unextracted residues comprised $\leq 20.76\%$ of the applied at the same test interval.

Based upon both supplemental and acceptable studies, parent alachlor appears to be highly mobile in soils. In a column leaching study, in three of the soils with lower organic matter, alachlor was very mobile: silt, sand, and loamy sand soil (0.7-2.4% OM) columns, the leachates contained 40.9-96.9% of the applied radioactivity. In another soil with a higher organic matter content, the mobility was lower: silt loam soil (3.4% OM), the leachates had only $\leq 0.6\%$ of the applied radioactivity; however, even though the water was added at a

rate slower than the infiltration capacity, substantial downward movement was observed through the column, with a total of 53.5-57.7% of the applied radioactivity found in the soil segments from 9- to 18-cm.

In a Terrestrial Field Dissipation study conducted in Chico, California, alachlor, at 4 lb. a.i./A, dissipated with a half-life of 11 days from loam/sandy clay loam soil planted to corn. This half-life agrees with the observed half-lives in various aerobic soil metabolism studies. Most of the alachlor was found in the 0- to 18-inch soil layers, with occasional detections in the 18- to 24-, 24- to 36-, and 36- to 48-inch layers, indicating a large extent of leaching. The four major water-soluble metabolites of alachlor were also monitored in this study. The soil composition data in this study shows increasing percent of clay with soil depth (to a maximum of 65% clay in the 24- to 36-inch soil depth). This "clay pan" reduces the flow of water into deeper soils layers, decreasing the possibility of leaching of both parent alachlor and degradates.

The major degradates in the Aerobic Soil Metabolism studies were DM-oxanilic acid (with a maximum of 17.0% of the applied), alachlor sulfonic acid (ESA; 24.9% of the applied), alachlor oxanilic acid (22.4% of the applied), and alachlor sulfinylacetic acid (16.2% of the applied). Of these major "water-soluble" degradates, alachlor sulfinylacetic acid was not observed in the valid aerobic soil metabolism study. However, it was observed in a supplemental study. All four degradates appear to be more persistent than alachlor, since significant concentrations remained in the soils at the end of the aerobic soil metabolism studies. At this time, EFGWB does not have data on the mobility of these degradates; however, the registrant submitted data for two structurally similar degradates of propachlor (propachlor sulfonic acid and propachlor oxanilic acid). Since all the major water soluble degradates of alachlor have carboxylic or sulfonic acid functional groups, which render a negative (anionic) character to the molecule under normal environmental conditions, it is expected that the degradates will be highly mobile in soils. This is supported by the available mobility data for the degradates of propachlor (propachlor sulfonic acid and propachlor oxanilic acid); these degradates are structurally similar to the degradates of alachlor and their data has been used as surrogate data in lieu of the original alachlor metabolites. This is also supported by the results of the Chico Terrestrial Field Dissipation study. The oxanilic acid, the sulfinylacetic acid, and the sulfonic acid derivatives were detected in the 0- to 6- and 6- to 12- inch soil depths at average concentrations of 0.010-0.045 ppm. Detections were observed through 36- to 48- soil depth for the oxanilic acid, 18- to 24-inch soil depth for the sulfinylacetic acid and sulfonic acid, and 6- to 12-inch soil depth for the DM-oxanilic acid. Generally, detections occurred through 44-90 days posttreatment in the subsoils. Once moved to the subsoils, these degradates appear to persist. There are also confirmed detections of alachlor sulfonic acid in groundwaters. It could not be determined if other major degradates mentioned above were also monitored in this study.

HED does not have any information about the human toxicity of the four major degradates of alachlor. At this time, EFGWB is requiring aged Leaching, or preferentially Batch Equilibrium study for the alachlor ethane sulfonic acid degradate. This will provide adequate information to assess the potential of this degradate to leach into ground waters. In addition, a new Terrestrial Field Dissipation study is currently being evaluated.

Alachlor has high solubility (240 ppm), and a relatively low octanol/water partition coefficient (434). Chemicals with these characteristics are not expected to bioaccumulate in fish extensively.

Volatilization is not expected to be an important route of dissipation for alachlor. The chemical has relatively low vapor pressure (2.2×10^{-5} mm Hg). Furthermore, the amount of volatiles in the aerobic soil metabolism studies were negligible. Alachlor can be aerially applied; therefore, drift is a possible route of dissipation for alachlor. Since alachlor was found to be highly toxic to nontarget plants, EFGWB is requiring Droplet Size Spectrum (201-1) and Drift Field Evaluation (202-1) data for the chemical.

Groundwater quality:

Alachlor exhibits the properties and characteristics associated with chemicals found in groundwater. The chemical has a high water solubility and mobility in soils. Once the chemical reaches deeper soil layers, it is persistent. Studies of alachlor half-lives at different depths indicate that in a sandy loam and a silt loam soil, alachlor degradation half-lives increased to about 250 to 600 days within the first 5 feet. Alachlor has been found to leach in the field at soil depths of up to 36- to 48-inches. Considering the nature of the chemical (i.e., moderately persistent and very mobile in many soils), there is a strong possibility of movement to ground water, especially in vulnerable areas. This has been confirmed by the detections reported in the "Pesticides in Ground Water Database" which indicate that alachlor has had a significant impact on ground-water quality. Although a major degradate of alachlor, alachlor ethanesulfonic acid (ESA), is widespread in ground water in alachlor use areas, no health levels of concern have been established by EPA at this time.

The lifetime Health Advisory for alachlor has been established at 2 ppb. Alachlor has been placed as an unclassified carcinogen, with a 1×10^{-6} cancer risk level of 0.4 ppb. Alachlor was detected in ground water in 25 states at concentrations ranging from trace levels to 3000 ppb.

Ground-water monitoring data collected, since 1991, by the USGS and the Acetochlor Registration Partnership (ARP) have found alachlor parent in two to fifteen percent of ground-water wells sampled. Less than 1.5 percent (0.03 to 1.1%) of these wells were found to have

alachlor residues above the MCL of 2.0 $\mu\text{g/L}$. These recent monitoring data are in agreement with earlier studies (e.g., those reported in Pesticides in Ground Water Data Base, Hoheisel et al., 1992). The maximum and minimum alachlor concentrations were 15.89 $\mu\text{g/L}$ and 0.05 $\mu\text{g/L}$, respectively.

Monitoring data collected by the USGS (Kolpin and Goolsby, 1995; Kolpin et al., 1995; Kolpin et al., 1996) also indicates that in addition to alachlor, more than 40 percent of the wells sampled in midcontinental US were contaminated with alachlor-ESA degradate and/or 16 percent were contaminated with the alachlor 2,6-diethylalanine degradate. There is no ground water monitoring data on the other two major degradates (alachlor oxanilic acid and sulfinylacetic acid). These results correspond with the fate data, which indicates that these alachlor degradates are more mobile and persistent than the parent compound.

These recent studies reflect that current alachlor use may still result in ground-water concentrations which exceed the LOCs for alachlor parent as detections have occurred which exceed the MCL of 2.0 $\mu\text{g/L}$. Since a much greater proportion of ground water wells are impacted by alachlor degradates, if an MCL or cancer risk level is established for alachlor-ESA at the same level as alachlor parent, levels-of-concern would be much greater than for the parent compound only.

Similar chemicals, acetochlor, metolachlor, and propachlor have also been found in ground water. Approximately, the same percentage of wells have been found to be contaminated by propachlor (1.2%) as alachlor (1.8%), although many fewer wells have been analyzed for propachlor. Although number of wells sampled for metolachlor and alachlor are similar, there are approximately twice as many wells with detections of alachlor (1.8%) residues then metolachlor (0.96%). Acetochlor, with a maximum of 2.17 $\mu\text{g/L}$, was detected in eight wells (4.6%) of 173 in the registrant's ground-water monitoring study.

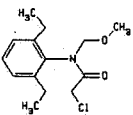
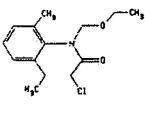
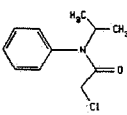
Surface Water Quality:

Alachlor can contaminate surface water at application via spray drift. Substantial fractions of applied alachlor could be available for runoff for several weeks post-application. The relatively low soil/water partitioning of alachlor indicates that most of alachlor runoff will occur via dissolution in runoff water (as opposed to adsorption to eroding soil). The persistence of alachlor in surface waters with high microbiological activities should be somewhat limited by its susceptibility to biodegradation. In waters with short hydrological residence times, its persistence will also be limited by flow out of the system. However, its resistance to abiotic hydrolysis and direct aqueous photolysis coupled with its low volatilization potential should make it more persistent in waters with low microbiological activities and long hydrological residence times. The relatively low soil/water partitioning of alachlor indicates that it

will readily partition into the water column and that at equilibrium, alachlor concentrations dissolved in sediment pore water will be comparable to or only slightly lower than concentrations on suspended and bottom sediment. Concentrations dissolved in the water column will be somewhat less than concentrations dissolved in sediment pore water.

The major degradates of alachlor in the aerobic soil metabolism study were DM-oxanilic acid, alachlor oxanilic acid, alachlor sulfinylacetic acid, and alachlor ethane sulfonic acid (ESA). The available data are inadequate to fully assess the persistence of those degradates. However, the results of terrestrial field dissipation studies indicate they are more persistent than alachlor. Available data indicates that such degradates are more mobile than alachlor. ESA has frequently been detected in midwestern reservoirs and streams at concentrations much greater than alachlor. That indicates that it is mobile and probably much more persistent than alachlor in surface water. High concentrations of ESA in flowing water even in early Spring before alachlor application may reflect discharges from ground water. The major degradates may be available for runoff longer than alachlor and will probably runoff primarily by dissolution in runoff water. They will probably readily partition into the water column and in addition to ESA, other degradates may also be more persistent in surface water than alachlor.

Comparison of the Environmental Fate Characteristics of Alachlor, Acetochlor and Propachlor:

Characteristic	Alachlor	Acetochlor	Propachlor
Chemical Structure			
Empirical Formula	C ₁₄ H ₂₀ NO ₂ Cl	C ₁₄ H ₂₀ NO ₂ Cl	C ₁₁ H ₁₄ NOCl
Molecular Weight	269.80	269.80	211.69
Vapor Pressure (mm Hg)	2.2x10 ⁻⁵	4.40x10 ⁻⁵	7.90x10 ⁻⁵
Log K _{OW}	2.64	3.0	2.30
Henry's Constant (atm m ³ /mol)	3.2x10 ⁻⁸	7.0x10 ⁻⁸	3.59x10 ⁻⁸
Solubility in water (ppm)	240	223	613
Hydrolysis	Stable at pH 3.0, 6.0, and 9.0	Stable at pH 5.0, 7.0, 9.0	Stable at pH 3.0, 6.0, 9.0
Photolysis in Water	Not expected to be important, based on UV absorption spectrum	Stable	Stable
Photolysis on soil	Not expected to be important, based on UV absorption spectrum	Stable	72 hours irradiated with sunlamp
Aerobic Soil Metabolism	2-3 weeks in three soil types	8-14 days one study reports 110 days	<3-<7 days
Anaerobic Soil Metabolism	Not available	230 days in sandy loam soil	

Mobility	Very mobile in loamy sand, silt and sand, mobile in silt loam in column leaching studies Estimated $K_{oc}=190$	K_{ads} variable between 0.81-7.5	Very mobile in loamy sand, sand, and silt, mobile in silt loam in column leaching studies $K_d=0.56$ in silt loam
Aged Mobility			propachlor oxanilic acid $K_{ads}=0.03-0.08$, propachlor sulfonic acid $K_{ads}=0.03-0.07$
Terrestrial Field Dissipation	11 days in Chico, CA	8-36 days at 5 sites in the US	<10 days half lives
Bioaccumulation in Fish	Not expected to be important, based on K_{ow} . In a supplemental study 5.8X in fillet, 11X in whole, and 15X in viscera	40X edible 780X non-edible 150X whole fish	

The above table shows that alachlor, acetochlor, and propachlor are not only structurally related, but they also exhibit similar fate properties. EFGWB has reviewed a number of batch equilibrium studies on acetochlor that were conducted on a number of soils. The studies show a range of K_d s from 0.81 to 7.5. Although no valid K_d s for alachlor are available at this time, they are expected to fall in the same range. EFGWB is not requiring additional mobility studies for alachlor at this time because a column leaching study has determined that alachlor is highly mobile. This is in agreement with ground water monitoring data which indicate that alachlor has had a significant impact on ground water quality.

TECHNICAL SUMMARIES OF ENVIRONMENTAL FATE STUDIES

THE FOLLOWING DATA SUMMARY IS DERIVED FROM STUDIES CONSIDERED ACCEPTABLE BY EFGWB

161-1 Hydrolysis

Suba, L.A., and D.A. Pearson. 1979. The environmental studies of alachlor. Report No. MSL-0860; Project No. 7824. (Accession Number 241135, GS0063-0036, MRID# 00134327)

[¹⁴C] Alachlor (carbonyl labeled), at 50 ppm, was relatively stable in sterile commercial pH 3, 6, and 9 buffer solutions, natural lake water, and deionized water that were incubated in the dark at 25°C for 30 days. [¹⁴C] Alachlor comprised 97.5-98.7% of the applied radioactivity in all test solutions, with no discernible pattern of decline. The degradate

2',6'-Diethyl-N-methoxymethyl acetanilide was ≤1.57% of the applied.

In nonsterile lake water, [¹⁴C] alachlor, at 2 ppm, degraded very slowly when incubated at an unspecified temperature for 30 days. After 30 days of treatment, alachlor was 88.8% of the applied concentration in the test solution. Five nonvolatile compounds were identified, at ≤2.7% of the applied.

162-1 Aerobic Soil Metabolism

Suba, L.A., and D.A. Pearson. 1979. The environmental studies of alachlor. Report No. MSL-0860; Project No. 7824. (Accession Number 241135, GS0063-0036, MRID# 00134327)

[¹⁴C] Alachlor, at 2 ppm, degraded with estimated half-lives of 2-3 weeks in silt, loamy sand, and silt loam soils incubated in the dark at 25°C and 75% of field moisture capacity for 175 days. In the silt loam soil, alachlor was 87.7% of the applied at the initiation of the study, 47.4% at 21 days, and 1.6% at 175 days. In the loamy sand, alachlor was 98.5% of the applied at 0 days, 52.4% at 14 days, and 2.5% at 175 days. In the silt soil, alachlor was 99.0% of the applied at day 0, 40.4% at day 14, and 0.7% at 175 days.

Four degradates were detected, with significant concentrations (≥ 10% of the applied):

2',6'-diethyloxanilic acid or [(2,6-diethylphenyl)amino]-2-oxoacetic acid (DM-oxanilic acid), which was a "water soluble" metabolite that increased gradually to a maximum of 5.3% of the applied at 50 days posttreatment in the silt loam, it decreased to 3.9% at 175 days. It increased to a maximum of 15.8-17.0% of the applied at 175 days posttreatment (last test interval) in the loamy sand and silt soils;

2',6'-diethyl-N-methoxymethyloxanilic acid or [2-(2,6-diethylphenyl) methoxymethyl) amino]-2-oxoacetic acid (alachlor

oxanilic acid), which was a "water soluble" metabolite, and was a maximum of 12.7-22.4% of the applied at 28-50 days posttreatment in all soil types and decreased to 2.9-13.4% of the applied at 175 days posttreatment;

2',6'-diethyl-N-methoxymethyl-2-sulfoacetanilide or [2-(2,6-diethylphenyl) (methoxymethyl)amino]-2-oxo-ethanesulfonic acid (alachlor sulfonic acid; ESA), which was a "water soluble" metabolite, which increased to a maximum of 24.9% of the applied at 50 days posttreatment in the silt loam, 16.9% of the applied at 175 days posttreatment in the loamy sand, and 16.0% of the applied at 21 days posttreatment in the silt soil. It decreased to 11.2-18.6% of the applied at 175 days posttreatment in the silt loam and silt soils.

2',6'-diethyl-2-hydroxy-N-methoxymethylacetanilide, which was the only major "methylene chloride soluble" degradate and increased to a maximum of 6.7-10.2% of the applied at 7-21 days posttreatment and decreased thereafter to $\leq 1.1\%$ of the applied at 175 days in all soil types.

Nine other degradates were also identified, at $\leq 10\%$ of the applied. After 175 days incubation, $^{14}\text{CO}_2$ was 16.17-30.00% of the applied. ^{14}C volatiles were $\leq 1.15\%$ of the applied, and unextracted ^{14}C residues totaled 19.25-20.76% of the applied.

163-1 Mobility, Leaching and Adsorption/Desorption

Suba, L.A., and D.A. Pearson. 1979. The environmental studies of alachlor. Report No. MSL-0860; Project No. 7824. (Accession Number 241135, GS0063-0036, MRID# 00134327)

The study is acceptable and partially satisfies the data requirement by providing information about the mobility of unaged alachlor.

To fully satisfy the data requirement, EFGWB requires that the registrant submit a Batch Equilibrium study conducted on the following major degradate observed in the aerobic soil metabolism studies: alachlor sulfonic acid (ESA).

^{14}C Alachlor (carbonyl labeled), at 3.5 lb a.i./A, was very mobile in 30 cm columns of silt, sand, and loamy sand soils that were leached with 20 inches of water. The leachate from the silt, sand, and loamy sand soil columns contained 40.9-96.9% of the applied radioactivity. This radioactivity was "mainly" alachlor. The following degradate was identified in these leachates, but not quantified:

2',6'-diethyl-N-methoxymethylacetanilide.

^{14}C Alachlor was mobile in columns of silt loam soil treated

under similar conditions. The leachate from the silt loam soil contained 0.5-0.6% of the applied radioactivity. The radioactivity remaining throughout the soil columns increased from 1.9-5.4% of the applied in the 0- to 2-cm segment, to 10.9-12.9% in the 10- to 14-cm segments, and declined to 0.1% in the 28- to 30-cm segment. The following compounds were detected in the leachates at 5-23% of the recovered radioactivity:

- 2',6'-diethyl-N-methoxymethylacetanilide,
- 2-chloro-2',6'-diethylacetanilide, and
- 2',6'-diethyl-N-methoxymethyl-2-methylthioacetanilide.

The analysis of selected soil extracts of all four soils indicated that the radioactivity was "mainly" alachlor. There was no clear correlation between the mobility of alachlor and the soil composition; however, it appears that higher organic matter contents favor adsorption of the chemical to the soil. A table summarizing the results obtained is as follows:

Soil type	% sand	% silt	% clay	% OM	%CEC	% found in leachates
sand	86.0	11.0	1.8	0.7	5.1	86.7-96.9
silt	4.6	84.2	10.0	1.2	10.4	78.2-82.2
loamy sand	75.1	17.8	4.8	2.4	11.3	40.9-43.4
silt loam	2.4	68.0	25.3	3.4	24.6	0.5-0.6

Even though this study had been found acceptable and provides information about the mobility of parent alachlor, the following details were noted since they could have had an effect on the observed results: In the study, the columns were packed using a wooden dowel; it is not reported if the columns were saturated prior to leaching. In addition, it is reported that the water "was added at a rate slower than the infiltration capacity of the soil." These conditions could have affected the observed leaching behavior. The parent alachlor could have leached even more under saturated flow conditions which would be the maximum flow rates.

164-1 Terrestrial Field Dissipation

- Kludas, R.S. 1991. PANAG Laboratory quality assurance and site information, terrestrial field dissipation of alachlor at two sites in California. (MRID# 42528004)
- Schlicher, M.A., and M.L. Schott. 1991. Terrestrial field dissipation of alachlor metabolites in Chico, California. (MRID# 42528002)
- Schneider, D.A. 1991. Storage stability of alachlor and alachlor metabolites in soil.

(MRID# 42528003)

●Schott, M.L., and M.A. Schlicher. 1990. Terrestrial field dissipation of alachlor at two sites in California. (MRID# 42528001)

The study conducted in Chico, California is acceptable and can be used to partially satisfy the Terrestrial Field Dissipation (164-1) data requirement. To fully satisfy the data requirement, a new study has been submitted. This study is currently under review.

Alachlor (Lasso 4-EC), applied once at 4 lb a.i./A, dissipated with an observed half-life of approximately 11 days from a plot of loam/sandy clay loam soil in Chico, California, that was planted to corn immediately after treatment. Alachlor was detected at a depth of 18- to 24-inches (at test intervals 7 and 14 days). In the 0- to 6-inch soil depth, alachlor averaged 0.781-0.798 ppm at 0-1 days posttreatment, 0.641 ppm at 7 days, and 0.350 ppm at 11 days. Two samples showed ≥ 0.124 ppm at 14 days, both in the 12- to 18- and 18- to 24-inch soil depths. In addition, five minor detections occurred at 36- to 48-inch soil depth at ≤ 0.016 ppm at 11-18 days. The rainfall plus irrigation totaled 6 inches through 18 days posttreatment.

The following degradates were detected in the soil:

[2-(2,6-diethylphenyl)methoxymethyl)amino]-2-oxoacetic acid (alachlor oxanilic acid), which was detected through 44 days posttreatment in the 0- to 6- and 6- to 12-inch soil depths, at averages ≤ 0.047 ppm. There were 15 individual detections through 44 days in the 0- to 6-inch soil depth and 10 individual detections through 21 days in the 6- to 12-inch soil depth. There were also sporadic detections in the soil depths up to 36- to 48-inch at ≤ 0.023 ppm. These included 5 detections in the 12- to 18-inch soil depth (14-120 days), 2 detections in the 18- to 24-inch soil depth (18 and 180 days), and 2 detections in the 36- to 48-inch soil depth (44 days);

[N-(2,6-diethylphenyl)-N-(methoxymethyl)-2-amino-2-oxo-ethyl]sulfinylacetic acid (alachlor sulfinylacetic acid), which was detected from 7 through 44 days posttreatment in the 0- to 6- and 6- to 12-inch soil depths, at averages ≤ 0.039 ppm. There were 13 individual detections through 44 days in the 0- to 6-inch soil depth and 11 individual detections through 44 days in the 6- to 12-inch soil depth. There were 5 sporadic detections in the soil depths up to 18- to 24-inch at ≤ 0.020 ppm at 14 and 18 days;

[2-(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxo-ethanesulfonic acid (alachlor sulfonic acid; ESA), which was detected from 1 through 44 days posttreatment in the 0- to 6- and 6- to 12-inch soil depths, at averages ≤ 0.027 ppm. There were 14 individual detections through 44 days in the 0- to 6-inch soil depth, 10 individual detections through 90 days in the 6- to 12-inch soil depth; and 4 detections each in the 12- to 18- and the 18- to 24-soil depths (at ≤ 0.022 ppm) at 14-78 days. Two sporadic

detections at ≤ 0.011 ppm were observed in the 24- to 36-inch soil depth, at 18, and 44 days.

[(2,6-diethylphenyl)amino]-2-oxoacetic acid (DM-oxanilic acid), with only sporadic detections at ≤ 0.061 ppm through 90 days after treatment, in the 0- to 6- and 6- to 12-inches depths. In addition, there was 1 detection each in the 12- to 18- and the 18- to 24-inch soil depths (90 and 44 days), and 2 detections in the 24- to 36-inch soil depth (14 and 78 days).

Three samples were tested per test intervals. The lowest limit at which the method was validated for each metabolite is 0.01 ppm. Detections below this level were reported as < 0.01 ppm.

Examination of the soil composition data of the Chico plot shows an increasing percent of clay with soil depth (to a maximum of 65% clay in the 24- to 36-inch soil depth). This "clay pan" reduces the flow of water into deeper soil layers, decreasing the possibility of leaching of both parent alachlor and its degradates. It is possible that under conditions that would favor the flow of water into deeper soil layers, further leaching would have been detected.

The study conducted at Madera, California was considered invalid since the alachlor concentrations found at all levels in the soils was ≤ 0.1 ppm. The application rate was 4 lb a.i./A. The concentrations were too low to assess the dissipation of alachlor. The study authors did not explain the low residue levels found. The registrant should try to provide the reason for the low recoveries observed in this study.

THE FOLLOWING DATA SUMMARY IS DERIVED FROM STUDIES CONSIDERED SUPPLEMENTAL BY EFGWB

162-1 Aerobic Soil Metabolism

Banduhn, M.C., and C.L. Livingston 1981. Comparative environmental fate and crop uptake studies of encapsulated and unencapsulated alachlor. (MRID# 00101531)

[^{14}C] Alachlor (phenyl ring-labeled), at 2 ppm, degraded with half-lives of 6-12 days in silt, loamy sand, and silt loam soils incubated in the dark at 25°C for 62 days. The soils were also treated with [^{14}C] alachlor encapsulated in a polyurea polymer. The rate of degradation is similar for the encapsulated [^{14}C] alachlor, with half-lives of 8-11 days.

Four major degradates were identified in the soil. These degradates were observed in all three soil types at 62 days; however, testing at various test intervals (monitoring through time) was performed only for the silt soil:

2',6'-diethyloxanilic acid or [(2,6-diethylphenyl)amino]-2-oxoacetic acid (DM-oxanilic acid), which comprised a maximum of

14.4% of the applied radioactivity in the silt soil at 62 days posttreatment. It comprised 2.9-7.3% of the applied at 62 days in the loamy sand and the silt loam;

2',6'-diethyl-N-methoxymethyl-oxanilic acid or [2-(2,6-diethylphenyl) methoxymethyl)amino]-2-oxoacetic acid (alachlor oxanilic acid), which comprised a maximum of 9.7-10.0% of the applied radioactivity in the silt soil at 20 days posttreatment. It decreased to \leq 3.7% of the applied at 62 days in the loamy sand and the silt loam;

(N-methoxymethyl-N-(2,6-diethylphenyl)-2-amino-2-oxoethyl) sulfinylacetic acid or [N-(2,6-diethylphenyl)-N-(methoxymethyl)-2-amino-2-oxo-ethyl] sulfinylacetic acid (alachlor sulfinylacetic acid), which comprised 15.9-16.2% of the applied radioactivity in the silt loam soil at 62 days posttreatment. It was a maximum of 12.6-13.3% of the applied in the silt soil at 20 days posttreatment, decreasing to \leq 9.7% at 62 days; and

2',6'-diethyl-N-methoxymethyl-2-sulfoacetanilide or [2-(2,6-diethylphenyl) (methoxymethyl)amino]-2-oxo-ethanesulfonic acid (alachlor sulfonic acid), which comprised a maximum of 6.5% of the applied radioactivity in the silt soil at 30 days posttreatment and \leq 5.1% at 62 days. It was 2.7-4.1% of the applied in the loamy sand and silt loam at 62 days.

This study provides supplemental information about the rate of degradation of alachlor and the identity of alachlor degradates under aerobic conditions. This study is deficient because up to 22.3% of the applied radioactivity was not characterized.

Sutherland, M.L.; Curtis, T.G.; Darlington, W.A.; et. al. (1972) Final Report on Lasso and the Environment; Part 6: Soil Dissipation of Lasso: Agricultural Research Report No. 264 (MRID# 00023014).

[¹⁴C] Alachlor, at 4 ppm, degraded appreciably, with a half-life of <18 days in sandy loam, silt loam, and silty clay loam nonsterile soils incubated at \leq 32°C in a greenhouse. [¹⁴C] Alachlor was \leq 0.5 ppm in all three soil types 72 days after treatment. The degradate 2-chloro-2',6'-diethylacetanilide was detected at all sampling intervals at \leq 0.8 ppm, with no definite pattern of formation or decline.

This study was conducted in a greenhouse. It provides supplemental information about the aerobic soil metabolism of alachlor by identifying one alachlor degradate. The study, however, is deficient when evaluated according to current guidelines because it was conducted in the greenhouse and material balances could not be confirmed.

Three different studies conducted on various soil types have shown similar degradation rates, ranging from 6 to \leq 18 days. The degradation products were identified only in two of the studies, one of which is

acceptable and the other is supplemental. Three of the four major degradates were observed in both studies. The compound

(N-methoxymethyl-N-(2,6-diethylphenyl)-2-amino-2-oxoethyl) sulfinylacetic acid,

which was up to 15.9% of the applied in one supplemental study (MRID# 00101531), was not observed in the acceptable study (MRID# 00134327). All major metabolites were monitored in the available Terrestrial Field Dissipation study.

163-1 Mobility, Leaching and Adsorption/Desorption

●Weidner, C.W. (1974) Degradation in Groundwater and Mobility of Herbicides. Master's thesis, Univ. of Nebraska, Dept. of Agronomy (MRID# 00027139)

●Lavy, T.L. (1974) Mobility and Deactivation of Herbicides in Soil-Water Systems (MRID# 00027140)

In a leaching study, [¹⁴C] alachlor residues leached through the columns, with ~96%, ~51%, and 0% of the recovered having leached through a gravelly sand, sandy loam, and a silty clay loam soil columns, respectively. The soil columns measured 20 cm (8 inches, recommended 30 cm), and were leached with 10 inches of water (recommended 20 inches).

Based on Adsorption/Desorption experiments [¹⁴C] alachlor, at 1-10 ppm, appears to have a high mobility in three soil types. The K_d values, calculated based on [¹⁴C] instead of actual alachlor concentrations, decreased with a decrease in soil organic matter. The mean K_d values were 3.74 for a silty clay loam, 2.88 for sandy loam, and 0.80 for a gravelly sand.

These studies were considered scientifically valid in the original DER's. However, EFGWB now believes that these studies only provide supplemental information because the soil column length used was 20 cm (Subdivision N Guidelines recommend a soil column length of 30 cm), and the columns were leached with 10 inches of water (recommended 20 inches). The studies provide supplemental information by indicating a high level of leaching in sand, sandy loam, and silty clay loam.

Guth, J.A. (1975) CGA-24705 Leaching Model Study with the Herbicide CGA-24705 in Four Standard Soils (MRID# 00078301)

Based on column leaching studies, alachlor, at 5 kg ai/A, appears to be very mobile in a Lakeland sand, with 59% of the applied alachlor recovered from the leachates of a 30 cm soil column, eluted with 8 inches (20 cm) of water. Alachlor was less mobile in other soils tested, with maximum leaching depths of 18 cm, 10 cm, and 4 cm in Collenbey sand, silt loam, and sandy clay loam columns, respectively. The level of leaching appeared to be related to the percent organic matter, with lower leaching of the soils associated with higher organic matter.

This study was also considered scientifically valid. However, the study does not meet the Subdivision N Guidelines because the columns

were eluted with only 8 inches of water (recommended 20 inches). In addition, no attempts were made to measure possible degradates or total residues. Therefore, EFGWB is concerned about the validity of the study since insufficient elution water was applied to demonstrate the mobility of alachlor in the soils. This study is now deemed supplemental and gives an indication of the level of leaching in sandy clay loam, silt loam, and sand.

Suba, L.A., and D.A. Pearson. 1979. The environmental studies of alachlor. (Accession Number 241135, GS0063-0036, MRID# 00134327)

Based on column leaching studies, aged (30 days) uncharacterized [¹⁴C] residues of alachlor were mobile in 30 cm columns with sandy loam soil, treated at 3.5 lb a.i./A, and leached with 20 inches of water. The radioactivity recovered in the leachate totaled 29.1-31.5% of the applied. Approximately 10 compounds were isolated from the leachates at ≤0.7% of the applied radioactivity. The major compound found in the soil samples was [¹⁴C] alachlor.

This portion of the study (aged) is not acceptable because the soil was aged for 30 days, which may be a period of time considerably longer than one half-life. The aerobic soil metabolism studies show estimated half-lives between 2 and 3 weeks. After the aging period, and prior to leaching, the soil was not characterized; therefore, it is not possible to determine if sufficient parent compound remained at the time of leaching, and what was the ratio of the degradates formed.

EFGWB considers that the mobility of aged alachlor and its metabolites has not been adequately assessed by the studies submitted. Based upon the studies available and the structural features of the chemicals, it appears that alachlor degradates, as well as parent alachlor, have a high potential to leach. To confirm the leaching behavior of the alachlor degradate alachlor ethane sulfonic acid (ESA), EFGWB requires that the registrant submit a Batch Equilibrium study.

THE FOLLOWING DATA REQUIREMENTS WERE WAIVED BY EFGWB

161-2 Photolysis in Water

This data requirement was waived, based on the UV absorption spectrum of alachlor in water.

A UV absorption spectrum of alachlor in water (MRID# 00023012), shows no absorption at wavelengths above 290 nm. In accordance with the current Branch Policy, EFGWB would concur with waivers for the Photolysis in Water (161-2) data requirement if the electronic spectrum of the chemical does not show significant absorption between 290 and 800 nm. Since photodegradation can only take place when there is an overlap between absorption regions of the spectrum of the chemical and the irradiation spectrum of the light source.

EFGWB will require no additional information on the Photolysis in

Water for the following reason:

- (1). The absorption spectrum of the chemical in water does not show significant absorption at wavelengths above 290 nm.

161-3 Photodegradation on Soil

EFGWB will require no additional data to support the Photodegradation on Soil data requirement at this time. Although EFGWB does not have any information about the photolytic behavior of any of the major degradates of alachlor at this time, the branch will not require a new study for the following reason:

- (1). The absorption spectrum of the chemical in water does not show significant absorption at wavelengths above 290 nm.

163-1 Mobility of Alachlor Degradates

Based on the submitted data, EFGWB agrees that no additional data are necessary for **DM-oxanilic acid, alachlor sulfinyl acetic acid, and alachlor oxanilic acid**. Because **alachlor sulfonic acid (ESA)** is a widely detected degrade in water resources, EFGWB recommends that the registrant be requested to **submit a mobility/batch equilibrium study** on this degrade as confirmatory data.

The registrant indicated that the alachlor metabolites have also been identified in crop metabolism studies, presumably because of plant uptake from the soils. They are included in the tolerance expressions for alachlor, which are currently expressed as alachlor and its metabolites (currently range from 0.05-3 ppm). The alachlor ethane sulfonic acid (ESA) had been detected in well waters in Indiana at levels between 0.007 and 0.017 ppm, with one sample at 0.023 ppm. The registrant found similar results from a study in Wisconsin (not further specified). EFGWB could not confirm these numbers.

Toxicology and mutagenicity studies appear to suggest that alachlor ethane sulfonic acid poses no toxicological concerns. According to the registrant in a 91-day study in which rats were provided drinking water containing ESA, a 200 ppm NOEL has been established. This value could not be confirmed with HED. The registrant believes that the other three metabolites of alachlor (alachlor oxanilic acid, alachlor DM-oxanilic acid, and alachlor sulfinyl acetic acid) are similar to alachlor ethane sulfonic acid because all of them result from metabolic changes to alachlor by replacement of the chlorine atom with an acidic functional group.

Additionally, the registrant indicated that all these degradates are anions at physiological pH, which make them not readily bioavailable, and facilitating excretion. The registrant cited three studies (MRID# 43525201, 43525202, and 43525203) containing information about acute toxicity of the alachlor degradates. According to the registrant "none of the three" (degradates) "showed serious acute

toxicological properties." The registrant also argued that these four degradates have little herbicidal activity. These facts could not be confirmed by EFGWB.

EEB confirmed that the oxanilic and sulfonic acids of alachlor show little if any toxicity to daphnia and trout LC50 levels were >100 ppm for these species.

Mobility of Alachlor Degradates:

The registrant, Monsanto, submitted Adsorption/Desorption studies for two propachlor soil metabolites. Propachlor is structurally related to alachlor. The registrant proposed to use this mobility data on propachlor degradates as surrogate data for alachlor degradates. Results obtained for the propachlor degradates are as follows:

Mobility and Adsorption/Desorption for Propachlor Oxanilic Acid:

This study is acceptable and can be used to partially satisfy the data requirement for the chemical propachlor. Based on batch equilibrium studies, propachlor oxanilic acid was determined to be very mobile in loamy sand, sandy loam, loam, and silty clay loam soil: solution slurries. Freundlich K_{ads} values ranged from 0.03 to 0.08. The following table summarizes results obtained in the study.

	K_{ads}	K_{oc}	K_{des}	K_{oc}
loamy sand	0.03	8	4.48	1120
sandy loam	0.04	2	15.86	886
loam	0.08	7	4.34	391
silty clay loam	0.06	10	20.91	3428

Mobility and Adsorption/Desorption for Propachlor Sulfonic Acid:

This study is acceptable and can be used to partially satisfy the data requirement for propachlor. Based on batch equilibrium studies, propachlor sulfonic acid was determined to be very mobile in sand, sandy loam, loam, and silty clay loam soil: solution slurries. Freundlich K_{ads} values ranged from 0.03 to 0.07. The following table summarizes results obtained in the study.

	K_{ads}	K_{oc}	K_{des}	K_{oc}
sand	0.03	7	1.33	317
sandy loam	0.06	6	6.24	624
loam	0.05	5	1.73	156

silty clay loam	0.07	3	1.23	47
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Mobility of alachlor vs. propachlor:

An examination of the adsorption coefficients of alachlor and propachlor show that both are very mobile. Generally, propachlor is more mobile than alachlor (except in the Ray silt). It is observed that %CEC and %OM are good predictors of alachlor mobility (higher mobility when %CEC is lower, and higher mobility when %OM is lower), while this trend is only general for propachlor. EFGWB believes, however, that for both alachlor and propachlor degradates, the negative charges play an important role in predicting the mobility.

Mobility Characteristics for Alachlor

Soil type	% sand	% silt	% clay	% OM	% CEC	% found in leachates
sand	86.0	11.0	1.8	0.7	5.1	86.7-96.9
silt	4.6	84.2	10.0	1.2	10.4	78.2-82.2
loamy sand	75.1	17.8	4.8	2.4	11.3	40.9-43.4
silt loam	2.4	68.0	25.3	3.4	24.6	0.5-0.6

Mobility Characteristics for Propachlor

Soil type	% sand	% silt	% clay	% OM	% CEC	Ave. % found in leachates
Lintonia sand	86.0	11.0	1.8	0.7	5.1	83.1-95.9
Ray silt	4.6	84.2	10.0	1.2	10.4	40.6-71.4
Spinks loamy sand	75.1	17.8	4.8	2.4	11.3	71.0-84.0
Drummer silt loam	2.4	68.8	25.3	3.4	24.6	2.9-7.9

EFGWB Comments:

EFGWB believes that the mobility requirements for alachlor

metabolites have been partially satisfied with the submission of mobility data of the propachlor degradates: propachlor oxanilic acid and propachlor sulfonic acid. EFGWB believes that these degradates show substantial structural similarity to alachlor degradates, they can be used to preliminarily assess the mobility of alachlor degradates. EFGWB believes that the available data confirms the premise that all the four major degradates of alachlor are very mobile under normal environmental conditions.

To better assess the mobility of alachlor ethane sulfonic acid (ESA), which is the most detected degradate in ground water, EFGWB recommends that the registrant be requested to submit a batch equilibrium study on this degradate. This data would confirm the Branch conclusion and result in a realistic K_d for this degradate.

163-2,3 Laboratory and Field Volatility

This data requirement was waived, based on the relatively low vapor pressure and levels of volatiles in the aerobic soil metabolism study.

Alachlor has a vapor pressure of 2.2×10^{-5} mm Hg @24°C². EFGWB believes that this value is relatively low and that volatility may not be an important route of dissipation for alachlor. In addition, the acceptable Aerobic Soil Metabolism study (MRID# 00134327) showed the presence of small amounts of [¹⁴C] volatiles ($\leq 1.15\%$ of the applied after 175 days of incubation). In a supplemental aerobic soil metabolism study (MRID# 00101531) [¹⁴C] volatiles were $\leq 4.84\%$ of the applied after 40-62 days. This suggests that volatilization is not a significant route of dissipation for alachlor.

165-4 Bioaccumulation in Fish

This data requirement was waived. Alachlor has a relatively high water solubility (240 ppm), and a low octanol/water partition coefficient of 434 (one study reports as low as 35). Chemicals with these physico/chemical properties are not expected to bioaccumulate substantially in fish. Therefore, EFGWB will require no additional information on the Bioaccumulation in Fish (165-4) data requirement for alachlor at this time.

THE FOLLOWING DATA REQUIREMENTS ARE RESERVED BY EFGWB AT THIS TIME

201-1/-2 Spray Drift/ Droplet Spectrum and Field Evaluation

Alachlor was found to be highly toxic to nontarget plants. Since the chemical can be applied aerially, the data requirement has been

². MRID# 00152209, Brightwell, B.B., and Rueppel, M.L., 1976, "Lasso^R and Ramrod^R: Physical Properties and Their Relationship to the Environment."

imposed (Memorandum from S. Syslo to Amy S. Rispin dated May 14, 1991). The results would be used to assess the extent of exposure to nontarget plants. This data requirement is not satisfied. It will be held in Reserve, pending the evaluation of the work of the industry's Spray Drift Task Force (SDTF), of which Monsanto, the registrant of alachlor, is a member.

GROUND WATER ASSESSMENT OF ALACHLOR

Detections of alachlor degradates in ground water are important because ground water may represent an important means of exposure. Four major degradates have been identified for alachlor: alachlor DM oxanilic acid, alachlor sulfinylacetic, alachlor sulfonic acid (ESA), and alachlor oxanilic acid. As noted above, the four degradates are more persistent than the parent compound. The Branch previously requested batch equilibrium studies on the degradates to assess their mobility. The registrant has proposed using adsorption data from two propachlor degradates as surrogate data for the alachlor degradates. The Branch has accepted this for two degradates, but will still require the determination of the mobility for the alachlor-ESA degradate.

Ground-water monitoring data collected, since 1991, by the USGS and the Acetochlor Registration Partnership (ARP) have found alachlor parent in two to fifteen percent ground-water wells sampled. Less than 1.5 percent (0.03 to 1.1%) of these wells were found to have alachlor residues above the MCL of 2.0 $\mu\text{g/L}$. These recent monitoring data are in agreement with earlier studies (e.g., those reported in Pesticides in Ground Water Data Base, Hoheisel et al., 1992). The maximum and minimum alachlor concentrations were 15.89 $\mu\text{g/L}$ and 0.05 $\mu\text{g/L}$, respectively.

Monitoring data collected by the USGS (Kolpin and Goolsby, 1995; Kolpin et al., 1995; Kolpin et al., 1996) also indicates that in addition to alachlor, more than 40 percent of the wells sampled in midcontinental US were contaminated with alachlor-ESA degradate and/or 16 percent were contaminated with the alachlor 2,6-diethylalanine degradate. There is no ground water monitoring data on the other degradates. These results correspond with the fate data, which indicates that these alachlor degradates are more mobile and persistent than the parent compound.

These recent studies reflect that current alachlor use may still result in ground-water concentrations which exceed the LOCs for alachlor parent as detections have occurred which exceed the MCL of 2.0 $\mu\text{g/L}$. Since a much greater proportion of ground water wells are impacted by alachlor degradates, if an MCL or cancer risk level is established for alachlor-ESA at the same level as alachlor parent, levels-of-concern would much greater than for the parent compound only.

Similar chemicals, acetochlor, metolachlor, and propachlor have also found in ground water. Approximately, the same percentage of wells have been found to be contaminated by propachlor (1.2%) as alachlor (1.8%), although many fewer wells have been analyzed for propachlor. Although number of wells sampled for metolachlor and alachlor are similar, there are approximately twice as many wells with detections of alachlor (1.8%) residues then metolachlor (0.96%). Acetochlor, with a maximum of 2.17 $\mu\text{g/L}$, was detected in eight wells (4.6%) of 173 in the registrant's ground-water monitoring study.

CURRENT AND RECENT GROUND WATER MONITORING DATA

Because of their similarity (both chemically and/or use) with alachlor, monitoring results for alachlor and the herbicides acetochlor, atrazine, metolachlor, and propachlor are presented and discussed. These monitoring data are summarized in Tables 2 and 3 (attached).

USGS Midcontinent Ground Water Monitoring Studies:

In 1991, the USGS sampled 303 wells from a reconnaissance well monitoring network in near-surface aquifers distributed across 12 midwestern states (Kolpin et al., 1995) (Table 1). These wells were distributed geographically and hydrogeologically by state, aquifer class (unconsolidated vs bedrock), and relative depth. At least 25% of the land within a 3.2 km radius of the well was in corn or soybean production during the 1990 growing season. One hundred wells were resampled during 1992 by selecting wells using a stratified random design based upon State and aquifer class.

The USGS found that five of the six most frequently detected pesticide compounds detected in ground water of 12 midwestern states were pesticide metabolites (Kolpin et al., 1995). Kolpin et al. (1996) also demonstrated that as the analytical reporting limits are decreased, there is an increase in the differences in frequencies of detections. Alachlor-ESA is reported almost 10 times more frequently than parent alachlor at the 0.05 $\mu\text{g/L}$ level.

Alachlor was detected in 6 wells (2%) out of 303 wells in 1991 and 5 wells (5%) out of 100 wells in 1992 in near-surface aquifers in 12 midwestern states (Kolpin et al., 1995). The alachlor reporting limits were 0.05 and 0.002 $\mu\text{g/L}$ for 1991 and 1992, respectively. The degradate alachlor-ESA was the most frequently detected compound detected in 1992 found in 33 wells (45%) of 73 wells for which the degradates were analyzed, with a reporting limit of 0.10 $\mu\text{g/L}$. In the same study, metolachlor was detected in 12 wells (4%) out of 303 in 1991; and, 11 wells (11%) out of 100 in 1992, with the same reporting limits as stated for alachlor. None of the metolachlor detections exceeded existing drinking water standards.

Additional samples were collected in 1993 (110 wells) and 1994 (38 wells) from unconsolidated aquifers (Kolpin et al., 1996). Alachlor was detected in 10 wells (3.3%) out of 303 wells. Alachlor parent was found in 5.9% of the 153 wells for which metabolites were analyzed for. The maximum alachlor concentration detected was 4.27 $\mu\text{g/L}$, with a reporting limit of 0.05 $\mu\text{g/L}$. The alachlor degradate ESA was found in 70 wells (45.3%) of 153 wells analyzed for degradates. Maximum concentration for ESA was 8.63 $\mu\text{g/L}$, with a 0.10 $\mu\text{g/L}$ reporting limit. A second alachlor degradate, 2,6-diethylalanine, was also detected in 15 wells (16%) of 94 wells analyzed. The maximum concentration was 0.02 $\mu\text{g/L}$ with a reporting limit of 0.003 $\mu\text{g/L}$. Atrazine degradates deisopropylatrazine (10% of 303 well; maximum

concentration of 1.17 $\mu\text{g/L}$) and deethylatrazine (22.8% of 303 wells; maximum concentration 2.20 $\mu\text{g/L}$) were also detected. Metolachlor was also detected at levels above 0.05 $\mu\text{g/L}$ in 8 wells (2.7%) out of 300 (Goolsby et al., 1995).

Acetochlor State Ground Water Monitoring Program (ARP-GWMP):

As a requirement for the registration of acetochlor, the two acetochlor registrants are conducting a ground-water monitoring program in seven major use states. Analytes are parent (no degradates) alachlor, acetochlor, and atrazine, dimethenamid, and metolachlor (only the first three were reported). Ground-water samples are collected monthly from 175 wells located in corn producing areas. The annual report from the first year of monitoring (only for acetochlor, alachlor, and atrazine) has been submitted by the registrants which includes a computer disk with a number of EXCEL data files (DP Barcode D225973). The report covers the 13-month period, beginning in December 1994 and ending December 1995. Only parent compounds were reported. The limits of detection and quantification for all analytes are 0.03 $\mu\text{g/L}$ and 0.05 $\mu\text{g/L}$, respectively.

The text of the annual report indicates that alachlor was detected in 45 samples (2.6%) out of 1720 (27 of which were greater than 0.1 $\mu\text{g/L}$). Acetochlor residues were detected in 25 of 1720 samples (15 of which were greater than 0.1 $\mu\text{g/L}$) and atrazine was detected in 651 samples (427 were greater than 0.1 $\mu\text{g/L}$) out of 1720.

The computer disk contained EXCEL files with 13 months (December 1994 to December 1995) worth of data from 180 wells (includes replacement wells as does Tables 16, 17, and 18 in the annual report) was also submitted by the ARP. [The numbers of wells and samples do not correspond exactly to the narrative (e.g., 175 well vs 180 wells, number of samples 1720 vs 2340 as values less than 0.05 $\mu\text{g/L}$ are not differentiated from no data). Results for the three pesticides are summarized in Table 2. Fourteen of the wells had alachlor detects greater than limit of quantification (LOQ - 0.05 $\mu\text{g/L}$), six had detections of acetochlor above the LOQ, and 75 had atrazine detections above the LOQ. Twenty-seven wells had alachlor detections above the limit of detection (LOD) of 0.03 $\mu\text{g/L}$, 93 wells had detections of atrazine above the LOD, and eight wells has acetochlor levels above the LOD.

Approximately 36 percent of the alachlor detections exceeded the MCL (2.0 $\mu\text{g/L}$) and 54 percent exceeded a one-in-million cancer risk level of 0.4 $\mu\text{g/L}$. Approximately 75 percent of the detections exceeded 0.11 $\mu\text{g/L}$ for alachlor, acetochlor and atrazine. These current studies should reflect the impact to ground water from the current alachlor use and demonstrates that LOC's are still exceeded for alachlor parent.

Two of the fourteen wells with alachlor detections had detections on more than one sampling date. One of these wells was located in Illinois. The first detection of alachlor for this well (May 1995) was

also the greatest (13.05 $\mu\text{g/L}$) concentration. Alachlor concentrations in this well declined with time, reaching 0.42 $\mu\text{g/L}$ by December 1995. The second well with multiple detections occurred in Kansas. The first detection (0.3 $\mu\text{g/L}$) was reported in March 1995. The highest detections for this well occurred in May 1995 (14.17 $\mu\text{g/L}$) and June (15.89 $\mu\text{g/L}$) and generally declined, reaching 3.64 $\mu\text{g/L}$ by December 1995. Seven other wells also had alachlor detections in March 1995.

Other Considerations

Since the degradation of alachlor appears to be much slower in aquifers than in the soil root zone and since alachlor-ESA is reported more frequently than alachlor in ground water, Kolpin et al. (1996) concluded that the degradation of alachlor occurs prior to being transported to the aquifer. They theorize that if alachlor degradation occurred after reaching the aquifer, the frequency of detections of alachlor and alachlor-ESA would be more similar. They also report that alachlor-ESA appears to be persistent in shallow aquifers, because 90 percent of the wells having alachlor-ESA concentrations exceeding 0.10 $\mu\text{g/L}$ remained at that level during all subsequent samples (1-year time interval). If an MCL or cancer risk level is established for alachlor-ESA at the same level as alachlor parent and because of the much higher percentages of wells having degradate detections, the concern for the population being exposed to levels of alachlor exceeding levels of concern is much greater than for the parent compound only.

Irrigation appears to increase the probability of contaminating ground water. The frequency of herbicide detection (35%) with irrigation within a radius of 3.2 km was greater than the frequency of herbicide detections (19%) without irrigation (Kolpin and Goolsby, 1995). They also suggest that ground water recharge from streamflow may also be a source of herbicide contamination.

Health Effects and Drinking Water Levels

The cancer grouping of alachlor has been recently redesignated as a **known carcinogen**, but the specific classification has not been determined. Alachlor was previously classified as a B2 carcinogen, with a one-in-a-million cancer risk level of 0.4 $\mu\text{g/L}$. The MCL has been set as 2.0 $\mu\text{g/L}$, by the Office of Water. There have been no health advisories or cancer risk levels established for any of the degradates.

Table 1. Summary of wells with detection of alachlor parent by study.

Study ¹	Number of Wells			Percent			
	Sampled	With Detects			All	<MCL	≥MCL
		All	<MCL	≥MCL			
PGWDB	25933	467	368	99	1.8	1.4	0.4
NPS	1300	1	0	1	<0.1	0	<0.1
NAWWS	1430	28	26	2	2.0	1.8	<0.1
USGS (1991)	303	6	5	1	2.0	1.7	0.3
USGS (1992)	100	5	-	-	5.0	-	-
ARP-GWMP	173	27	25	2	15.6	14.5	1.2

¹ PGWDB - Pesticides in Ground Water Data Base, NPS - National Survey of Pesticides in Drinking Water Wells, NAWWS - National Alachlor Water Well Study, USGS - U.S. Geological Survey Midcontinent Study, ARP-GWMP - Acetochlor Registration Partnership Ground Water Monitoring Program.

Table 2. Detections and concentrations (in $\mu\text{g/L}$) of acetochlor, alachlor, and atrazine in study conducted by the registrants of acetochlor (DP Barcode D225973) and submitted as EXCEL data files.

Statistic	Acetochlor	Alachlor	Atrazine
Number of Samples with Detects $>0.10 \mu\text{g/L}$ (% of samples)	18 (0.8)	27 (1.2)	529 (22.6)
Number of Wells (% of 180)	8 (4.4%)	14 (7.8%)	74 (41.1%)
Number of Samples ¹	2322	2311	1811
Mean	0.39	3.38	0.75
Standard Deviation	0.52	4.89	5.88
Minimum	0.06	0.05	0.05
1st Quartile	0.11	0.12	0.11
Median	0.25	0.73	0.24
3rd Quartile	0.38	5.06	0.56
Maximum	2.17	15.89	131.53 ²

¹ It was not possible to determine whether data identified as missing were no data or below detection limit.

² The next highest value for atrazine was $30.03 \mu\text{g/L}$.

Table 3. Summary of alachlor, metolachlor, and propachlor ground water monitoring data from the Pesticides in Ground Water Data Base (Hoheisel et al., 1992).

Detection Information	Alachlor	Metolachlor	Propachlor
	Number of Wells (Percent of Wells)		
MCL ($\mu\text{g/L}$)	2	70	90
\geq MCL	99 (0.38)	3 (0.01)	0 (0.00)
$<$ MCL	368 (1.42)	210 (0.94)	33 (1.21)
Total Detections	467 (1.80)	213 (0.96)	33 (1.21)
Total Sampled	25993	22255	2718
Number States with detections	25	20	5
Number of States with monitoring	35	29	11
Range of concentrations ($\mu\text{g/L}$)	trace to 3000	0.001 to 157	0.02 to 3.5

Detections of Alachlor in Ground Water

Pesticides in Ground Water Database

There is a substantial database of evidence that alachlor leaches through soil to ground water. The 1992 Pesticides in Ground Water Database (PGWDB) reports that alachlor was detected in 25 states, in 467 wells of 25993 sampled (Table 3). Of these wells with detections, 99 had concentrations above the MCL of 2 ppb. A review of studies with alachlor detections in the PGWDB (see attached table) indicates that many of the detections above the 2 $\mu\text{g/L}$ MCL likely result from point-source mechanisms. Detections over the MCL in the PGWDB that appear to have resulted from nonpoint-source mechanisms do not generally contain the high levels of alachlor that are seen in the point-source detections. PGWDB data seem to indicate that the median concentration of detections not likely due to point-sources is around 0.2 ppb. Monsanto's NAWWS study data, which are not included in the PGWDB, are discussed below.

Alachlor, metolachlor and propachlor in the pesticides in ground water

The PGWDB (Hoheisel et al., 1992) reported propachlor detections in 33 (1.2%) wells [in five states] out of 2718 wells sampled in eleven states (Table 3). The concentrations ranged from 0.02 to 3.5 $\mu\text{g/L}$, thus the maximum concentration exceeded the MCL of alachlor (2 $\mu\text{g/L}$), but not for propachlor (90 $\mu\text{g/L}$) (Table 3).

The PGWDB (Hoheisel et al., 1992) also summarizes a number of studies which included metolachlor (Table 3). Metolachlor has been analyzed for in 29 states and detected in 20 states. Detections occurred in 213 (1%) wells out of 22,255 wells sampled, with concentrations ranging from 0.02 to 157 $\mu\text{g/L}$. Three exceeded the lifetime Health Advisory (LHA) of 70 $\mu\text{g/L}$ for metolachlor, but typically appear to less than 10 $\mu\text{g/L}$.

National Pesticide Survey (NPS)

The EPA National Pesticide Survey (NPS) was conducted to provide a statistical estimate of the frequency and concentration of pesticide contamination of drinking water wells. From April 1988 to February 1990, EPA collected water samples and well information from over 1300 community water systems and rural domestic drinking water wells. Based on these data, EPA estimated that alachlor contamination occurred in 0.03% of drinking water wells nationwide. The detection limit for alachlor in the NPS was quite high (0.5 ppb); this probably resulted in an estimate of exposure well below actual contamination rates. Degradates of alachlor were not analyzed in the study, and therefore are not included in the estimates.

Monsanto NAWWS Study

A "snapshot" of exposure to alachlor via ground water used for drinking is provided in Monsanto's large-scale retrospective monitoring study, the "National Alachlor Well Water Survey" (NAWWS). The NAWWS study was a statistically designed one-time sampling of rural private drinking-water wells within the alachlor use area, with some bias to high-sales areas, and higher vulnerability counties. Estimates of hydrologic vulnerability were drawn from statistical data. Because this was a study of possible exposure, and not of actual alachlor leaching potential, the study did not include consideration of field-scale soil conditions or hydrology. In addition, Monsanto did not analyse ground water samples for alachlor degradates.

Of the 1430 wells sampled in the NAWWS, 28 wells contained detections; two of these wells exceeded the MCL. Based on these data, Monsanto estimated that approximately 10 percent of the wells with alachlor detections in ground water are over 1 ppb, and about 20 percent of the wells with alachlor detections in ground water were estimated to have greater than 0.4 ppb. An estimated 7 percent of the wells with alachlor detections in ground water are over 1.5 µg/L. Based on the results of the NAWWS, Monsanto estimated that 1200 wells (0.02% of an estimated 6 million private rural wells in the alachlor use area) had levels of alachlor greater than or equal to 2.0 ppb.

USGS Near-Surface Aquifer Study

The United States Geologic Survey examined the contamination of near-surface aquifers by selected pesticides and metabolites in the corn- and soybean-producing region of the Midwest in 1991 and 1992. Wells included in the program were no deeper than 15 meters. In sampling during the spring and summer of 1991, alachlor was detected in 2.0% of 303 wells sampled, with a maximum concentration detected of 1.05 ppb. The following year, 100 wells were resampled for an expanded suite of pesticides and degradates. Alachlor was detected in 5.0% of the wells sampled, with a maximum concentration of 0.99 ppb.

Included in the expanded sampling menu were the alachlor degradates 2,6-diethylaniline and ESA. With a detection rate of 47.0%, ESA was the most widely detected chemical in the study. Degradate 2,6-diethylaniline was detected in 16% of the samples, a rate greater than for any chemical except for ESA and atrazine and its metabolites. The highest concentration of ESA detected was 4.95 ppb; the highest for 2,6-diethylaniline was 0.022 ppb. The report concluded that "these results show how the affects (sic) of pesticides on the quality of water resources can be substantially underestimated without data on metabolites."

State of Wisconsin Monitoring Program

The State of Wisconsin currently has a major monitoring program underway focused on ESA, a metabolite of alachlor. Over 1000 wells

have been screened in vulnerable areas. Official results will be available in August 1994.

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State of Florida Monitoring Program

Prior to the ban on the use of alachlor in the State of Florida, Monsanto conducted a groundwater monitoring study for alachlor in conjunction with the Florida Department of Agriculture and Consumer Services (FDACS). The main focus of this study was the monitoring of alachlor in open hole bedrock wells in Jackson County, in northernmost Florida. After confirmed detections of alachlor in 13 of 100 wells, the sampling was expanded to include 310 wells in 10 counties.

Alachlor was detected in 189 samples from 46 of 310 wells during sampling from July 1989 to May 1990. This does not include multiple detections in samples split between the State and Monsanto. Concentrations ranged from trace levels to 135 ppb in a well in Levy county. This high concentration is significantly above the **one-day, 10-kg. child health advisory for the chemical** of 100 ppb. Concentrations in that particular well above the 100 ppb level were still detected after 18 months. This pattern was reflected in many wells with lesser concentrations above the MCL. The Florida Department of Agriculture and Consumer Services stated that although Jackson County is underlain by karstified limestone, these conditions were not found throughout the 10 county area where there were significant detections. The State of Florida does not consider the detections in this study to be the result of point-source contamination.

State of New York- Suffolk County

From 1990 to 1992, the Suffolk County Department of Health Services (SCDHS) analyzed private wells near a nursery for alachlor residues. Alachlor was detected in 14 of the 63 wells, 11 of which had at least one detection equal to or greater than the 2.0 ppb MCL. The highest concentration detected was 49 ppb. Subsequent sampling of 92 wells near nurseries resulted in a single detection of alachlor at 0.6 ppb. The SCDHS did not find any evidence to suspect point source contamination.

State of North Carolina- UNC-Asheville

Researchers from the University of North Carolina-Asheville Environmental Quality Institute (EQI) conducted a three-year study (1989-1991) to increase the information available concerning the presence and persistence of pesticides in the ground water of a four-county area in eastern North Carolina. Alachlor was among the 8 chemicals investigated. In sampling over the three summers, alachlor was detected in 13 of 139 samples, with a range of concentrations from 0.30 to 18.30 ppb. Five of the detections were above the 2.0 ppb MCL. Two of three wells studied in a seven-month resampling program

maintained levels of alachlor above the MCL over 3 sampling efforts. The third had a concentration of 0.30 that declined below the detection level of 0.17 ppb.

The EQI study concluded that the detections of alachlor encountered in the study appeared to be the result of normal agricultural use.

SURFACE WATER ASSESMENT OF ALACHLOR

Alachlor can contaminate surface water at application via spray drift. Substantial fractions of applied alachlor could be available for runoff for several weeks post-application (aerobic soil metabolism half-life of 2-3 weeks; terrestrial field dissipation half-life of 11, 15, and 18 days). The relatively low soil/water partitioning of alachlor (SCS/ARS database K_{oc} of 170; K_d values of 3.74, 2.88, and 0.88) indicates that most of alachlor runoff will occur via dissolution in runoff water (as opposed to adsorption to eroding soil).

The persistence of alachlor in surface waters with high microbiological activities should be somewhat limited by its susceptibility to biodegradation. In waters with short hydrological residence times, its persistence will also be limited by flow out of the system. However, its resistance to abiotic hydrolysis and direct aqueous photolysis coupled with its low volatilization potential (Henry's Law constant = 3.2×10^{-8} atm*m³/mol) should make it more persistent in waters with low microbiological activities and long hydrological residence times. The relatively low soil/water partitioning of alachlor indicates that it will readily partition into the water column and that at equilibrium, alachlor concentrations dissolved in sediment pore water will be comparable to or only slightly lower than concentrations on suspended and bottom sediment. Concentrations dissolved in the water column will be somewhat less than concentrations dissolved in sediment pore water.

The major degradates of alachlor in the aerobic soil metabolism study were DM-oxanilic acid, alachlor oxanilic acid, alachlor sulfinylacetic acid, and alachlor ethane sulfonic acid (ESA). The available data are inadequate to fully assess the mobility and persistence of those degradates. However, the results of terrestrial field dissipation studies indicate they are more persistent than alachlor and their anionic properties indicate they are probably more mobile. ESA has frequently been detected in midwestern reservoirs and streams at concentrations much greater than alachlor. That indicates that it is mobile and probably much more persistent than alachlor in surface water. High concentrations of ESA in flowing water even in early Spring before alachlor application may reflect discharges from ground water.

The major degradates may be available for runoff longer than alachlor and will probably runoff primarily by dissolution in runoff water. They will probably readily partition into the water column and in addition to ESA, other degradates may also be more persistent in surface water than alachlor.

The octanol/water partition coefficient of alachlor and the mobility of alachlor and its major degradates suggests that their bioaccumulation potential is low.

Acetochlor Registration Partnership 1995 Data on Alachlor

The most recent and extensive data on alachlor in surface water was supplied to OPP by the Acetochlor Registration Partnership. It has been analyzed and summarized in detail by R. David Jones in a May 24, 1996 memo from him to EEB. Samples were collected at 175 sites in the following 12 states: DE, IL, IN, IA, KS, MD, MN, MO, NE, OH, PA, and WI. Samples were collected once every two weeks from April through September 1995. Two additional samples were collected at each site, one in the Fall and the other in the Winter. Unfiltered samples were analyzed for total alachlor.

Cumulative exceedence curves for peak, annual maximum 96-day time weighted mean, and annual time weighted mean alachlor concentrations over the 175 sites are provided in Figures 1, 2, and 3 (from the D. Jones memo), respectively. The maximum peak, annual maximum 96-day, and annual time weighted mean alachlor concentrations were 4, 0.8, and 0.4 ug/L, respectively. The 90th percentile (upper 10th percentile site) peak, annual maximum 96-day, and annual time weighted mean alachlor concentrations were approximately 0.37, 0.17, and 0.1 ug/L, respectively.

USGS 1989, 1994, and 1995 Midwestern Stream Reconnaissance Studies

Since the data submitted by the Acetochlor Registration Partnership was for samples collected at set intervals once every two weeks, it is probable that the data are generally substantially lower than peak alachlor concentrations associated with post-application runoff events. Such peak alachlor concentrations are probably more closely represented by post-application data collected by the USGS in reconnaissance studies conducted on numerous midwestern streams. The USGS (Goolsby/Thurman 1991; Goolsby 1995; Goolsby 1996) conducted reconnaissance surveys of numerous midwestern streams in 1989, 1994, and 1995 to determine post-application, and in some cases pre-application and Fall concentrations of various herbicides including alachlor. Pre-application samples collected in 1989 and 1994 and Fall samples collected in 1989 had alachlor concentrations much less than 1 ug/L and generally below the detection limit of 0.05 ug/L.

Cumulative frequency curves for post-application alachlor concentrations are given for 129 streams in 1989 and 50 of those streams in 1994 and 1995 in Figures 4, 5, and 6, respectively. Since post-application samples were generally collected during the first major runoff event after application, the concentrations in those samples should generally approximately represent peak alachlor concentrations. The maximum post-application alachlor concentrations for 1989, 1994, and 1995 were 51.3, 10.1, and 19.9 ug/L, respectively. The 90th percentile (upper 10th percentile) post-application alachlor concentrations for 1989, 1994, and 1995 were 12, 6.5, and 2.0 ug/L, respectively. The substantially lower concentrations in 1994/1995 than in 1989 may reflect reported decreases in alachlor use.

In 1989, a pre-application sample, a post-application sample, and a Fall sample were collected from 48 of the sites. A cumulative frequency curve for annual time weighted mean concentrations (TWMCs) based on 3 samples from each site is given in Figure 7. The maximum and 90th percentile (upper 10th percentile) annual TWMCs were 11.6 and 3.4 ug/L, respectively. Annual TWMCs based on 4 quarterly samples (as specified to determine compliance with the Safe Drinking Water Act) probably would have been somewhat lower but not more than 25% lower.

In 1994 and 1995, samples were analyzed for ESA as well as alachlor. Consequently, ESA is also included on the post-application cumulative frequency curves for alachlor for 1994 (Figure 5) and 1995 (Figure 6). As can be seen, ESA concentrations are much higher than alachlor. That also appears to be true in early Spring even before alachlor application as can be seen from Figure 8.

Because of the much greater concentrations in surface water of ESA than alachlor even in samples collected in the early spring prior to alachlor application, EFGWB strongly recommends that both HED and EEB accurately determine the toxicity of ESA so that a risk assessment can be performed for it.

USGS 1991-1992 Study of 8 River Locations Mississippi River Basin

The USGS (Coupe et. al. 1995) sampled 8 locations on rivers within the Mississippi Basin from April 1991 through March-September 1992 (depending on location) and analyzed the samples for numerous insecticides and herbicides including alachlor. Samples were collected twice per week from May 6 to July 15 1991, once per every two weeks from November 1991 to February 1992, and once per week at other times. The samples were filtered (0.7 μ) and analyzed for dissolved alachlor. Alachlor 1991 peaks and 1991 annual time weighted mean concentrations are listed in Table 1 and are plotted as cumulative frequency curves in Figures 9 and 10. The maximum peak and 1991 annual time weighted mean concentrations over the 8 sites were 3.6 μ g/L and 0.43 μ g/L, respectively (both in the Platte River at Louisville NE).

Concentration versus time plots for the three sites with the highest 1991 alachlor concentrations are provided in Figures 11, 12, and 13. The shapes of the plots are similar to those commonly seen for atrazine and cyanazine, but the peak concentrations are lower. Pre-application concentrations of less than 0.1 ppb in early Spring rapidly increase to several ppb during post-application runoff events in May and June, then rapid decline to background levels by mid-late summer. The White River at Hazelton IN site was the only one of those three sites at which sampling was performed far enough into 1992 to give a second set of alachlor peaks (1992) in addition to the 1991 set. It can be seen from Figure 11 that alachlor concentrations in 1992 were lower than in 1991 at that site.

USGS 1992 Midwestern Reservoir Reconnaissance Study

The USGS (Goolsby et. al. 1993) sampled each of 76 midwestern reservoirs four times during 1992 and analyzed them for various herbicide degradates and herbicides including alachlor and ESA. Alachlor was detected above a detection limit of 0.05 $\mu\text{g/L}$ in 36%, 48%, 26% and 16% of the samples collected in late April to mid-May, late June to early July, late August to early September and late October to early November, respectively. ESA was detected more frequently (72, 79, 77, and 64%) and at higher concentrations than alachlor. A box plot showing the distributions of alachlor and ESA over the 76 reservoirs is given in Figure 14 which is a copy of Figure 4 in the Goolsby et. al. 1993 article. The highest alachlor and ESA concentrations were for samples collected in June or July of 1992. The maximum and 95th percentile alachlor concentrations for June-July over the 76 reservoirs appear to be between 5 and 10 $\mu\text{g/L}$. The maximum and 95th percentile ESA concentrations for June-July appear to be between 10 and 20 $\mu\text{g/L}$. After June-July, alachlor concentration appear to decrease more substantially than ESA concentrations. We are currently attempting to obtain the raw data necessary to perform further analyses.

Missouri River Public Water Supplies Association 1990 Study

The Missouri River Public Water Supplies Association (MRPWSA) sampled the raw water of 8 surface water supplies within the Missouri River Basin. Samples were collected daily May-July 1990. The peak and mean concentrations are listed in Table 2 and are plotted as cumulative frequency curves in Figures 15 and 16. The maximum peak and May-July mean concentrations were 14.9 and 0.47 $\mu\text{g/L}$, respectively (both at Kansas City MO). However, the second highest peak and May-July mean concentrations were 2.9 and 0.29 $\mu\text{g/L}$, respectively. The annual mean concentrations should be greater than 25% of the May-July means.

State of Illinois 1986-1988 Study

The State of Illinois (Moyer and Cross 1990) collected 4-7 samples per year from each of 30 flowing surface water sites during 1986-1988 and analyzed the unfiltered samples for numerous pesticides including alachlor. The peak concentration for each year, the annual TWMC for each year, and the 3 year 1986-1988 TWMC are listed for each of the 30 sites in Table 3. Cumulative exceedence curves for the peak concentrations, annual TWMCs and the three year TWMCs are given in Figures 17, 18, and 19, respectively. The maximum alachlor peaks over the 30 sites were 5.6, 8.5, and 18 $\mu\text{g/L}$ for 1986, 1987, and 1988, respectively. The maximum alachlor annual TWMCs over the 30 sites were 0.65, 0.76, and 2.0 $\mu\text{g/L}$ for 1986, 1987, and 1988, respectively. The maximum three year TWMC over the 30 sites was 0.81 $\mu\text{g/L}$.

The State of Illinois (Taylor 1994) recently summarized pesticide data for surface water samples collected from 34 stations from 10/1/85 through 2/15/94. Thirty of the stations were the same ones discussed

in the Moyer and Cross 1990 document, but the Taylor summary represents a update to February 1992. A total of 1278 samples were analyzed for alachlor at a detection limit of 0.05 ug/L. Apparently assuming non-detects were equal to the detection limit, Illinois reported maximum, 95th percentile, 90th percentile, and mean total (unfiltered sample) alachlor concentrations over the 34 sites and 9 years of 18 ug/L, 0.90 ug/L, 0.32 ug/L, and 0.065 ug/L, respectively.

Monsanto 1986 Finished Surface Water Supply Study:

In 1986, Monsanto sampled 30 finished surface water supply systems approximately weekly from April through August or September (Smith etal, 1987) and analyzed the samples for 5 herbicides including principally alachlor. The community water systems sampled represented 4 combinations of Lasso (alachlor) use and average soil susceptibility to runoff (high use/high runoff, low use/high runoff, high use/low runoff, low use/low runoff). The susceptibility to runoff was estimated from the weighted average of hydrological classifications (A, B, C, D) of soils within the drainage area. Of the 30 community water systems sampled, 13, 2, and 15 were classified as using sources which drain areas with high, intermediate, and low susceptibility to runoff, respectively.

The total (unfiltered samples) alachlor peak and 1986 annual TWMCs for the 30 systems (along with population served) are listed in Table 4 and are plotted as cumulative exceedence curves in Figures 20 and 21. The maximum and 90th percentile (upper 10th percentile) peak alachlor concentrations over the 30 systems were 9.5 and approximately 6.0 ug/L, respectively. The maximum and 90th percentile (upper 10th percentile) alachlor annual TWMCs over the 30 systems were 1.1 and approximately 0.73 ug/L, respectively.

Monsanto 1985 Finished Surface Water Supply Study:

In 1985, Monsanto had sampled 30 finished surface water supply systems different from the ones sampled in 1986. They also sampled raw water. Samples were collected approximately weekly from April 1995 through August or September 1995 (Lauer etal, 1986) and analyzed only for alachlor. The community water systems sampled represented areas of high, medium and low alachlor use.

The total (unfiltered samples) alachlor peak and 1985 annual TWMCs for the 30 systems (along with population served) are listed in Table 5 and are plotted as cumulative exceedence curves in Figures 22 and 23. The maximum and 90th percentile (upper 10th percentile) peak alachlor concentrations in finished water over the 30 systems were 12 and approximately 4.2 ug/L, respectively. The maximum and 90th percentile (upper 10th percentile) alachlor annual TWMCs over the 30 systems were 1.5 and approximately 0.62 ug/L, respectively.

Due to the low soil/water partitioning of alachlor, the primary treatment processes employed by most surface water supply systems are

not expected to be effective in removing it. Figures 22 and 23 support that by showing that the alachlor concentrations in raw water were comparable to those in finished water.

USGS 1984-1985 Study on the Cedar River Basin IA

The USGS (Squillace and Engberg 1988) collected samples at 6 locations within the Cedar River Basin (5 along the Cedar River and one along the Shell Rock River. Samples were collected approximately monthly from May 1984 through September 1985 at the Floyd and Cedar Falls sampling locations, and from May 1984 through November 1985 at the other 4 locations.

Two sets of samples were collected. One set was centrifuged for the determination of the dissolved concentrations of herbicides. "Total recoverable" herbicide concentrations consisting of both the extractable adsorbed and dissolved herbicides were determined in the sample set not centrifuged.

Dissolved alachlor peak concentrations and annual TWMCs are plotted as cumulative frequency curves over the 12 site-years (6 sites each over 2 years) in Figures 24 and 25. Two year TWMCs are plotted over the 6 sites in Figure 26. The maximum peak and annual TWMC concentrations over the 12 site-years were 23 and 3.3 ug/L, respectively. The next highest peak and annual TWMCs were 21 and 1.9 ug/L, respectively. The maximum two year TWMC over the 6 sites was 1.7 ug/L.

Baker 1982-1985 Study on Ohio Tributaries to Lake Erie

Baker collected samples at various times including several times per week from mid-April to mid-August from 8 Ohio tributaries to Lake Erie during 1982-1985 and analyzed them for many pesticides including alachlor. Alachlor Peak and 4/15-8/15 TWMCs concentrations were reported. They are listed in Table 6 and plotted as cumulative exceedence curves over 30 site-years (8 sites over 3 years plus six of the sites over another year) in Figure 27 and over 24 site-years (8 sites over 3 years) in Figure 28.

The maximum and 90th percentile (upper 10th percentile) peak alachlor concentrations over the 30 site-years are 76 and 32 ug/L, respectively. The maximum and 90th percentile (upper 10th percentile) 4/15-8/15 TWMCs over the 24 site-years are 3.3 and 2.7 ug/L, respectively. Annual TWMCs should be greater than 33% of the 4/15-8/15 TWMCs.

Possible Concerns Over Alachlor and ESA in Surface Water:

According to EEB, the potential risks to fish and aquatic invertebrates posed by alachlor in surface water are low. Potential risks to aquatic plants posed by alachlor are currently being assessed by EEB. The potential risks of ESA to fish, aquatic invertebrates and

aquatic plants has not been well characterized.

In analyzing surface water concentration data, the EFED considers the frequency that annual averages exceed the drinking water MCL (for alachlor, 2 $\mu\text{g}/\text{l}$), and the frequency that peak concentrations exceed the MCL by a factor of 4 or more: Compliance with the Safe Drinking Water Act is based on comparison of the MCL to an arithmetic average of four quarterly measurements. Consideration of 4 times the MCL (4MCL) is of interest because if one or more of four measurements exceeds 4MCL, then the average of the measurements exceeds the MCL.

Most of our original concern over alachlor in drinking water was due to individual alachlor measurements frequently exceeding 4MCL. The frequency of exceedences of 4MCL was greatest in the 1989 USGS reconnaissance study in which samples were collected during major runoff events following application, and in the study by Baker (1988), in which samples were apparently collected at least 3 times a week and not time composited. They were less frequent in the 1994 and 1995 USGS reconnaissance studies (which were also designed to capture peak concentrations) possibly due to decreases in alachlor use.

With the exception of 2 site-years in the 1984-1994 USGS study of the Cedar River Basin and one site-year in the 1986-1988 Illinois EPA study, none of the annual TWMCs for alachlor exceeded the MCL of 2 $\mu\text{g}/\text{L}$. This includes the 1985-1986 Monsanto studies of drinking water supplies and the recent 1995 Acetochlor Registration Partnership study of 175 sites over 12 states. In that study, the maximum annual TWMC was only 0.4 $\mu\text{g}/\text{L}$. Although the study used set sampling intervals that may often miss peak concentrations associated with runoff events, the once every two weeks sampling from April through September and the Fall and Winter samples (a total of 14/site) is much more than the 4 quarterly samples required under the SDWA. Again, the relatively low alachlor concentrations compared to some earlier studies may reflect substantial decreases in alachlor use.

RECOMMENDATIONS

Environmental Fate of Alachlor:

At this time, the following environmental fate data requirements for alachlor have not been satisfied:

163-1 Mobility Leaching and Adsorption/Desorption: a Batch Equilibrium study for Alachlor Sulfonic Acid degradate of alachlor

201-1/202-2 Droplet Size Spectrum and Drift Field Evaluation

1. The Mobility/Leaching and Adsorption/Desorption (163-1) data requirement was partially satisfied by the following study reviewed in this package: Suban and Pearson, 1979, MRID# 00134327. No additional data on the mobility of unaged alachlor is required.

Alachlor has four major degradates with carboxylic or sulfonic acid functional groups. These functional groups render a negative (anionic) character to the molecules under normal environmental conditions. EFGWB believes that these degradates would have a high mobility in soils. This has been confirmed with data for structurally similar degradates of propachlor: propachlor sulfonic acid and propachlor oxanilic acid. To confirm the leaching behavior of alachlor degradate alachlor ethane sulfonic acid, a widely observed degradate of alachlor in ground waters, EFGWB requires that the registrant submit a Batch Equilibrium study for alachlor ethane sulfonic acid (ESA).

2. Alachlor was found to be highly toxic to nontarget plants. Since the chemical can be applied aerially, the Droplet Size Spectrum (201-1) and Drift Field Evaluation (202-2) data requirements have been imposed (Memorandum from S. Syslo to Amy S. Rispin dated May 14, 1991). The results would be used to assess the extent of exposure to nontarget plants. This data requirements are not satisfied. They will be held in Reserve, pending the evaluation of the work of the industry's Spray Drift Task Force (SDTF), of which Monsanto, the registrant of alachlor, is a member.

Alachlor in Groundwaters:

Because alachlor residues continue to exceed LOC's for ground water, EFGWB recommends the following previous recommendations (as suggested by K. J. Costello) be considered (note some of which have been agreed to by the registrant):

In its response to EFGWB's 1994 draft Reregistration Eligibility Document (RED) for alachlor, Monsanto accepted several ground-water

mitigation recommendations:

1. Monsanto agreed to classify alachlor as a Restricted Use Pesticide (RUP) for ground-water concerns;
2. Monsanto will change its alachlor labels to include an up-to-date ground-water advisory;
3. Monsanto has volunteered to add language calling for a 50-foot setback of mixing and loading activities from wells, rivers or lakes unless such activity is protected by an impervious pad, as well as other unspecified language meant to "avoid accidental water contamination."

The RED chapter should be edited to reflect Monsanto's agreement to RUP classification for alachlor for ground-water concerns, and to a revised ground-water label advisory, setbacks for mixing and loading areas, and other language meant to help avoid accidental water contamination.

1. The ground-water advisory located on the alachlor label under "Environmental Hazards" must be revised to read:

"This chemical is known to leach through soil into ground water under certain conditions as a result of registered uses. Use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground-water contamination."

2. The recommendation that alachlor be included in State Management Plans should not be removed from the final RED chapter.
3. The registrant must submit to EPA for validation analytical methods for alachlor degradates (including ESA) with minimum detection limits of equal to or less than 0.1 $\mu\text{g/L}$ in water, and make standards available for parent alachlor and its degradates through the Pesticide Repository.
4. The Registrant should identify mitigation measures to manage the use of alachlor in such a way that ground-water resources will not be contaminated as a result of normal uses. Ground-water monitoring studies should be developed and conducted to determine if these measures are effective at preventing any further contamination of ground-water resources from alachlor use. The Registrant should discuss mitigation measures and study design with EFGWB prior to initiation of these studies.

This could include such things as identifying areas that are vulnerable to ground-water contamination by alachlor, and recommend label restrictions that prevent this from occurring. Such restrictions should address:

- 1) rate reduction

- 2) use restrictions
- 3) soil or geographic restrictions (for example, karst areas).

Because the detection of alachlor is related to irrigation, more efficient irrigation methods could be adapted to reduce pesticide leaching. The registrant notes that there have been major alachlor use reductions, but recent monitoring studies still indicate that about the same percentage of wells exceed drinking water criteria as earlier studies.

5. EFGWB believes that it is appropriate to maintain the recommendation for mitigation triggers for alachlor, tied to results of sampling being done in the acetochlor ARP ground water monitoring program or some other monitoring program. Monsanto should enter into negotiations with SRRD to set the details of such triggers, such as number of detections and concentration levels. This recommendation is somewhat dependant upon the outcome of the new cancer risk determination and assessment of the toxicity or cancer potential for the degradates.

Alachlor in Surface Waters:

1. Alachlor is currently regulated under the Safe Drinking Water Act (SDWA). Water supply systems will be considered out of compliance with respect to alachlor if annual average alachlor concentrations exceed the MCL of 2 $\mu\text{g}/\text{L}$. Since water supply systems are required to sample and analyze for alachlor under the SWDA, EFED is not currently recommending that any monitoring of surface water source drinking water for alachlor be required as a condition for reregistration. However, EFED recommends the following: If the results of the monitoring programs indicate that the annual average concentration of alachlor exceeds the MCL at one or more surface water source supply systems, the following is recommended:

If any community water supply system (that derives its water primarily from surface water) has an annual time weighted mean concentration of alachlor exceeding the MCL of 2 $\mu\text{g}/\text{L}$, then either:

(1) The registrant will absorb 100% of treatment and monitoring costs required to restore the system to compliance (if alachlor is the only pesticide causing the system to be out of compliance). If other pesticides are also causing the system to be out of compliance, the treatment and monitoring costs may be shared among the registrants of the different pesticides.

or

(2) The use of alachlor on the related watershed (supplying most to all of the water to the system) will be canceled.

The more recent alachlor data supports the registrant's contention (in their rebuttal to the draft RED) that annual average alachlor concentrations at surface water supply systems are unlikely to exceed the MCL of 2 ug/L except possibly "in an extremely rare case". Nevertheless, Monsanto agreed that the recommended options for either covering the monitoring and treatment costs to bring any out of compliance systems with respect to alachlor back into compliance or canceling alachlor use on the related watershed "constitute reasonable mitigation steps". However, Monsanto wants to retain "the right to choose between the options" and to "fully investigate any data" indicating exceedences of the MCL. We have no objection to Monsanto generally choosing between the two options or examining any data which indicates a system is out of compliance.

- 2 Our original concerns over alachlor in surface source drinking water have been decreased somewhat by recent (1992-1995) and extensive data collected by the USGS in reconnaissance surveys of midwestern streams and reservoirs and by the Acetochlor Registration Partnership for 175 surface water sites. Such data may reflect reported substantial decreases in alachlor use. However, we have developed substantial concern over concentrations of ESA frequently greatly exceeding those of alachlor and often being several ppb even in early Spring prior to alachlor application. Consequently, we strongly recommend that the mammalian toxicology of ESA be accurately determined so that a risk assessment for ESA in drinking water can be performed.

We are also concerned about the possible exposure to and toxicity of other major degradates of alachlor such as DM-oxanilic acid, alachlor oxanilic acid, and alachlor sulfinylacetic acid.

3 Label Wording Recommendations

If a decision is made to require labeling precautions against to minimize runoff, EFGWB recommends the following wording:

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

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Table A. GENERIC DATA REQUIREMENTS FOR ALACHLOR

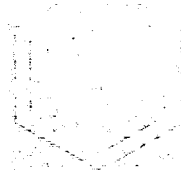
Data requirement	Use Pattern ¹	Does EPA have data to satisfy this requirement?	Bibliographic Citation	Must additional data be submitted under FIFRA Sec. 3(c)(2)(8)?
<u>DEGRADATION STUDIES - LAB.:</u>				
161-1 Hydrolysis	A, C	Yes	00134327	No ²
<u>PHOTODEGRADATION:</u>				
161-2 In Water	A, C	No		Waived ³
161-3 On Soil	A	No		Waived ⁴
161-4 In Air	A	No		Waived ⁵
<u>METABOLISM STUDIES:</u>				
162-1 Aerobic Soil	A, C	Yes	00134327	No ⁶
162-2 Anaerobic Soil	N/A	N/A		N/A ⁷
162-3 Anaerobic Aquatic	N/A	N/A		N/A
162-4 Aerobic Aquatic	N/A	N/A		N/A
<u>MOBILITY STUDIES:</u>				
163-1 Leaching and Adsorption-Desorption	A, C	Yes	00134327	No ⁸
163-2 Volatility (Lab.)	A	No		Waived ⁹
163-3 Volatility (Field)	A	No		Waived ⁹
<u>DISSIPATION STUDIES - FIELD:</u>				
164-1 Soil	A, C	No	42528001, 42528002, 42528003, 42528004	Yes ¹⁰
164-2 Aquatic (Sediment)	N/A	N/A		N/A
164-3 Forestry	N/A	N/A		N/A
164-4 Combination and Tank Mixes	N/A	N/A		N/A
164-5 Soil, Long Term	A	No		No ¹¹
<u>ACCUMULATION STUDIES:</u>				
165-1 Rotational Crops (Confined)	N/A	N/A		N/A ¹²
165-2 Rotational Crops (Field)	N/A	N/A		N/A ¹²
165-3 Irrigated Crops	N/A	N/A		N/A
165-4 In Fish	A, C	No		Waived ¹³
165-5 Aquatic Non-Target Organisms	N/A	N/A		N/A
<u>GROUNDWATER MONITORING:</u>				
166-1 Small Prospective	A	No		No ¹⁴
166-2 Small Retrospective	A	No		No ¹⁴
166-3 Large Retrospective	A	No		No ¹⁴
<u>SURFACE WATER:</u>				

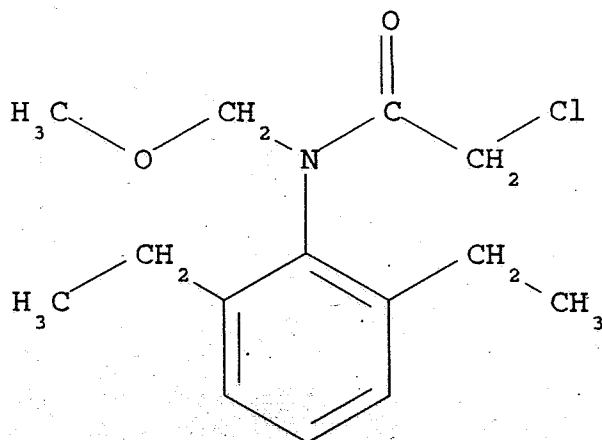
Data requirement	Use Pattern ¹	Does EPA have data to satisfy this requirement?	Bibliographic Citation	Must additional data be submitted under FIFRA Sec. 3(c)(2)(8)?
167-1 Field Runoff	A	No		No ¹⁵
167-2 Surface Water Monitoring	A	No		No ¹⁵
SPRAY DRIFT:				
201-1 Droplet Size Spectrum	A, C	No		Reserved ¹⁶
202-1 Drift Field Evaluation	A, C	No		Reserved ¹⁶

Footnotes:

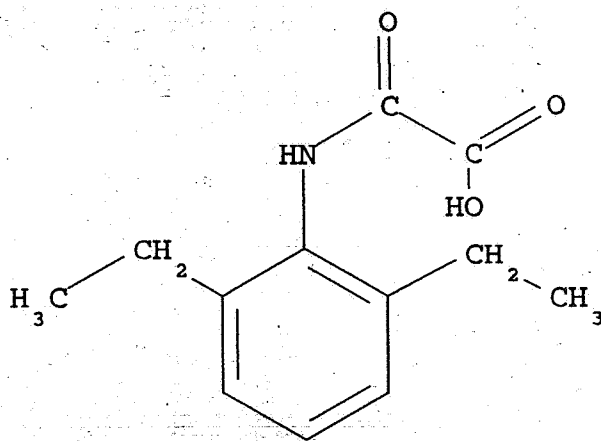
- Use Patterns N/A = Not Applicable; A = Terrestrial Food Crop, C = Terrestrial Non-Food.
- Alachlor is relatively stable in sterile pH 3, 6, and 9 buffer solutions, natural lake water, and deionized water.
- EFGWB is requiring no additional data on the Photolysis in Water for alachlor because the absorption spectrum of the chemical has no bands in the 290-800 nm region. One study (MRID# 00023012) is available. The study supports the conclusion that photolysis in water is not an important route of degradation for alachlor.
- EFGWB is not requiring any additional information to support the data requirement, based on supplemental information (MRID# 00134327) and the absence of absorption bands in the absorption spectrum of alachlor in water.
- Waived, based on the observed characteristics of alachlor (vapor pressure 2.2×10^{-5} mm Hg @ 24°C; low levels of [¹⁴C] volatiles in the aerobic soil metabolism study with $\leq 1.15\%$ of the applied after 175 days incubation, no Photolysis in Water), which suggest that Photolysis in Air is not an important route of dissipation of alachlor.
- Alachlor degraded with estimated half-lives of 2-3 weeks in silt, loamy sand, and silt loam soils. [¹⁴C] volatiles were $\leq 1.15\%$ of the applied after 175 days. Four degradates were detected: DM-oxanilic acid, alachlor oxanilic acid, alachlor sulfonic acid or ESA, and 2',6'-diethyl-2-hydroxy-N-methoxymethylacetanilide. In an available supplemental study, the degradate alachlor sulfinylacetic acid was also detected.
- The data requirement does not apply to this chemical; therefore, no additional data are required.
- The unaged portion of this study is acceptable and partially satisfies the Mobility data requirement. The aged portion provides only supplemental data. EFGWB will not require additional data for the following degradates of alachlor: 2',6'-diethyloxanilic acid, 2',6'-diethyl-N-methoxymethyloxanilic acid, 2',6'-diethyl-N-methoxymethyl-2-sulfoacetanilide, and 2',6'-diethyl-2-hydroxy-N-methoxymethylacetanilide. A Batch Equilibrium study is required for alachlor ethane sulfonic acid. Alachlor was very mobile in silt, sand, and loamy sand soils (40.9-96.9% of the applied radioactivity in the leachates), and mobile in a silt loam soil (0.5-0.6% of the applied radioactivity in the leachates).
- Waived, based on the observed characteristics of alachlor (vapor pressure 2.2×10^{-5} mm Hg @ 24°C; low levels of [¹⁴C] volatiles in the aerobic soil metabolism study with $\leq 1.15\%$ of the applied after 175 days incubation), which suggest that volatilization is not a significant route of dissipation of alachlor.
- Alachlor dissipated with an observed half-life of ≈ 11 days from a plot planted to corn immediately after treatment in Chico, California. Alachlor was detected as deep as 36- to 48-inch soil depth. Four degradates identified are: alachlor oxanilic acid, alachlor sulfinylacetic acid, alachlor sulfonic acid, and DM-oxanilic acid. An additional study is currently under review.
- Study is not required, based on the short half-lives observed in the Aerobic Soil Metabolism and the Terrestrial Field Dissipation studies.
- Confined and Field Rotational Crops data requirements have been transferred to RCB/HED.
- Waived, based on the properties of the chemical. Alachlor has a relatively high water solubility (240 ppm), and a relatively low octanol/water partition coefficient ($K_{ow} \approx 434$, one study reports as low as 35). Chemicals with these physico/chemical properties are not expected to bioaccumulate in fish.
- The Registrant should identify mitigation measures to manage the use of alachlor in such a way that ground-water resources will not be contaminated as a result of normal uses.
- EFGWB is not currently recommending that any monitoring of raw surface waters for alachlor to support aquatic non-target organism risk assessments be required as a condition for reregistration. Alachlor is currently regulated under the Safe Drinking Water Act (SDWA). Since water supply systems are required to sample and analyze for alachlor under the SDWA, EFGWB is not currently recommending that any monitoring of surface water source drinking water for alachlor be required as a condition for reregistration.
- Studies are being held in Reserve, pending the evaluation of the work conducted by industry's Spray Drift Task Force, of which Monsanto, the registrant of alachlor, is a member.

APPENDIX
ALACHLOR AND ITS DEGRADATES

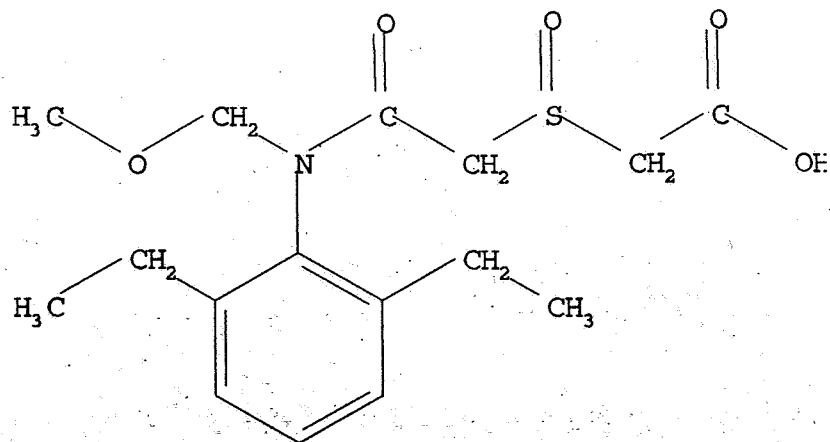




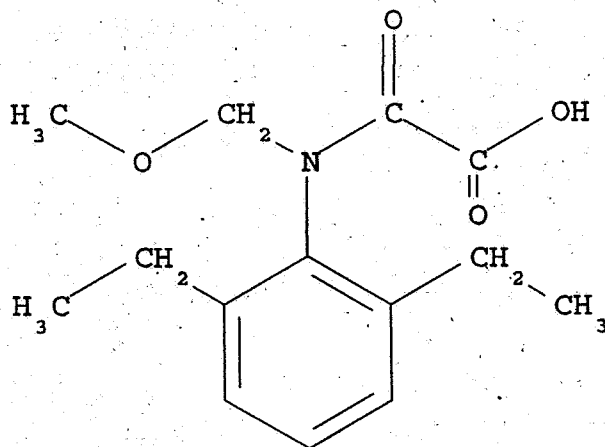
2-Chloro-2',6'-diethyl-N-methoxymethylacetanilide
(Alachlor)



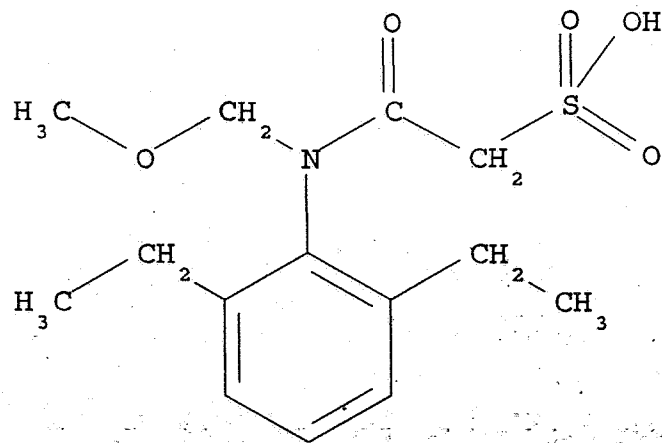
2',6'-Diethyloxanilic acid
(DM-Oxanilic acid)
(Compound III)



(N-Methoxymethyl-N-(2,6-diethylphenyl)-2-amino-2-oxoethyl)-
sulfinylacetic acid
(Alachlor sulfinylacetic acid)
(Compound VIII)



2',6'-Diethyl-N-methoxymethyloxanilic acid
(Alachlor oxanilic acid)
(Compound X)



2',6'-Diethyl-N-methoxymethyl-2-sulfoacetanilide
(Alachlor sulfonic acid)
(Compound XI)

Figures

Alachlor

1995 Annual Peak Concentrations (Acetochlor Registration Partnership)

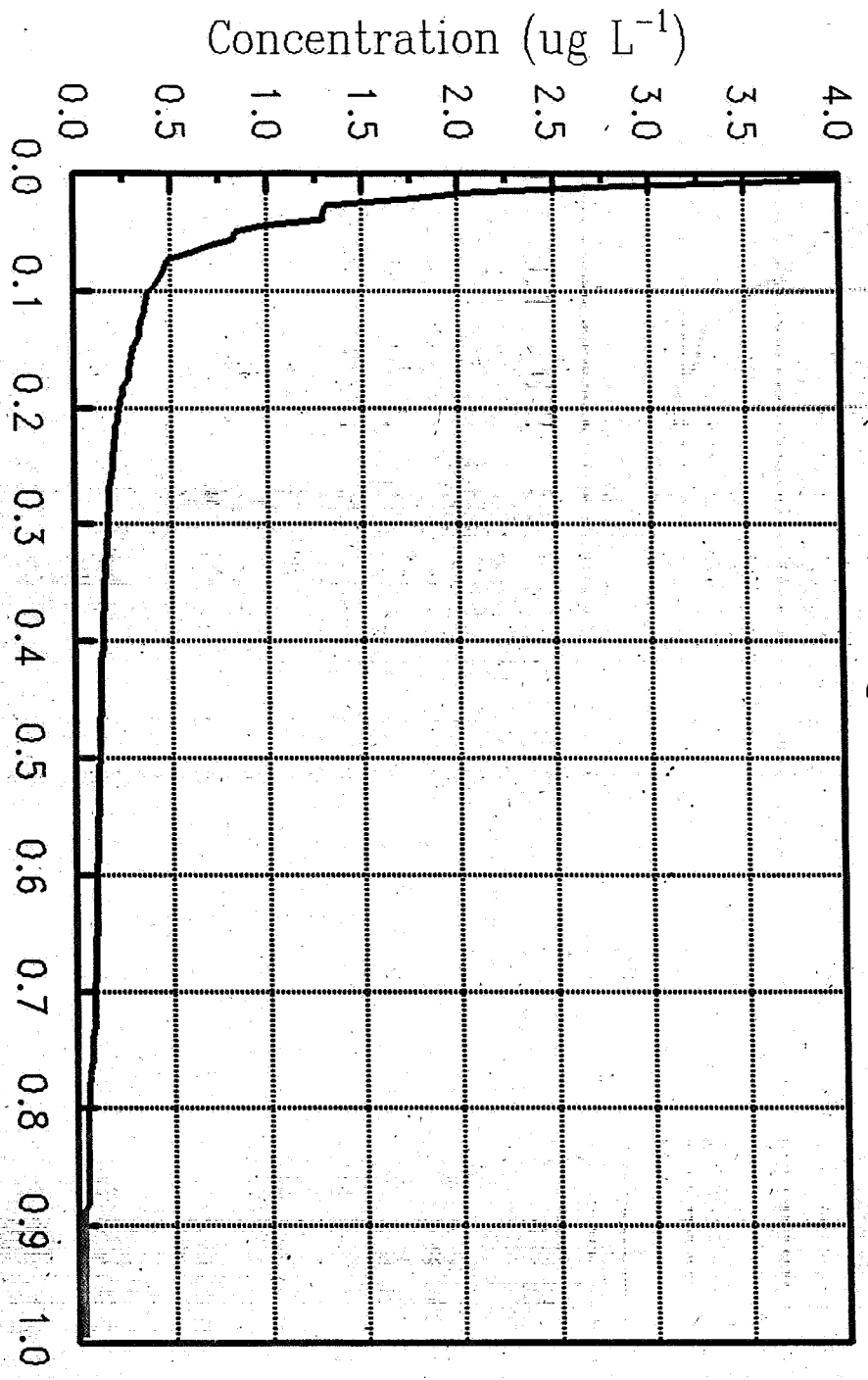


Figure 1.

Site Exceedance Probability

001, 1996
al4p95.psg, 5/28/96

Alachlor

1995 Annual Maximum 96 Day Means
(Acetochlor Registration Partnership)

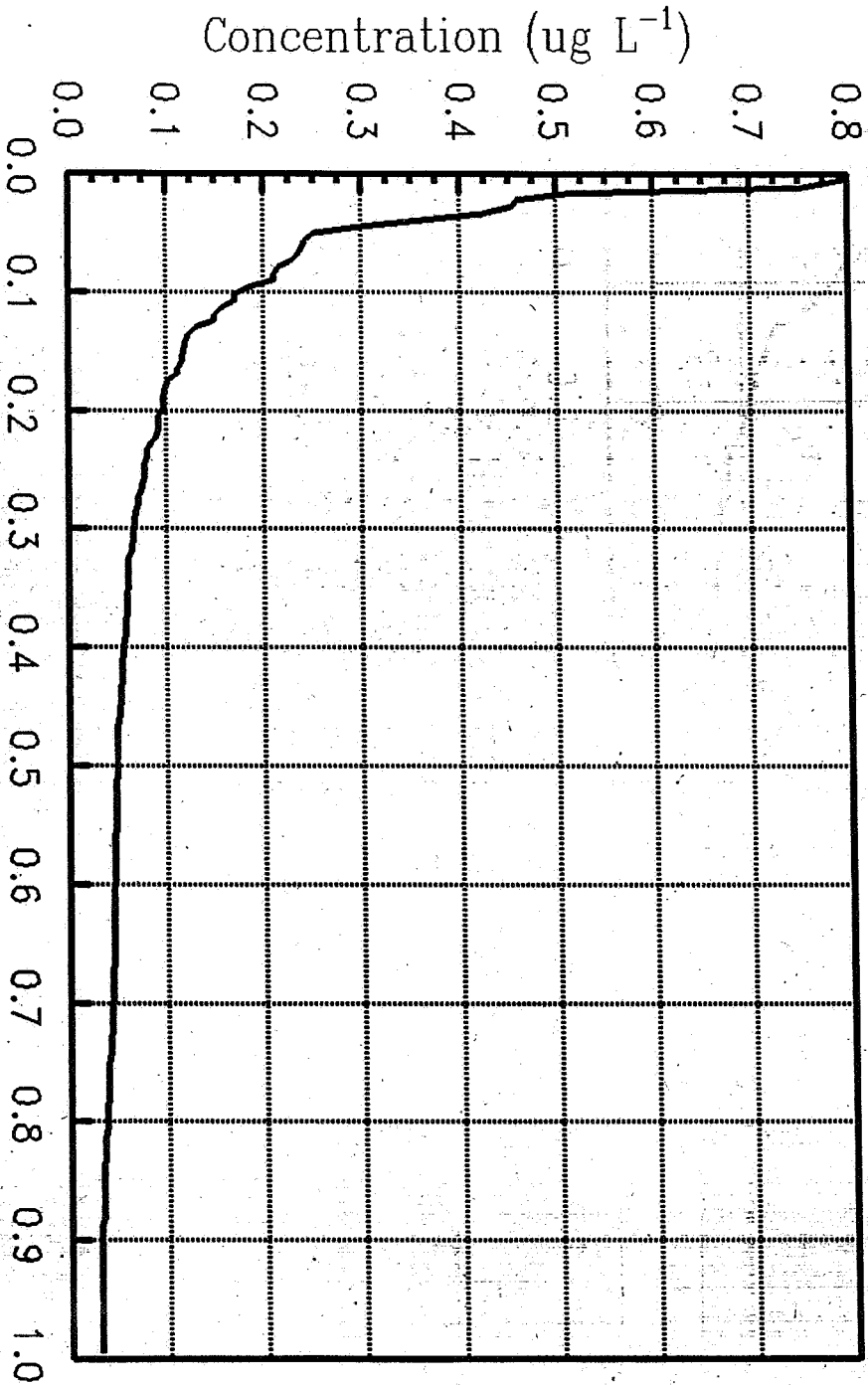


Figure 2.

Site Exceedance Probability

Alachlor

1995 Annual Mean Concentrations (Acetochlor Registration Partnership)

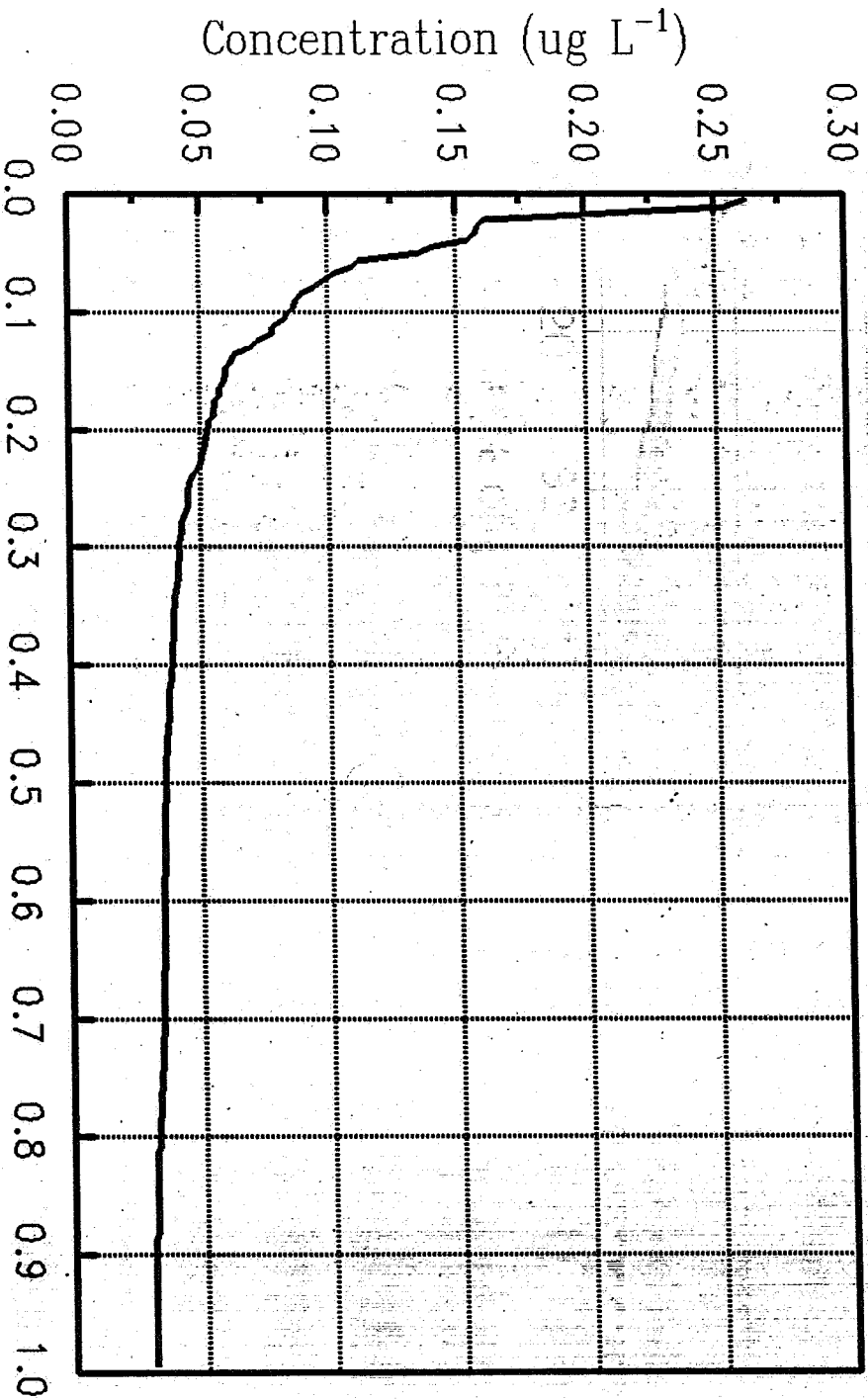


Figure 3.

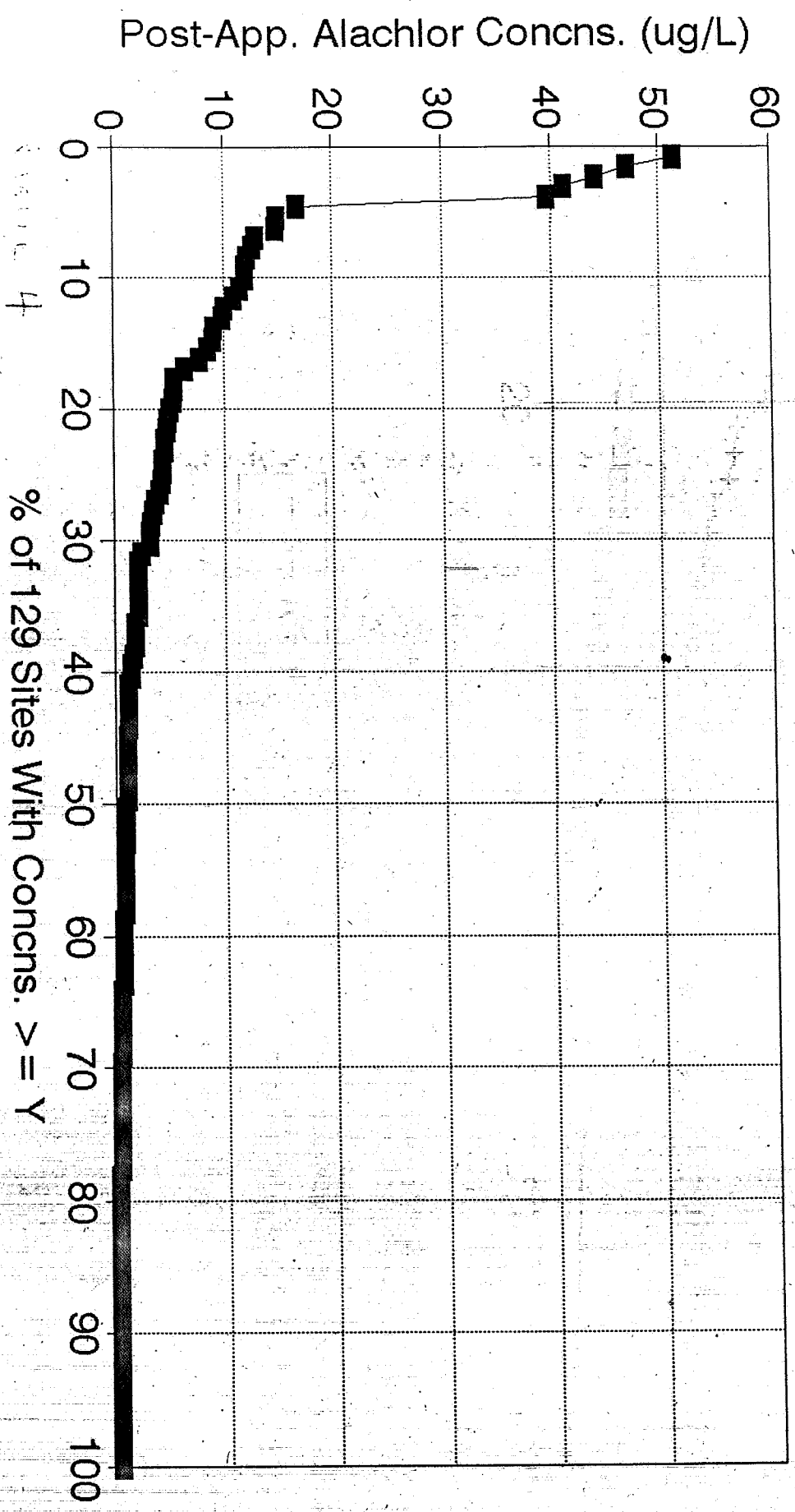
Site Exceedance Probability

R01, 1996
alant05.psq, 5/28/96

Post-App. 10 Midwestern States 1989

Goolsby/Thurman (1991) Data

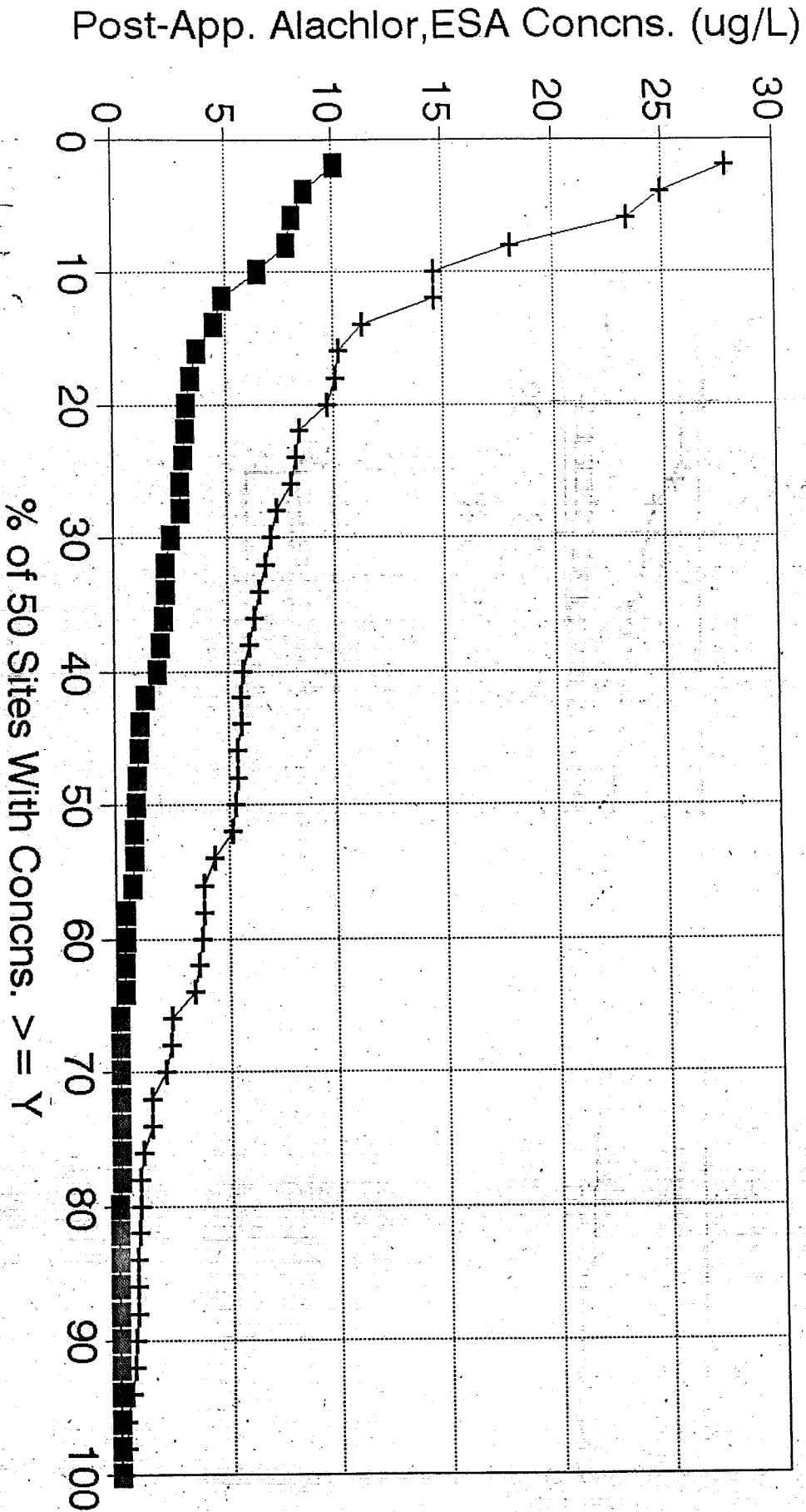
5



■ Alachlor

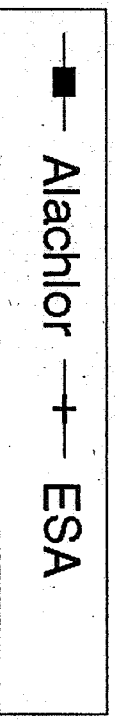
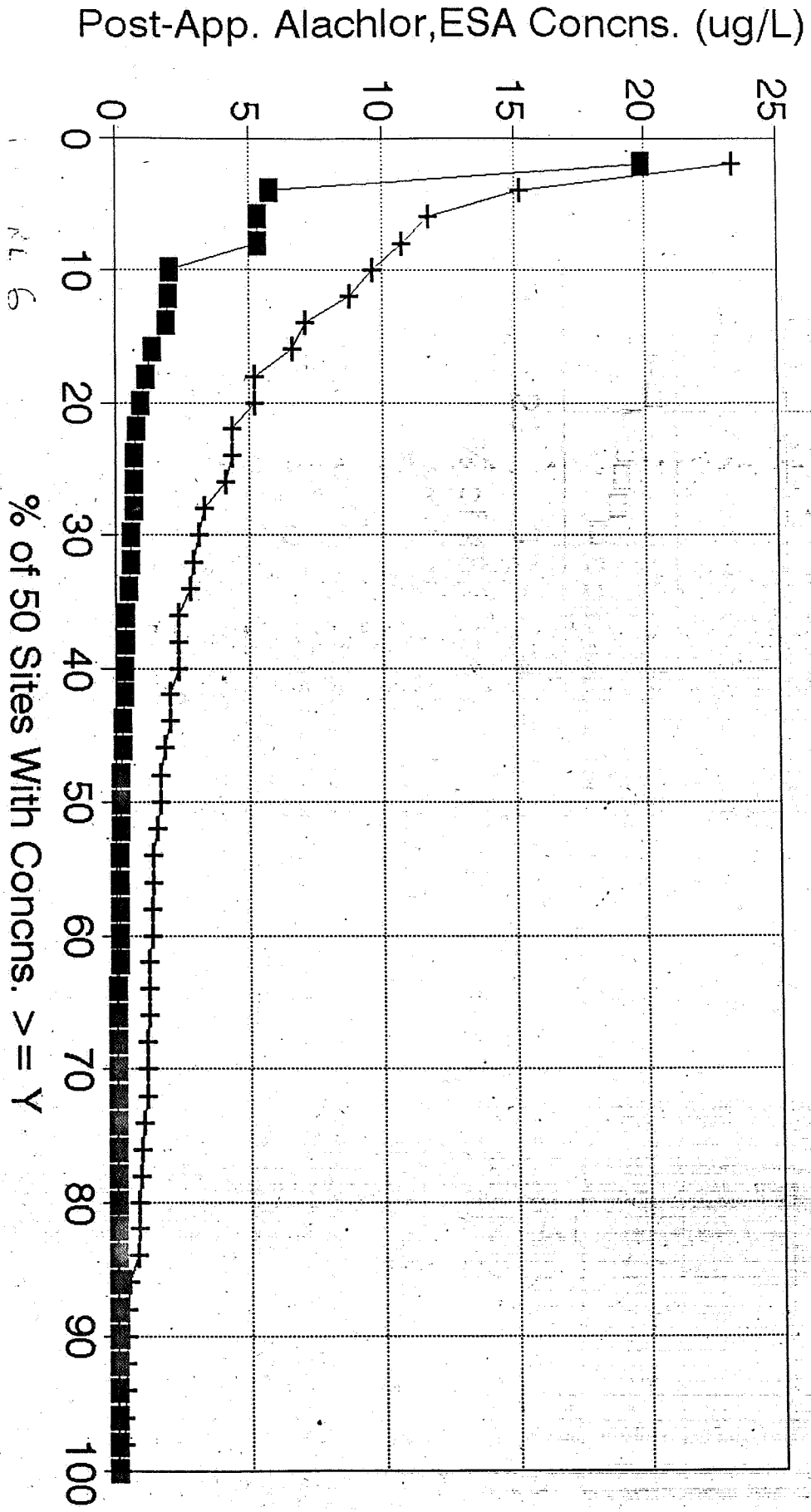
Post-App. 8 Midwest States 1994

Goolsby (1996) Data



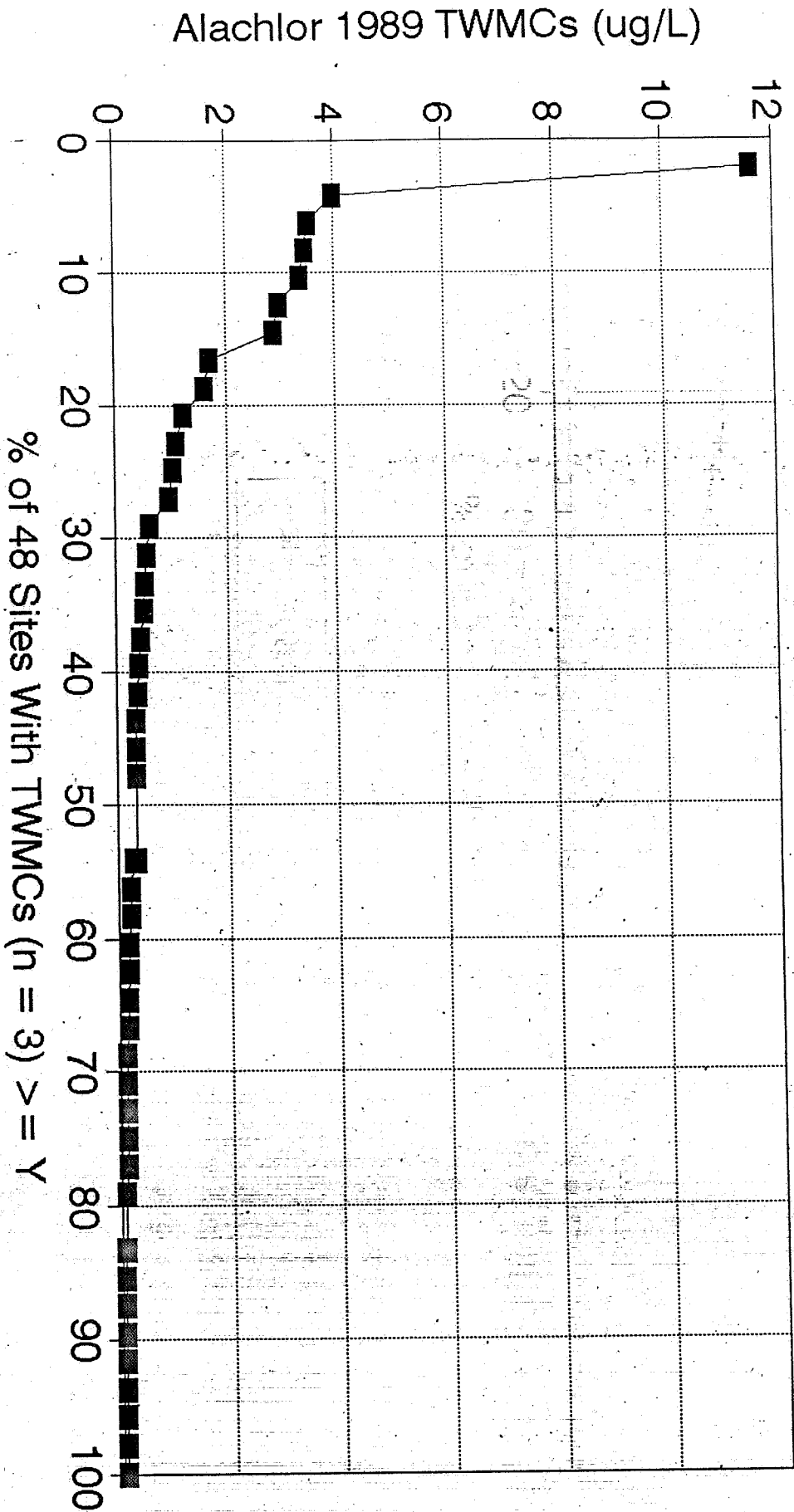
Post-App. 8 Midwest States 1995

Goolsby (1996) Data



Ann. TWMCs 10 Midwestern States 1989

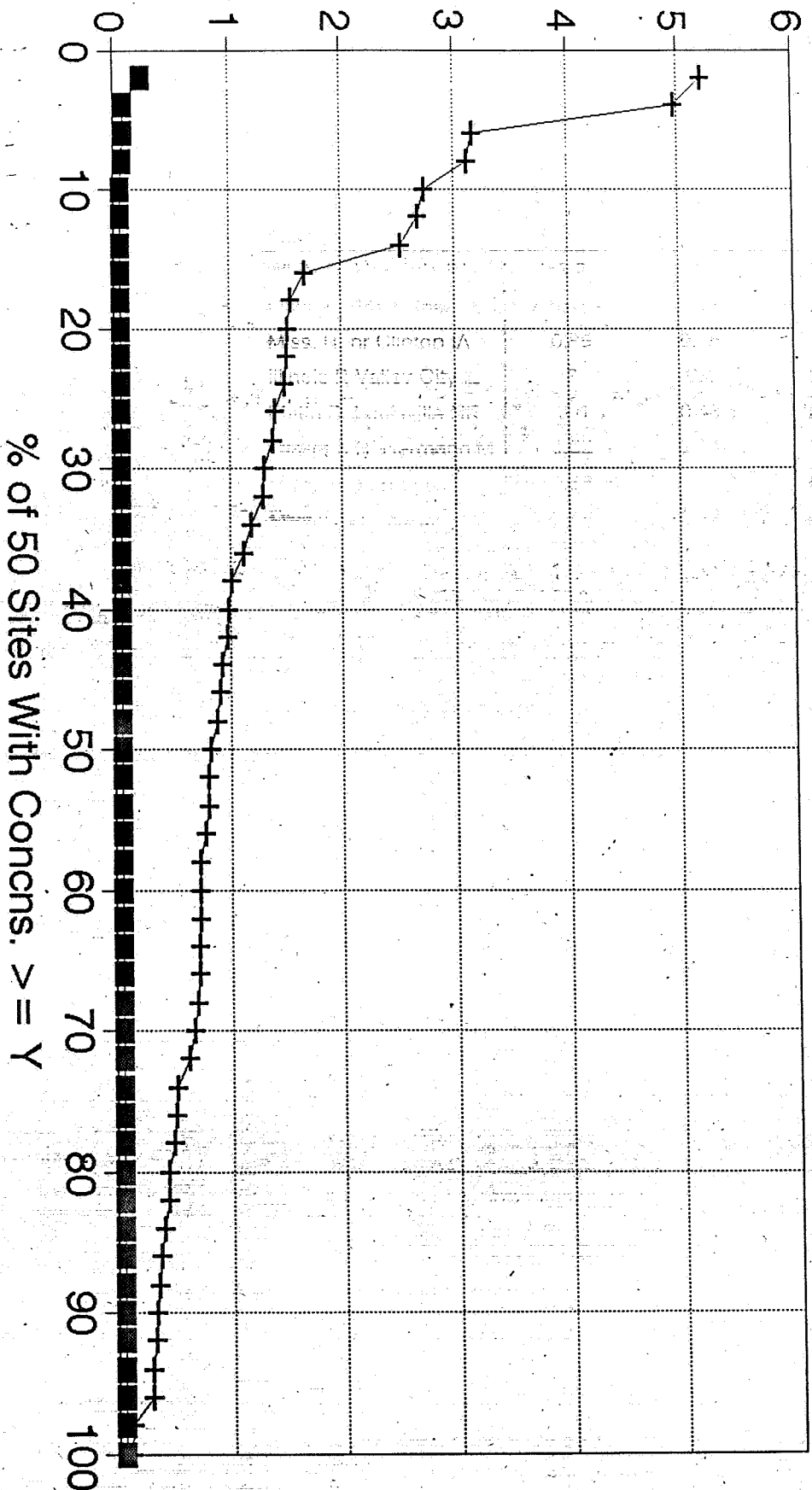
Goolsby/Thurman (1991) Data



Pre-App. 8 Midwest States 1994

Goolsby (1996) Data

Post-App. Alachlor, ESA Concns. (ug/L)



■ Alachlor + ESA

Data from Goolsby, Coup, and Markovchick (1991)

Mississippi River Basin (8 sites)

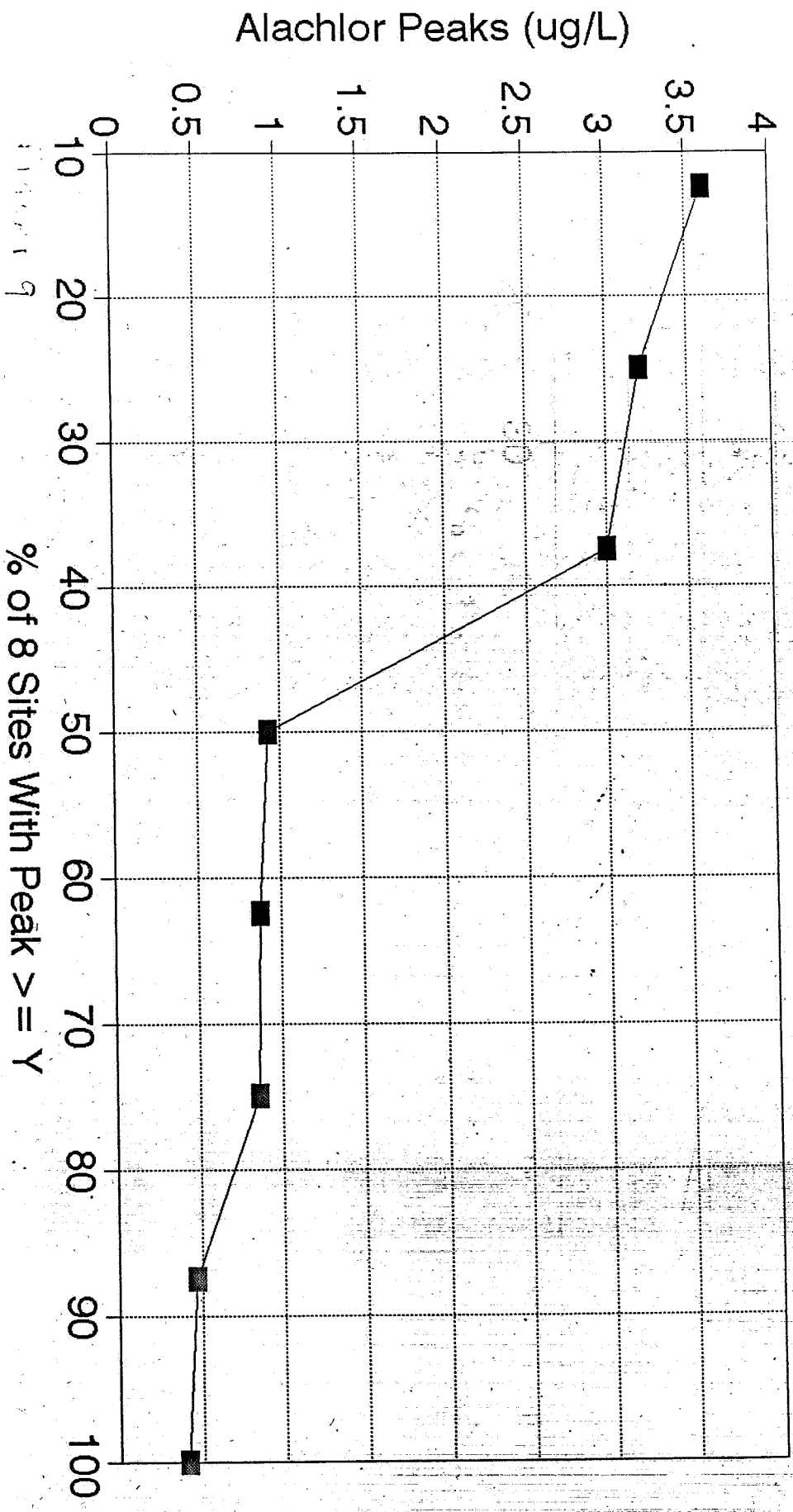
Biweekly samples May-Aug., Weekly samples Apr., Sept.-Dec. 1

Site	Alachlor Peak Concn. (ug/L)	Alachlor Arith. Mean (ug/L)	Alachlor Annual TWMC (ug/L)
White R. Hazelton IN	3.2	0.3	0.22
Ohio R. Grain Chain IL	0.4	0.08	0.07
Miss. R. nr Clinton IA	0.85	0.16	0.1
Illinois R Valley City IL	3	0.4	0.22
Platte R. Louisville NE	3.6	0.43	0.22
Missouri R. Hermann M	0.92	0.19	0.12
Miss. R. nr Thebes IL	0.86	0.27	0.23
Miss. R. B. Rouge LA	0.46	0.12	0.09

Alachlor Peaks 1991

Mississippi R. Basin (Goolsby et al 1991)

7

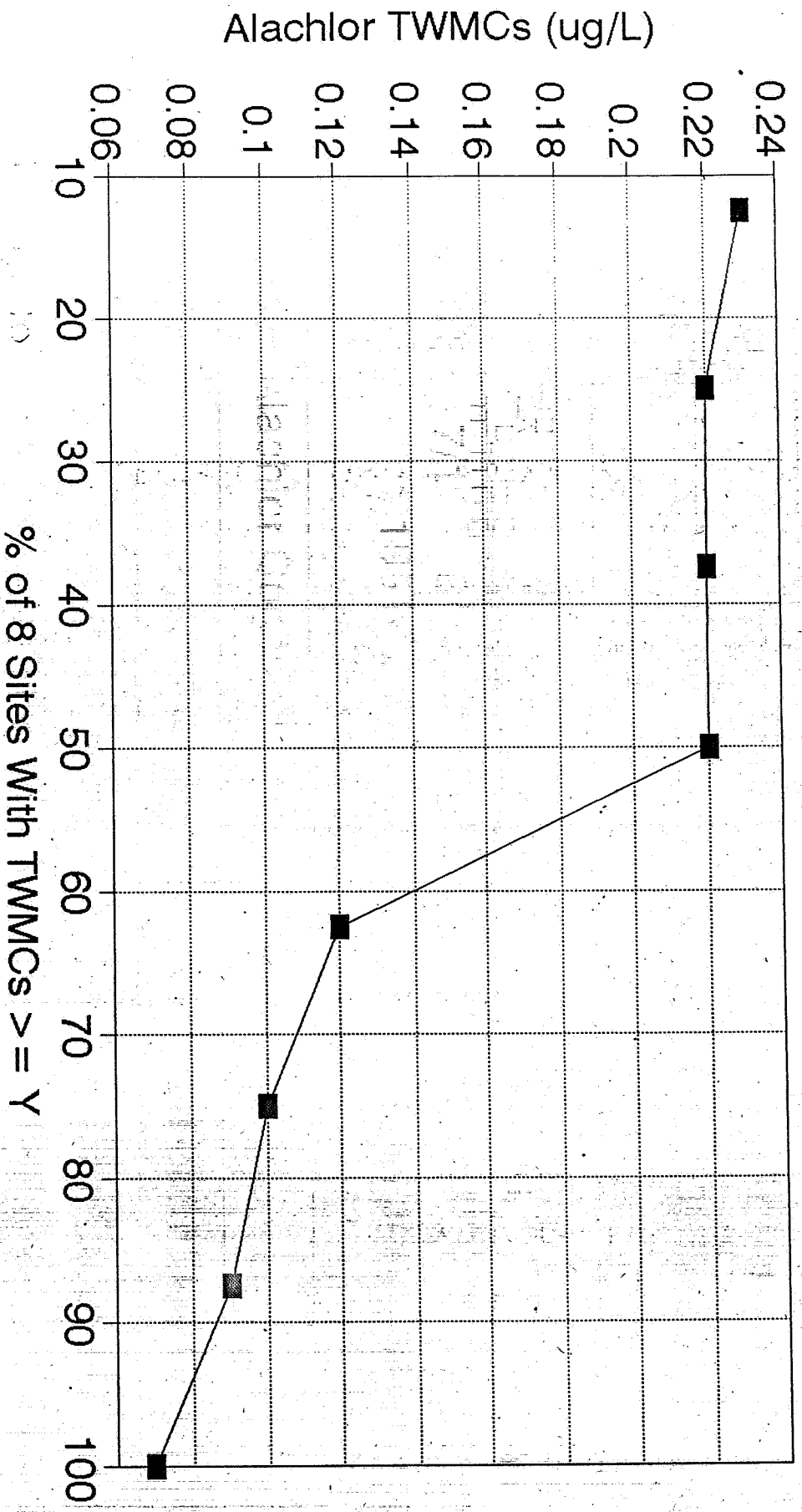


Alachlor

Alachlor Annual TWMCs 1991

Mississippi R. Basin (Goolsby et al 1991)

72

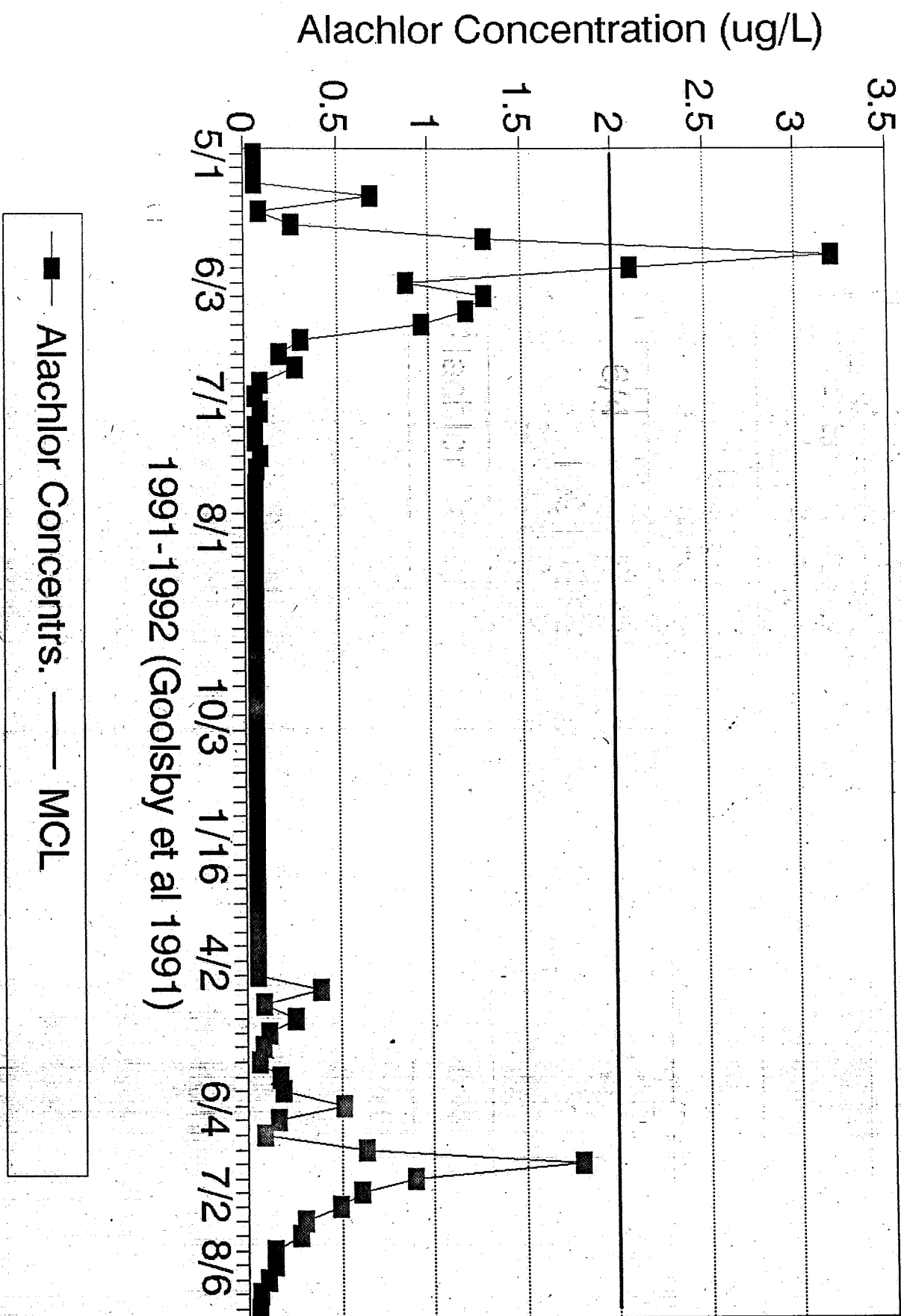


■ Alachlor

Alachlor Time Series

White River near Hazelton, IN

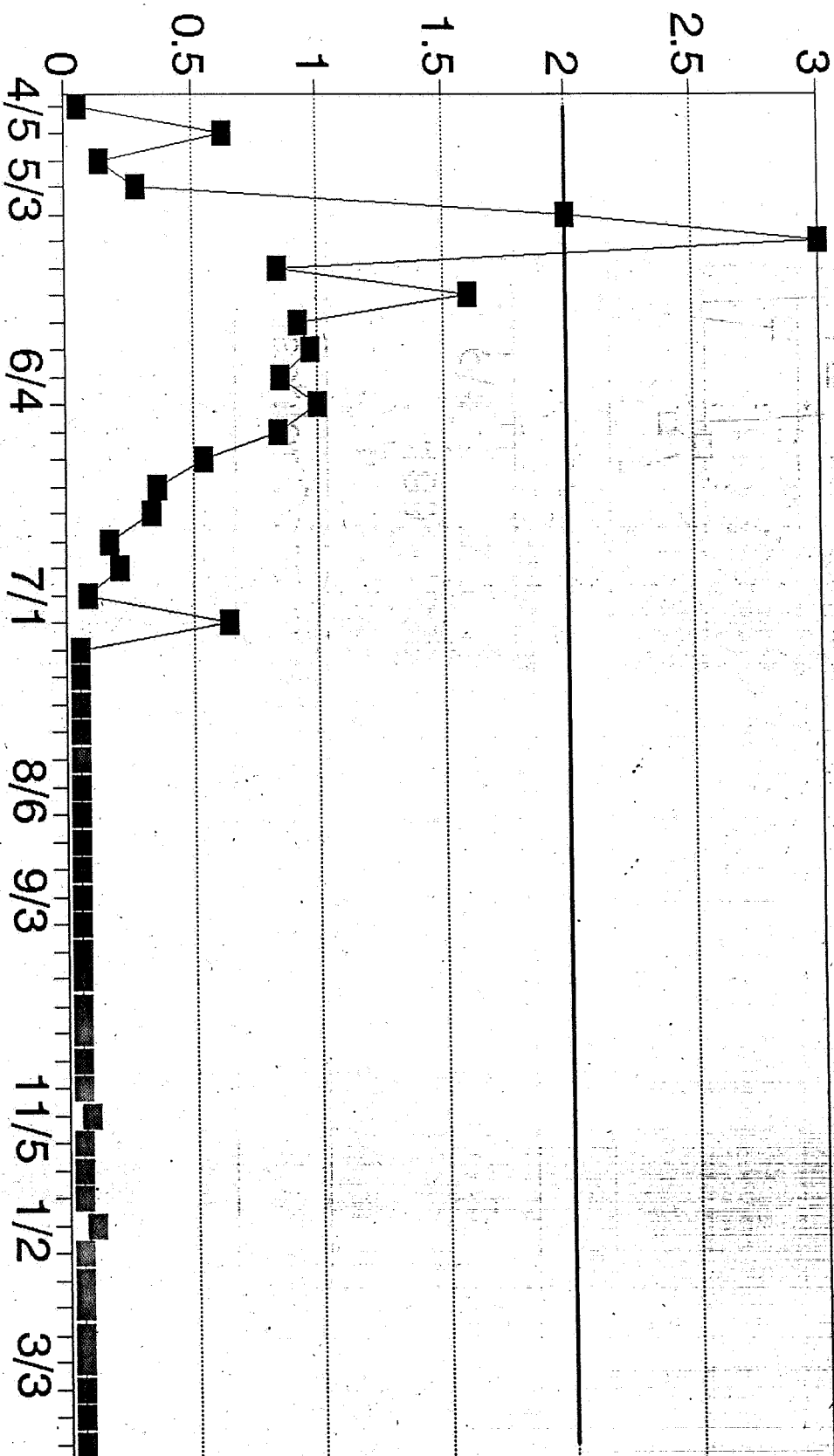
73



Aalachlor Time Series

Illinois R. nr. Valley City IL

Aalachlor Concentration (ug/L)



■ Aalachlor Concentrs. — MCL

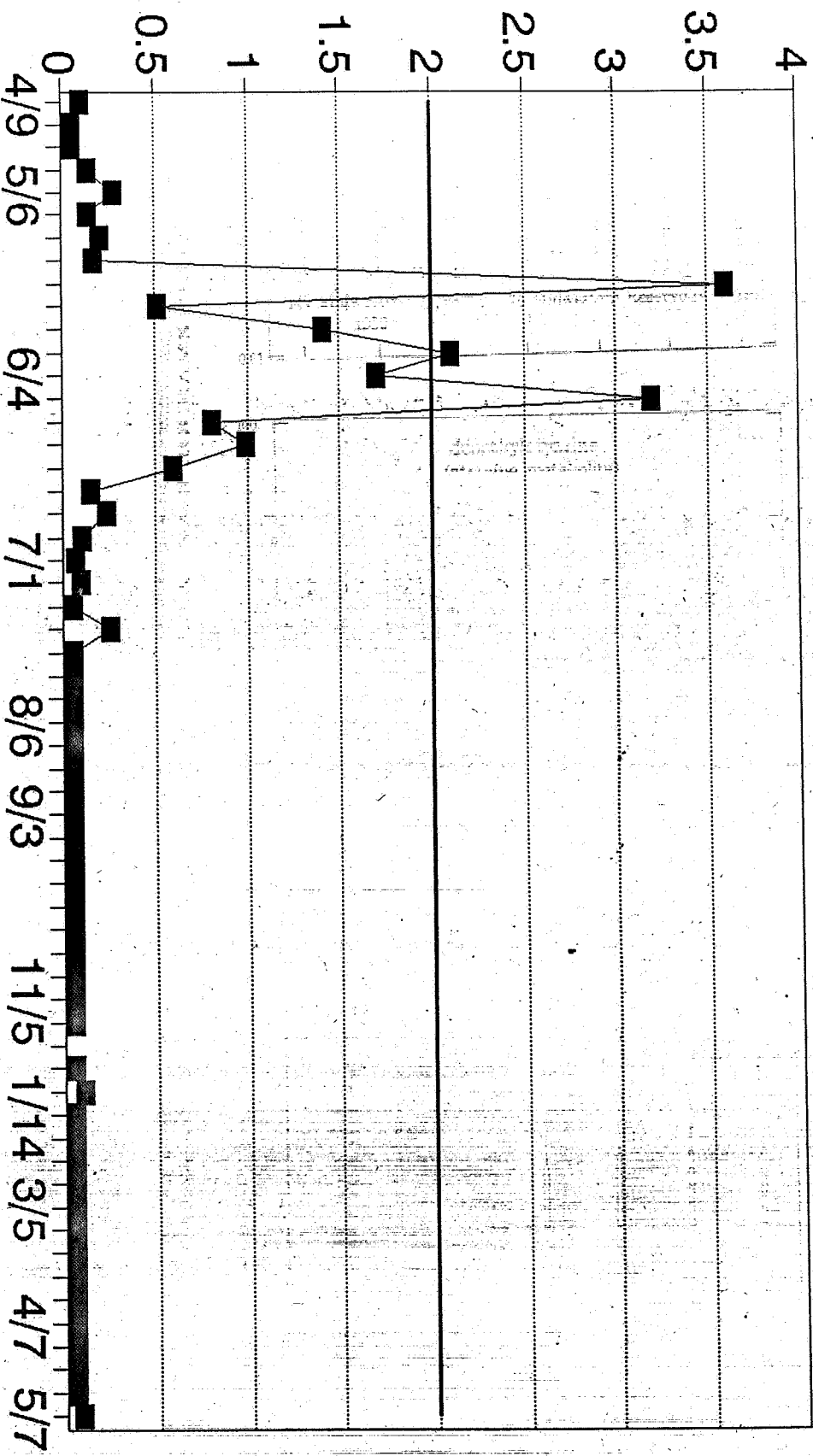
1991-1992 (Goolsby et al 1991)

Aalachlor Time Series

Platte R. nr. Louisville NE

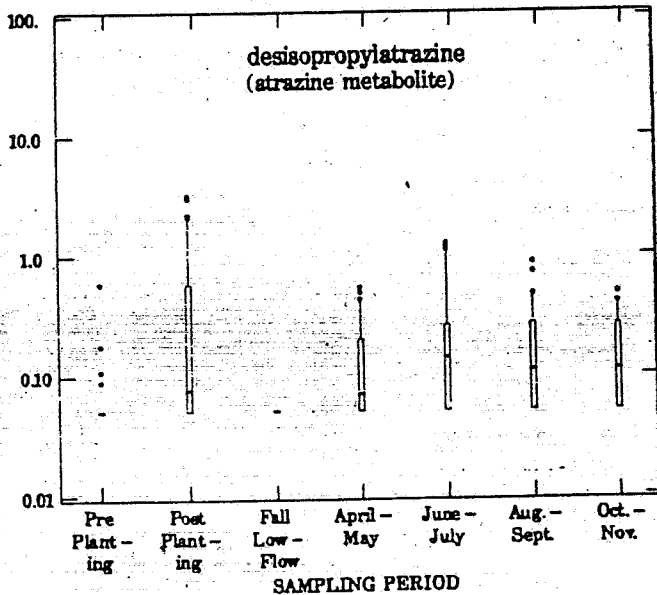
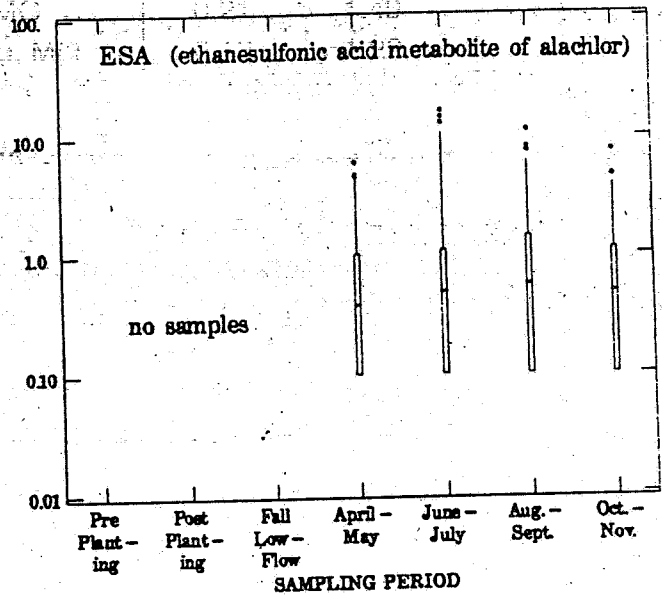
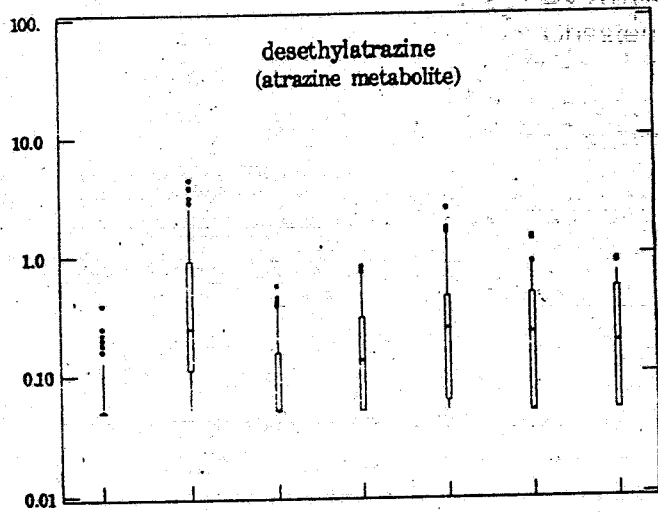
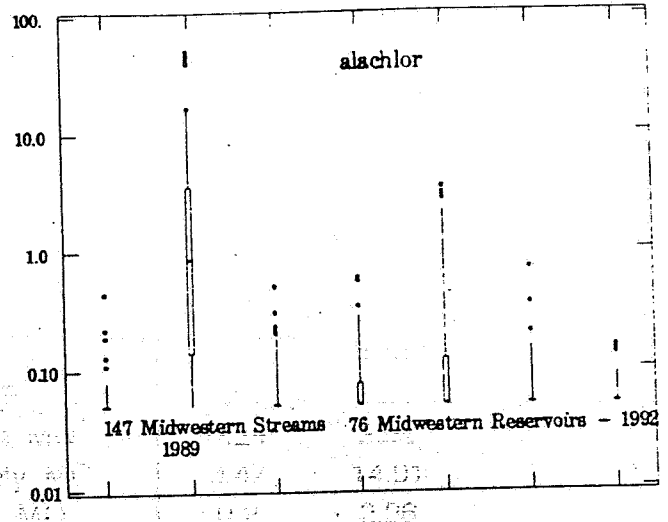
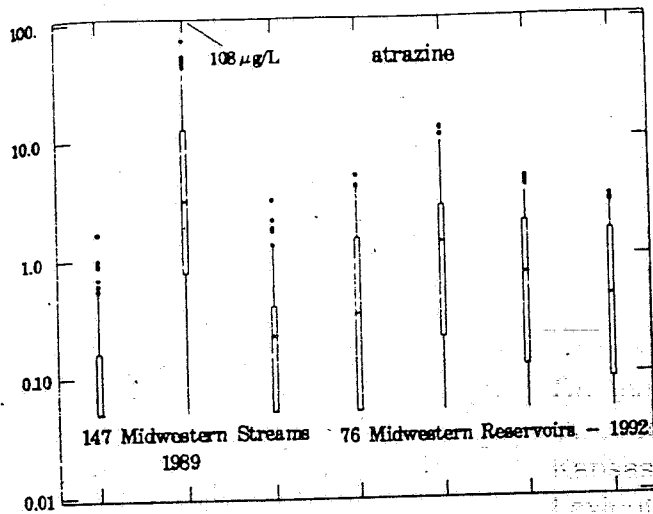
75

Aalachlor Concentration (ug/L)



■ Aalachlor Concentrs. — MCL

1991-1992 (Goolsby et al 1991)



EXPLANATION

- — maximum concentration
- 95th percentile
- 75th percentile
- median
- 25th percentile
- 5th percentile
- — reporting limit or minimum concentration

14
Figure 4. Temporal distribution of atrazine, alachlor, and three metabolites in midwestern reservoirs during 1992 and in midwestern streams during 1989.

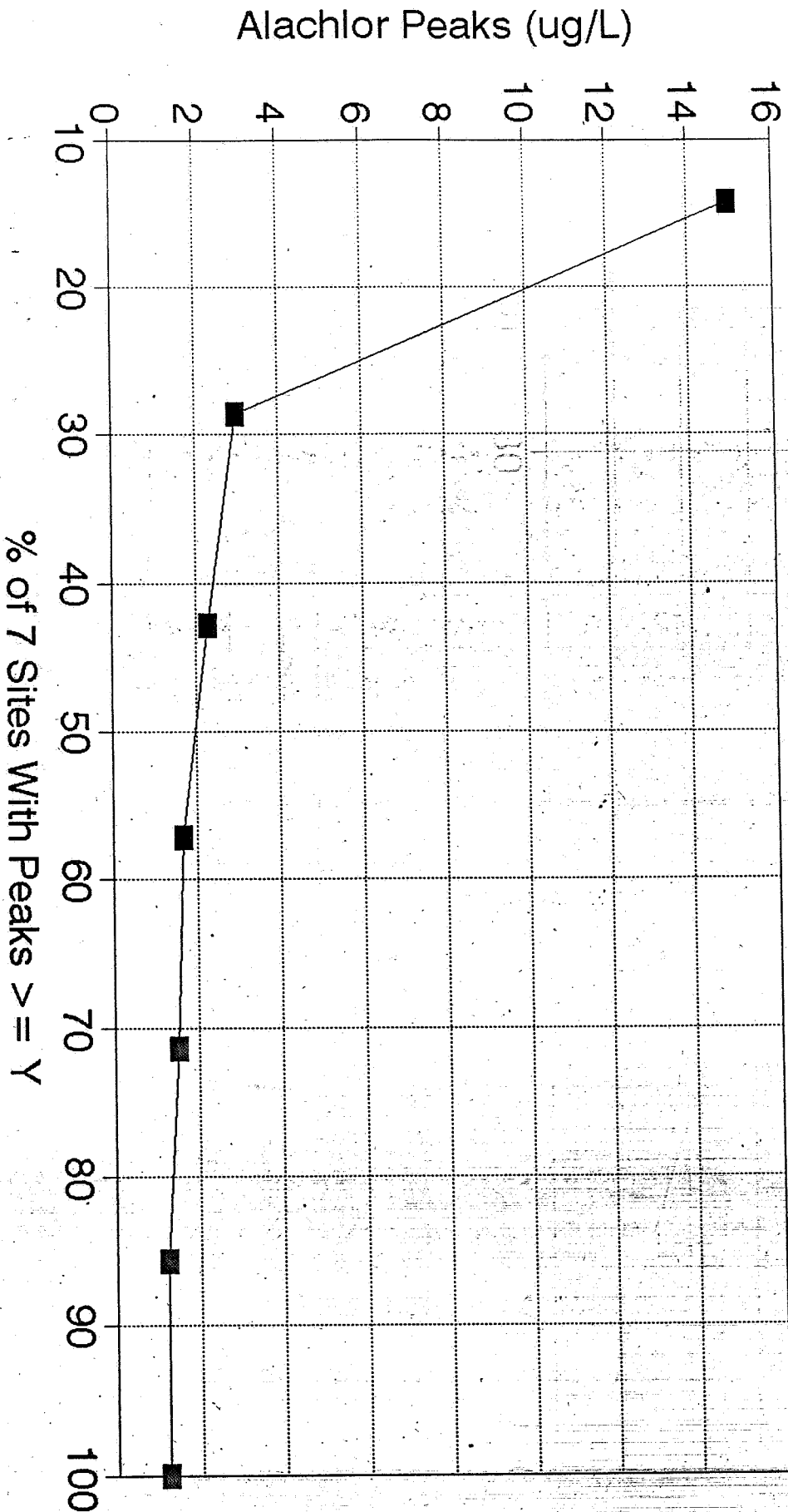
76

Data from Keck (1991)
Missouri River Basin (7 locations)
Daily samples May-July 1990

Location	Alachlor Mean (ug/L)	Alachlor Peak (ug/L)
Sioux City, IA	0.03	1.64
Omaha, NE	0.07	1.21
St. Joseph, MO	0.29	2.94
Kansas City, MO	0.47	14.91
Lexington, MO	0.2	2.26
Boonville, MO	0.21	1.49
Chesterfield, MO	0.12	1.22

Aalachlor Peaks 1990

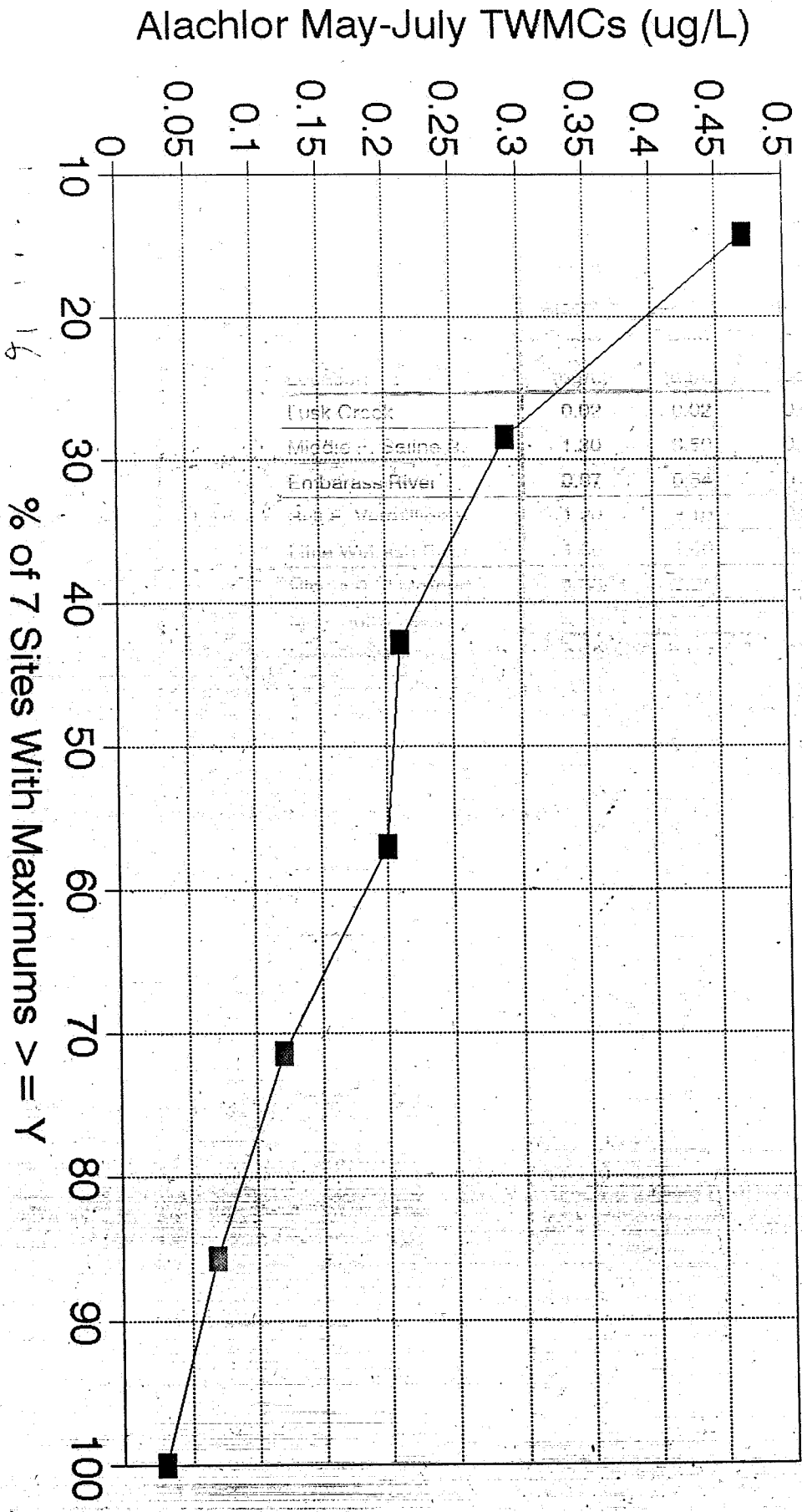
Missouri R. Basin (Keck 1991)



Alachlor May-July TWMCs 1990

Missouri R. Basin (Keck 1991)

67



■ Alachlor

Data from Moyer and Cross (1990)

Illinois Surface Waters (30 sites)

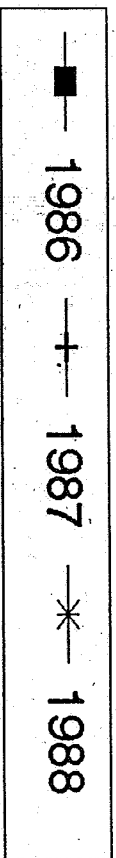
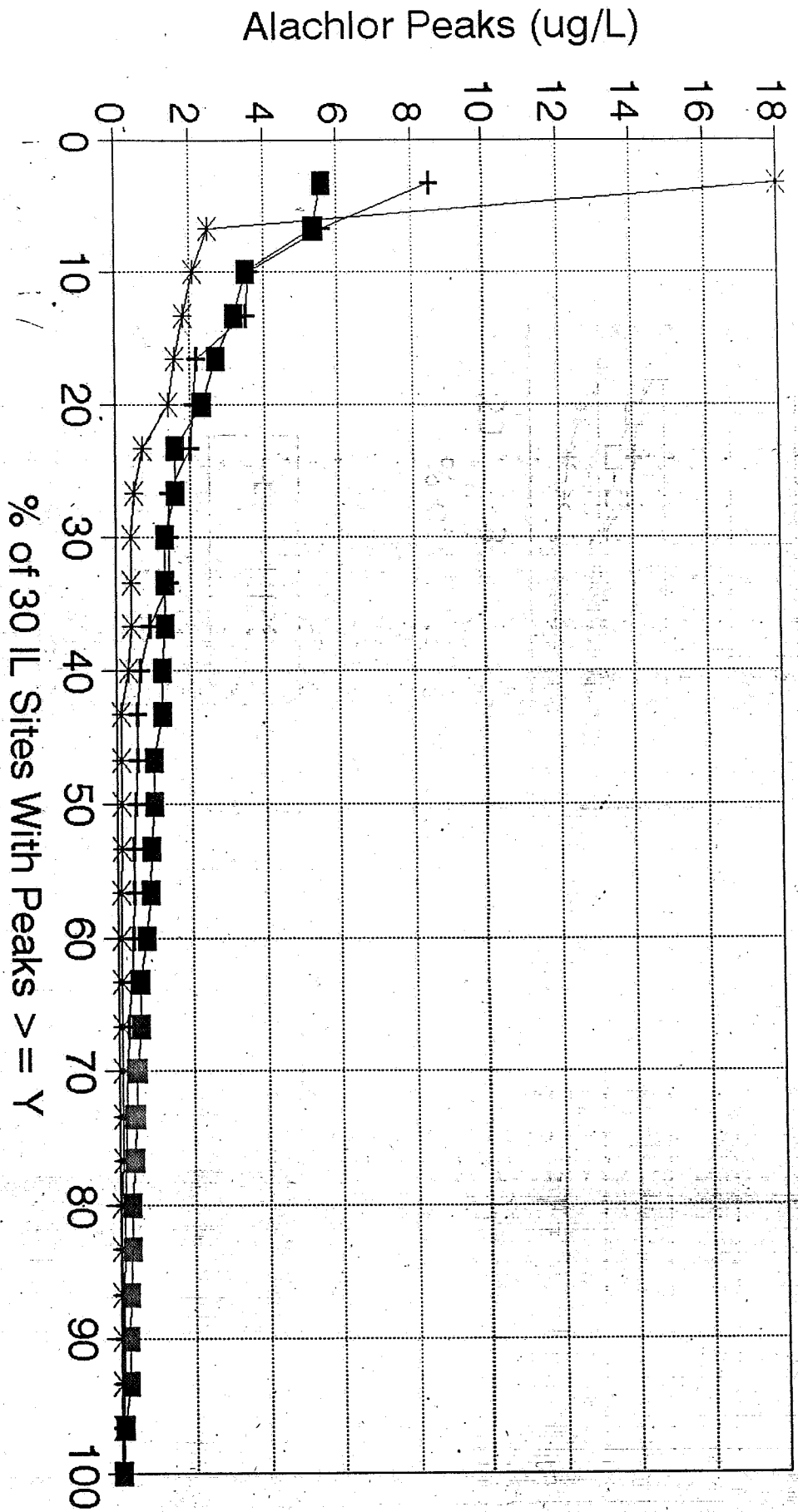
4-7 Samples collected per year at each site from 1986-1988

Location	1986	1987	1988	1986	1987	1988	86-88	86-88
	Alachlor Peak (ug/L)	Alachlor Peak (ug/L)	Alachlor Peak (ug/L)	Alachlor TWMC (ug/L)	Alachlor TWMC (ug/L)	Alachlor TWMC (ug/L)	Alachlor Arith. Mean (ug/L)	Alachlor TWMC (ug/L)
Lusk Creek	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Middle F. Saline R.	1.30	8.50	0.11	0.20	0.86	0.04	0.60	0.37
Embarass River	0.97	0.54	0.13	0.18	0.18	0.06	0.16	0.14
Salt F. Vermillion R.	1.20	2.10	0.46	0.19	0.29	0.07	0.24	0.18
Little Wabash River	1.60	1.40	0.08	0.25	0.36	0.04	0.31	0.22
Illinois R. (Harbour)	1.30	0.24	2.10	0.25	0.09	0.28	0.34	0.21
Maucopin Creek	2.30	0.91	0.04	0.31	0.13	0.03	0.19	0.16
Lamoine R. (Ripley)	3.20	1.40	0.09	0.51	0.18	0.05	0.30	0.24
Lamoine R. (Colmar)	0.75	0.36	0.11	0.16	0.07	0.05	0.12	0.09
Spoon R. (Wyoming)	0.37	0.07	0.08	0.06	0.03	0.03	0.04	0.04
Spoon R. (Seville)	0.24	0.22	0.07	0.06	0.05	0.03	0.06	0.05
Mackinaw River	0.30	3.50	0.08	0.07	0.43	0.03	0.24	0.18
Big Bureau Creek	0.85	0.45	0.39	0.11	0.11	0.07	0.13	0.10
Vermillion River	5.30	1.40	0.72	0.53	0.19	0.11	0.52	0.28
Sangamon R. (Oakfor)	0.08	0.45	0.04	0.04	0.18	0.03	0.06	0.09
Sangamon R. (Montic)	0.90	0.12	0.10	0.11	0.03	0.04	0.09	0.06
Salt Creek	0.57	0.14	2.50	0.10	0.04	0.30	0.20	0.15
Kankakee River	1.30	2.20	0.40	0.20	0.32	0.10	0.26	0.20
Des Plaines River	1.00	0.06	0.02	0.13	0.04	0.02	0.08	0.06
Bay Creek	0.44	2.00	18.00	0.11	0.31	2.00	1.25	0.81
Bear Creek	2.70	0.47	1.80	0.39	0.09	0.25	0.34	0.25
Henderson Creek	1.20	0.04	0.32	0.16	0.02	0.05	0.10	0.08
Edwards River	5.60	0.37	0.05	0.65	0.09	0.02	0.35	0.25
Plum River	1.60	5.60	0.04	0.16	0.61	0.02	0.42	0.26
Apple River	0.46	0.53	0.02	0.06	0.07	0.02	0.07	0.05
Big Muddy River	0.32	0.12	0.04	0.06	0.04	0.02	0.04	0.04
Kaskaskia River	0.57	0.07	0.09	0.11	0.03	0.03	0.07	0.05
Silver Creek	3.50	3.60	1.40	0.46	0.76	0.15	0.69	0.46
Green River	0.22	0.60	1.60	0.10	0.11	0.23	0.18	0.14
Elkhorn Creek	0.21	0.16	0.41	0.04	0.05	0.07	0.07	0.05

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Alachlor Peaks 1986-1988

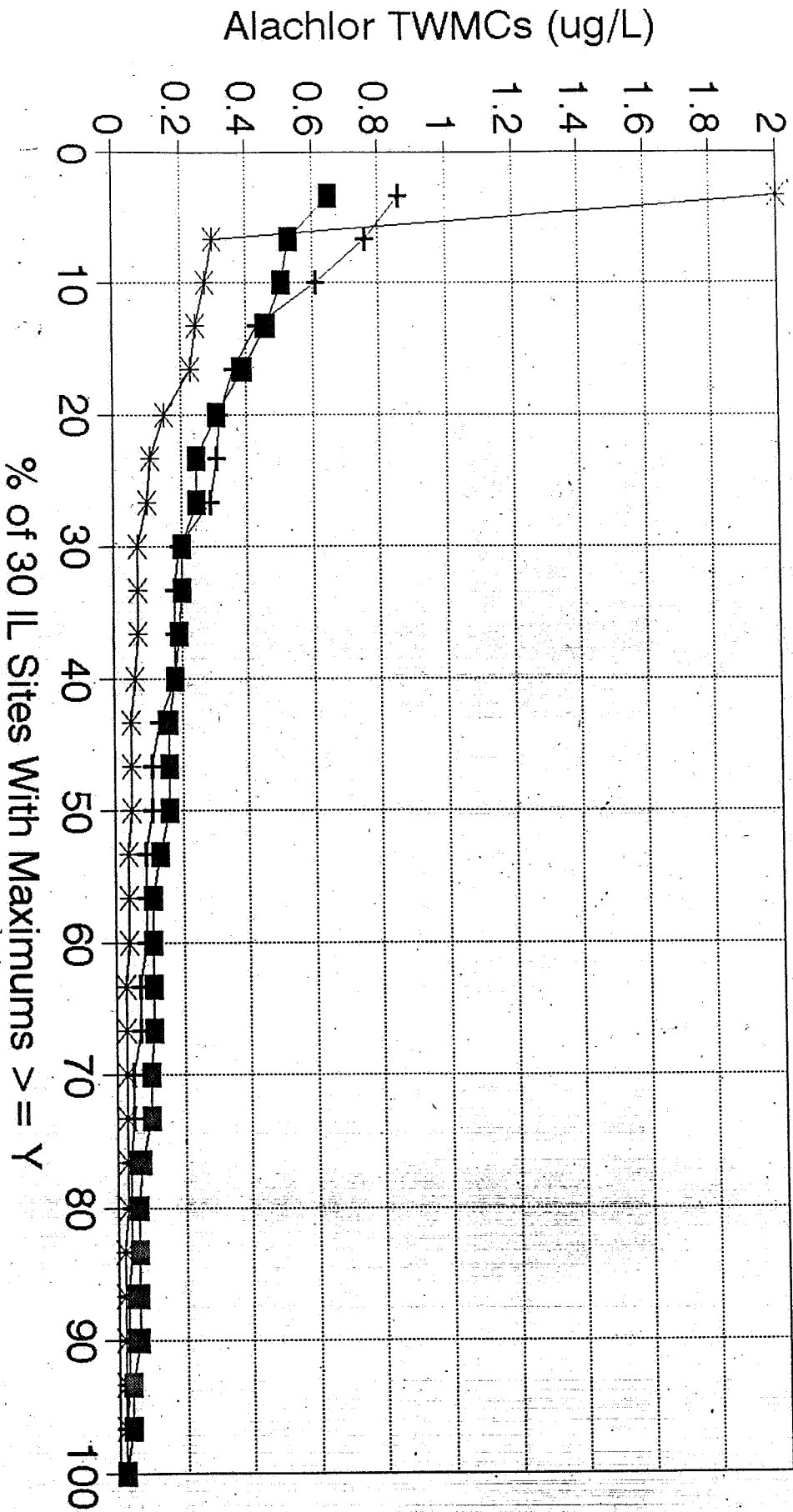
30 IL Sites (Data from Moyer&Cross)



Aalachlor Ann. TWMCs 1986-1988

30 IL Sites (Data from Moyer&Cross)

82

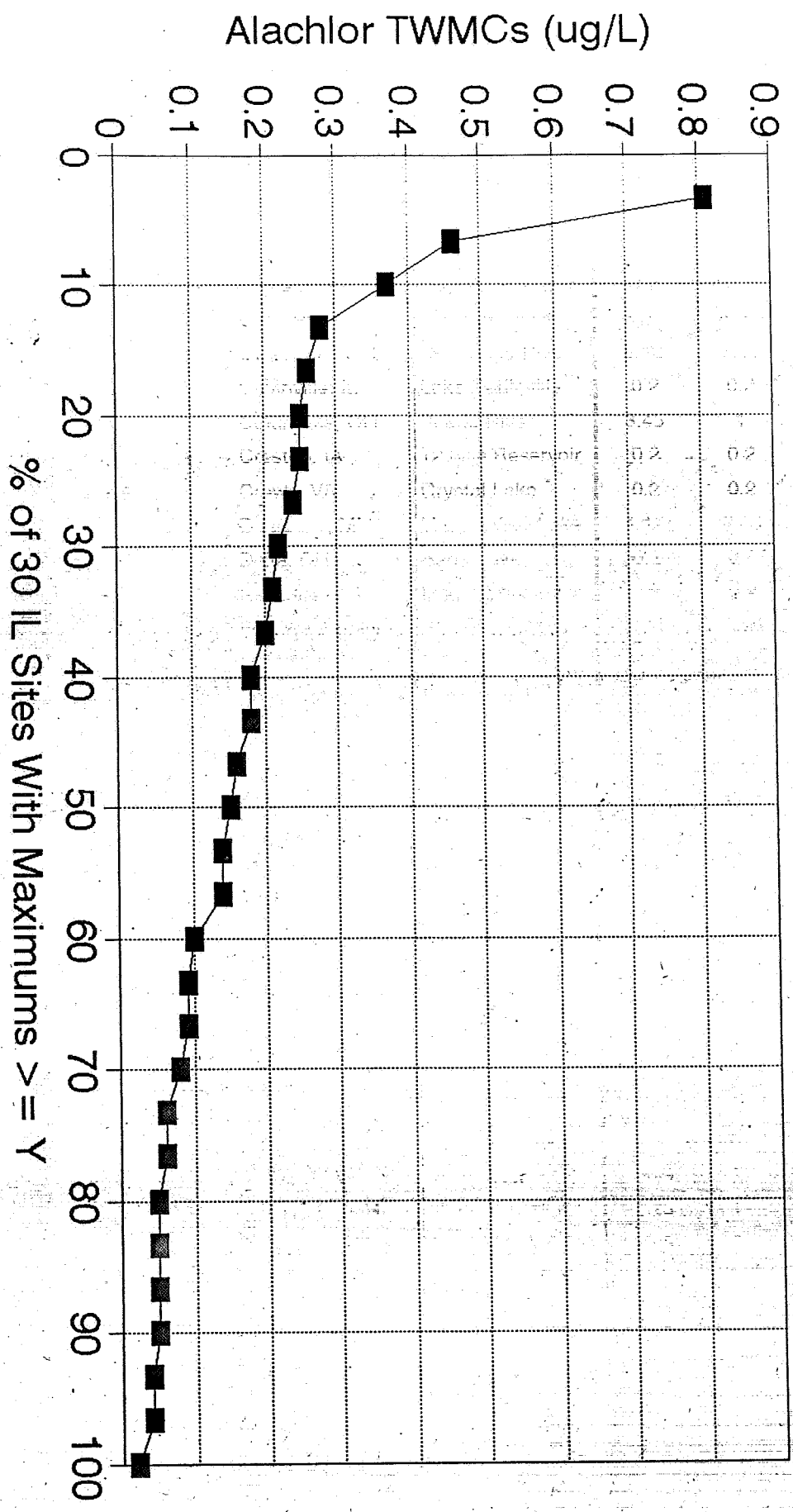


■ 1986 + 1987 * 1988

'86-88 Alachlor 3 Year TWMCs

30 IL Sites (Data from Moyer&Cross)

22



■ '86-88 3 Yr. TWMCs

Data from Smith etal (1987)

30 Finished water supplies in areas of alachlor use (primarily corn belt)

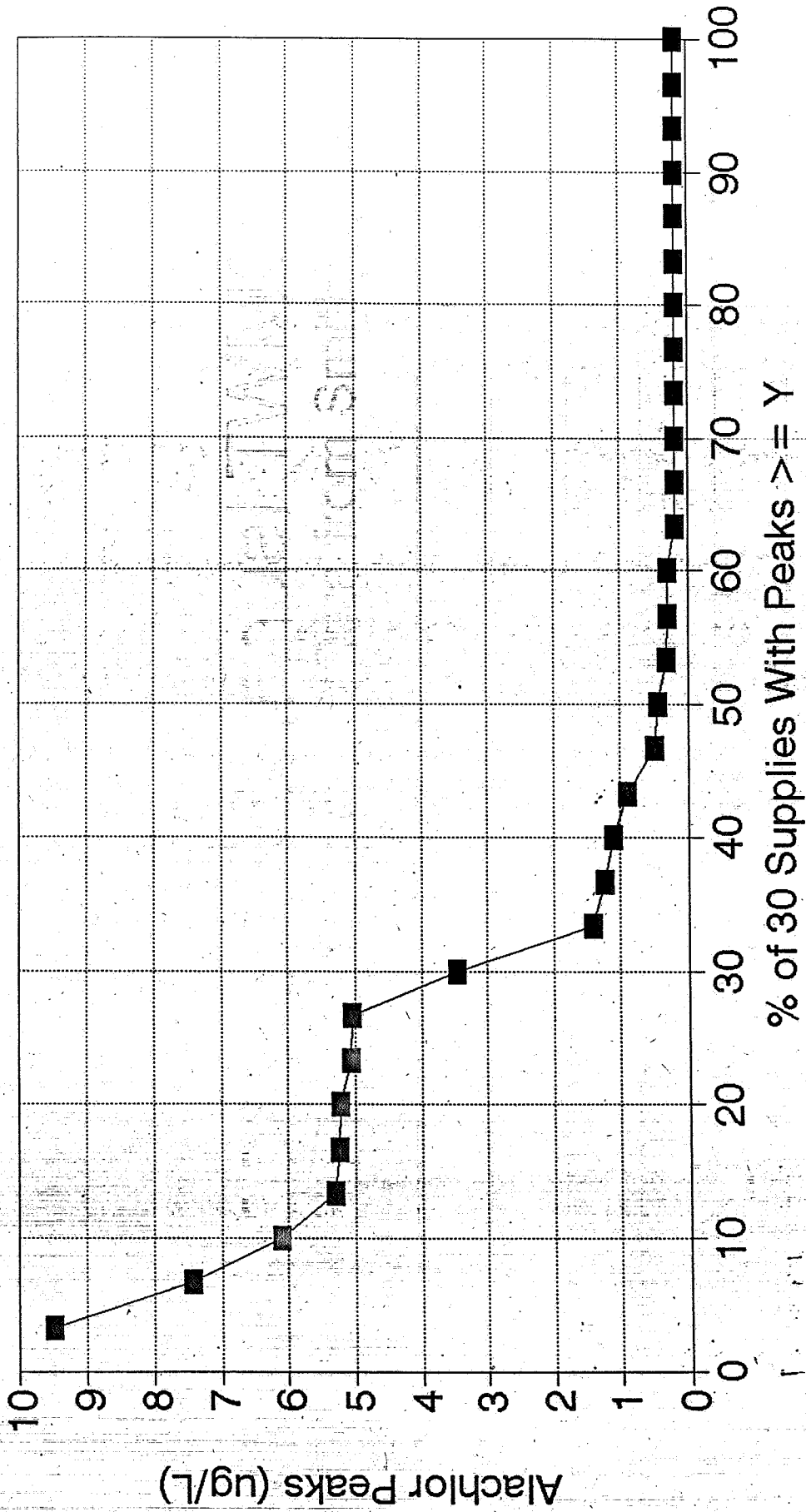
Most of the samples were collected weekly from April through August or September 1986

System	Source	Alachlor		
		Alachlor Peak (ug/L)	Arith. Mean (ug/L)	Alachlor Annual TWMC (ug/L)
Appleton, WI	Lake Winnebago	0.2	0.2	0.2
Bowling Green, O	Maumee River	5.21	1.25	0.66
Caledonia, OH	Olentangy River	9.48	1.41	0.73
Carlinville, IL	Lake Carlinville	0.2	0.2	0.2
Columbus, OH	Scioto River	3.45	1	0.59
Creston, IA	12 Mile Reservoir	0.2	0.2	0.2
Crewe, VA	Crystal Lake	0.2	0.2	0.2
Dearborn, MI	Unspecified Lake	1.12	0.35	0.26
Delta, OH	Bad Creek	0.2	0.2	0.2
Eskridge, KS	Lake Wabaunese	0.2	0.2	0.2
Fort Wayne, IN	St. Joseph River	5.03	1.25	0.6
Hettick, IL	Lake Treesen	0.2	0.2	0.2
Iowa City, IA	Iowa River	5.07	1.06	0.56
Jacksonville, IL	Mauviasterre R.	6.12	1.99	1.07
Jaratt, VA	Nottaway River	0.2	0.2	0.2
Jefferson Co., KS	Perry Lake	0.29	0.21	0.2
Macomb, IL	Spring Lake	1.42	0.36	0.27
Maysville, OH	Frasier's Quarry	0.2	0.2	0.2
Olathe, KS	New Olathe Lake	0.51	0.25	0.22
Ottawa, KS	Maraisdes Cygnes	0.2	0.2	0.2
Plattsburg, MO	Unspecified Lake	0.2	0.2	0.2
Pomona Lake, KS	Pomona Lake	0.45	0.26	0.22
Sabetha, KS	Sabetha Lake	0.91	0.4	0.29
Shelbina, MO	Shelbina Lake	0.3	0.21	0.2
Shipman, IL	Shipman R./Res.	7.43	0.91	0.91
Swanton, OH	Swan Creek	0.33	0.21	0.2
Univ. of IA	Iowa River	5.29	1.16	0.62
Waterville, OH	Maumee River	5.25	1.08	0.62
Westerville, OH	Alum Creek	1.25	0.26	0.23
White House, TN	Old Hickory Lake	0.2	0.2	0.2

84

Alachlor 1986 Peaks

30 Finished Supplies (Data from Smith)



■ Alachlor

Alachlor 1986 Annual TWMCs

30 Finished Supplies (Data from Smith)

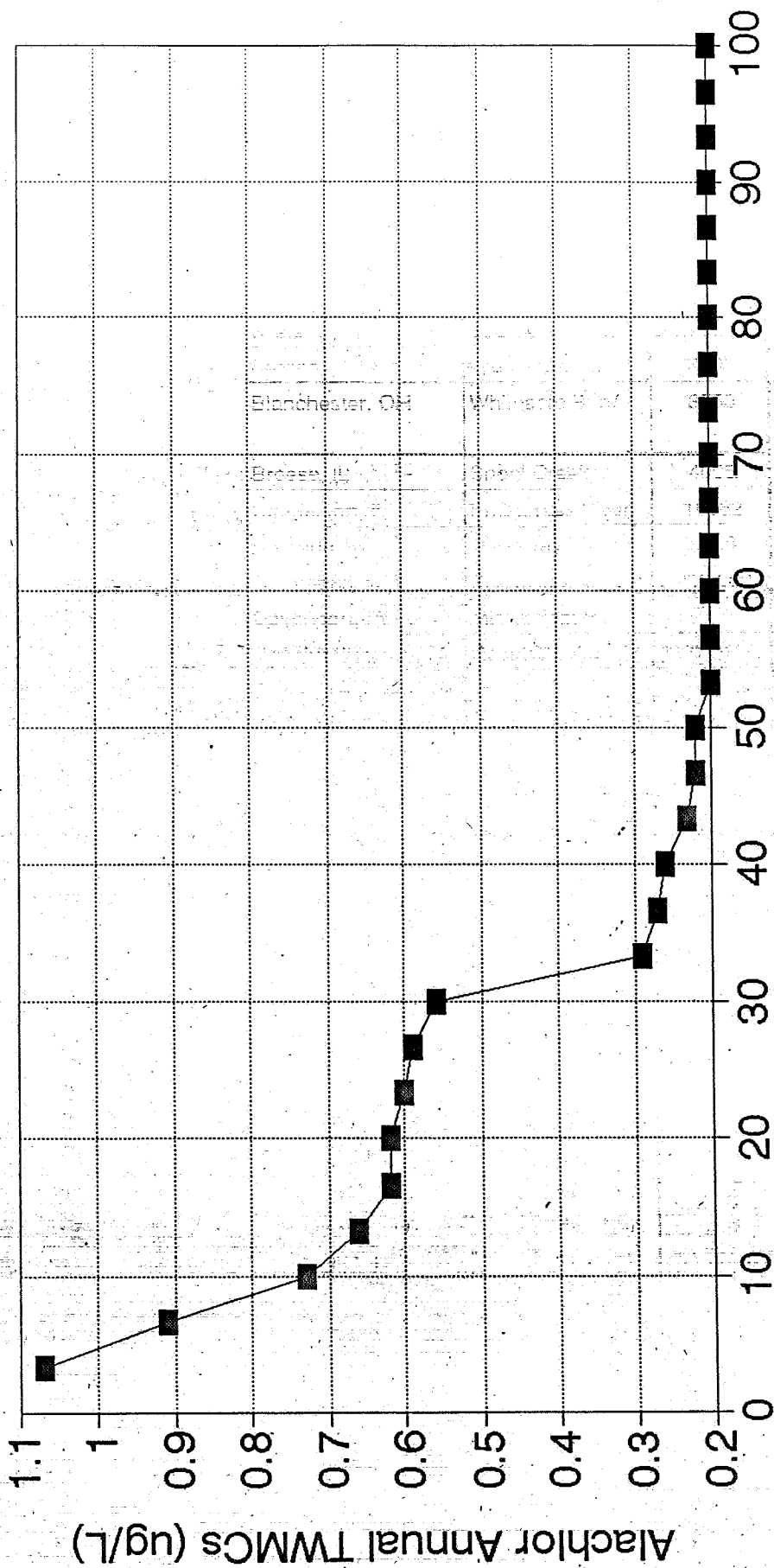


FIGURE 2.1 % of Supplies With Annual TWMCs \geq Y

TABLE 5
Data from Lauer et al (1986)

30 Water supplies mostly in areas of low to high alachlor use
Most of the samples collected weekly April 1985-Jan. or Feb. 1986

System	Source	Population	Raw Alachlor Peak (ug/L)	Raw Alachlor Arith. Mean (ug/L)	Raw Alachlor TWMC(1) (ug/L)	Finished Alachlor Peak (ug/L)	Finished Alachlor Arith. Mean (ug/L)	Finished Alachlor TWMC(1) (ug/L)
Bethany, MO	Old L./New L.	3090	0.2	0.2	0.2	0.2	0.2	0.2
Blanchester, OH	Whiteacre Run/	3750	1.26	0.36	0.33	1.1	0.34	0.31
Breese, IL	Shoal Creek	4095	4.57	0.51	0.47	4.45	0.49	0.45
Charleston, IL	Embarrass River	18162	0.2	0.2	0.2	0.2	0.2	0.2
Clarinda, IA	Nodaway River	5458	0.2	0.2	0.2	0.2	0.2	0.2
Columbus, OH	Scioto River	250,000	10.7	1.74	1.53	12	1.68	1.48
Davenport, IA	Mississippi R.	133,264	0.72	0.22	0.21	0.35	0.2	0.2
Decatur, IL	Decatur Lake	91,018	0.28	0.2	0.2	0.3	0.21	0.21
Greenville, NC	Tar River	37,000	0.26	0.2	0.2	0.28	0.2	0.2
Kankakee, IL	Kankakee River	56,232	0.85	0.26	0.25	0.79	0.25	0.24
Lexington, MO	Missouri River	5356	0.84	0.25	0.26	0.59	0.22	0.22
Marion, IL	Crab Orchard Lake	14,016	0.2	0.2	0.2	0.2	0.2	0.2
Michigan City, IN	Lake Michigan	36,250	0.2	0.2	0.2	0.2	0.2	0.2
Monroe, MI	Lake Erie	23,531	0.2	0.2	0.2	0.2	0.2	0.2
Mt. Vernon, IN	Ohio River	7610	1.46	0.26	0.25	1.21	0.24	0.24
Muncie, IN	White River	80,000	2.54	0.44	0.41	2.86	0.43	0.4
Piqua, OH	Miami River	21,500	1	0.25	0.24	0.63	0.22	0.22
Quincy, IL	Mississippi R.	48,000	0.54	0.22	0.22	0.64	0.24	0.23
Richmond, IN	Whitewater River	41,260	3.49	0.82	0.7	3.55	0.83	0.72
Roanoke Rapids, NC	Roanoke River	48,000	0.2	0.2	0.2	0.2	0.2	0.2
Toledo, OH	Lake Erie	388,000	0.2	0.2	0.2	0.2	0.2	0.2
Univ. of Iowa	Iowa River	8560	1.71	0.3	0.28	1.83	0.31	0.29
Wyaconda, MO	Wyaconda River	356	0.29	0.21	0.21	0.2	0.2	0.2
Ypsilanti, MI	Huron River	24,031	0.2	0.2	0.2	0.2	0.2	0.2

Alachlor 3/85-2/86 Peaks

30 Water Supplies (Data from Lauer 1986)

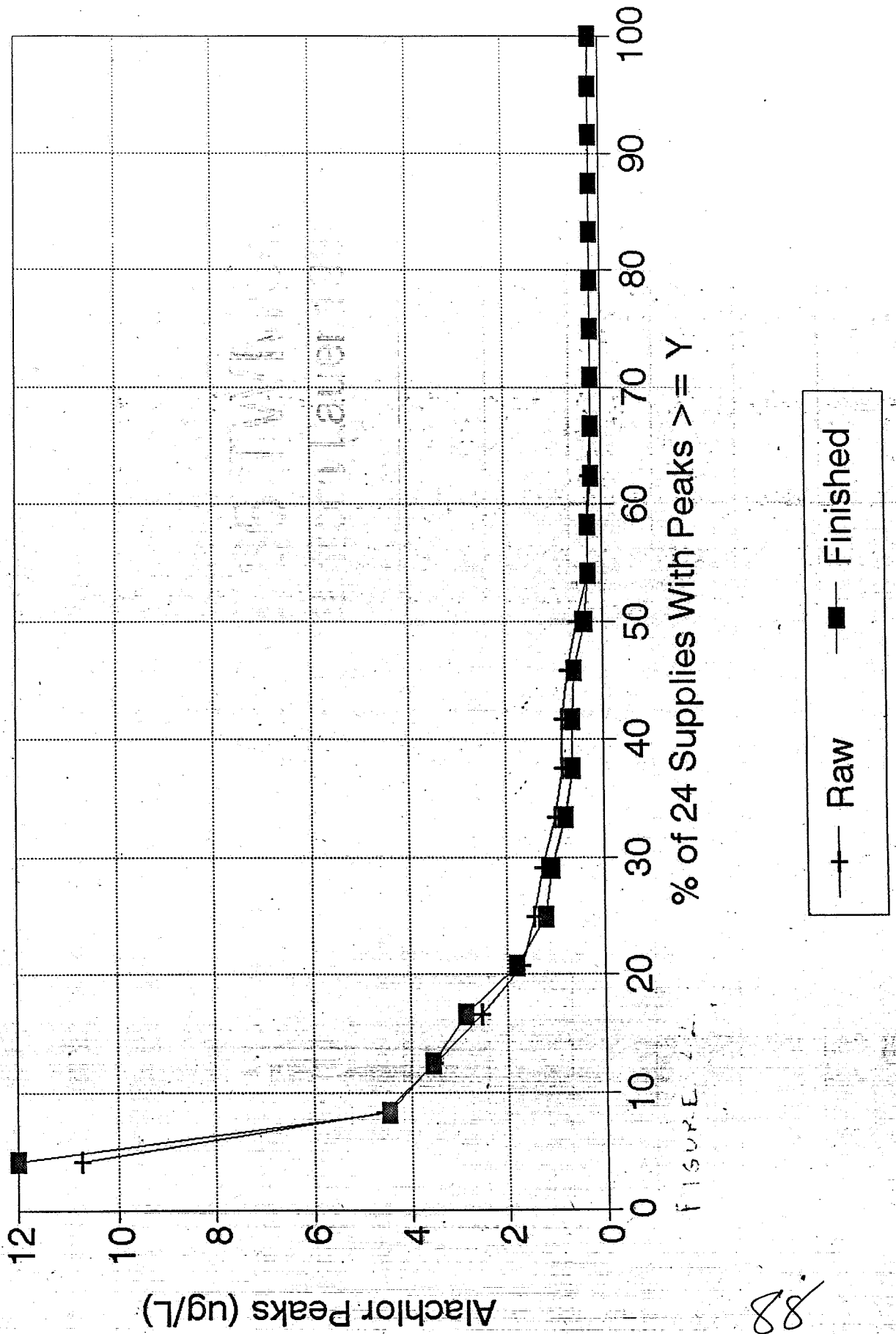


FIGURE 4.2

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Alachlor 3/85-2/86 TWMCs

30 Water Supplies (Data from Lauer 1986)

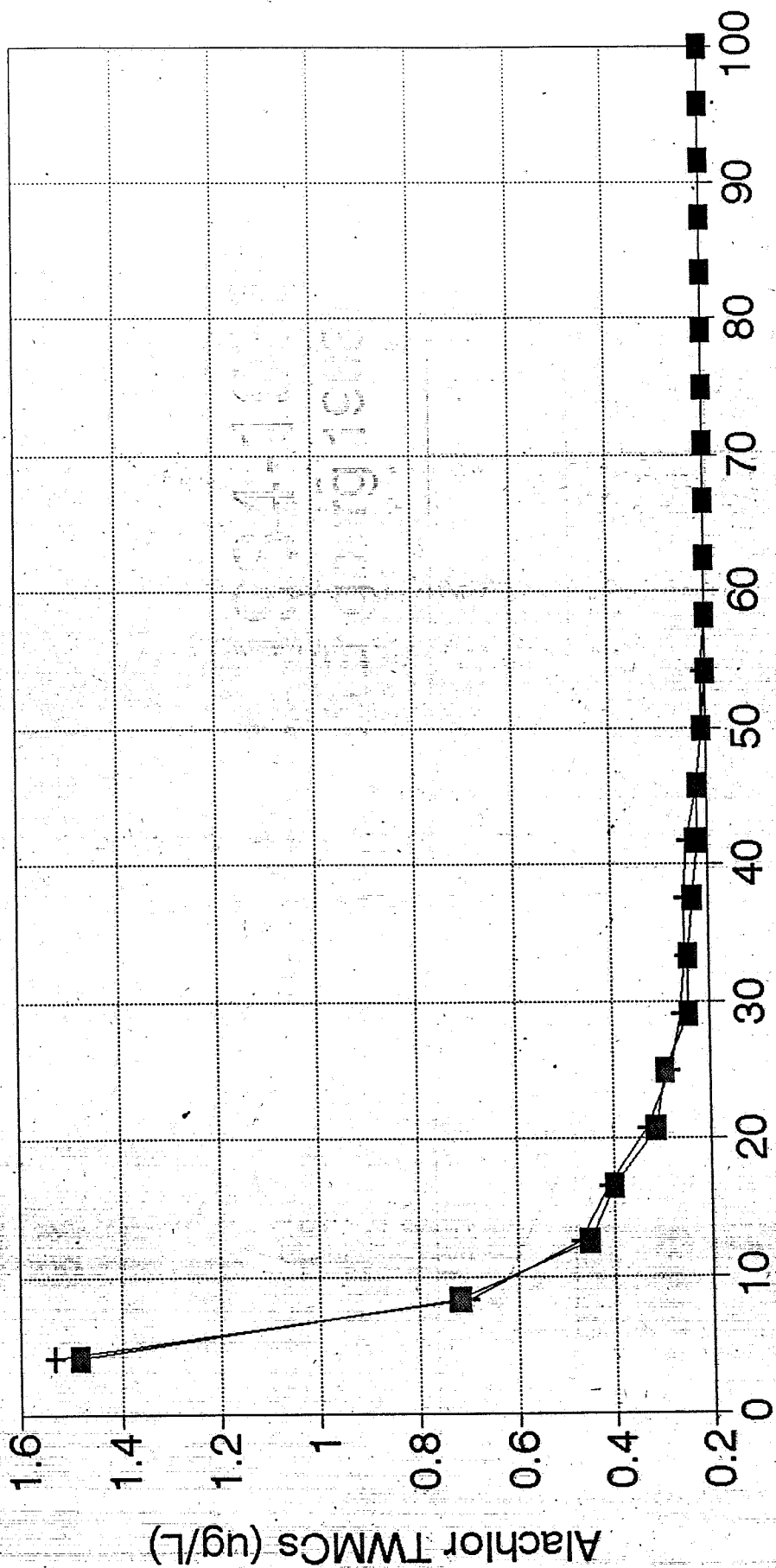


FIGURE 2-3 % of 24 Supplies With TWMCs $\geq Y$

Alachlor Peaks 1984-1985

6 IA Sites (Squillace & Engberg 1988)

(CEDAR RIVER BASIN)

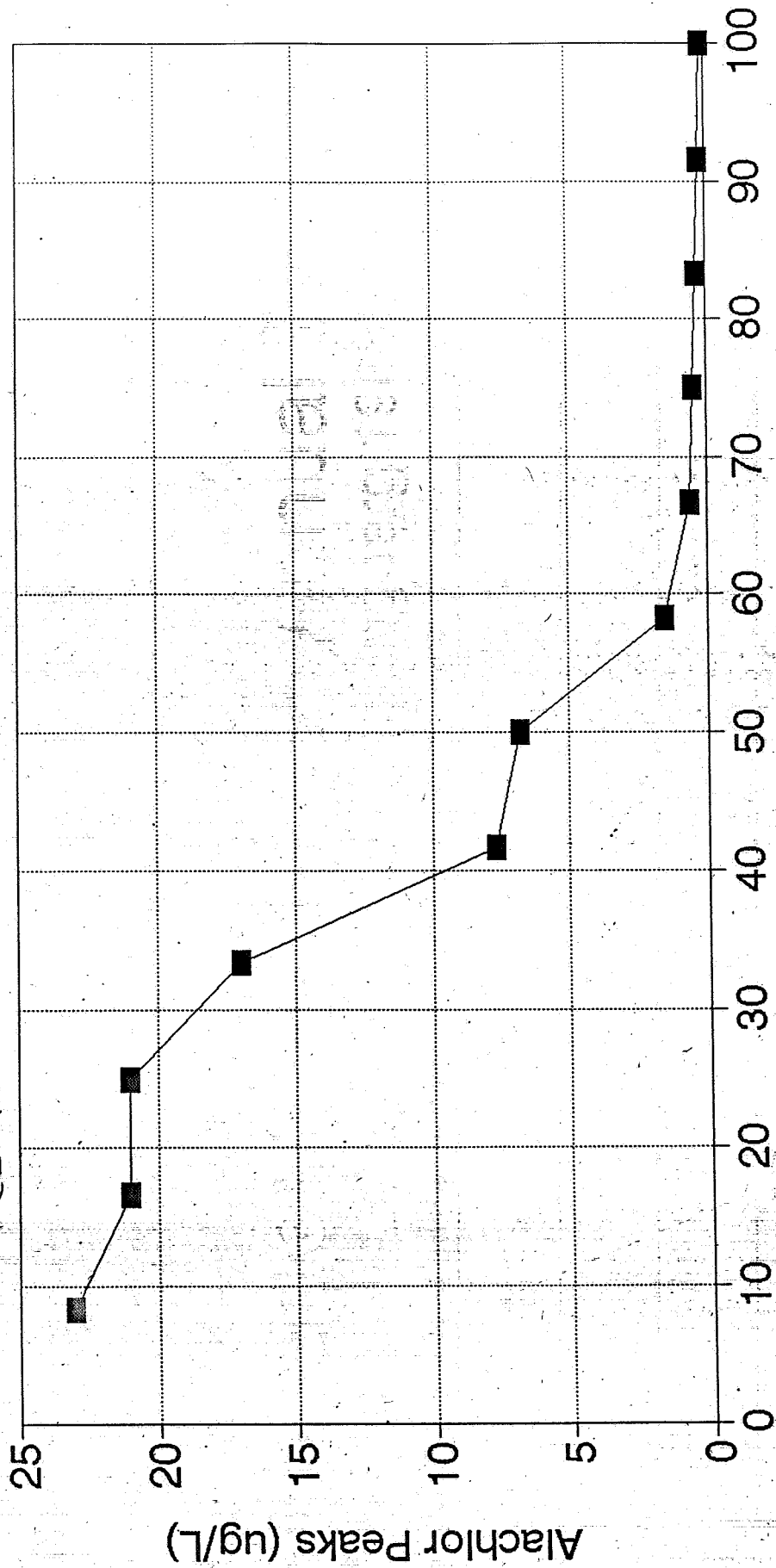
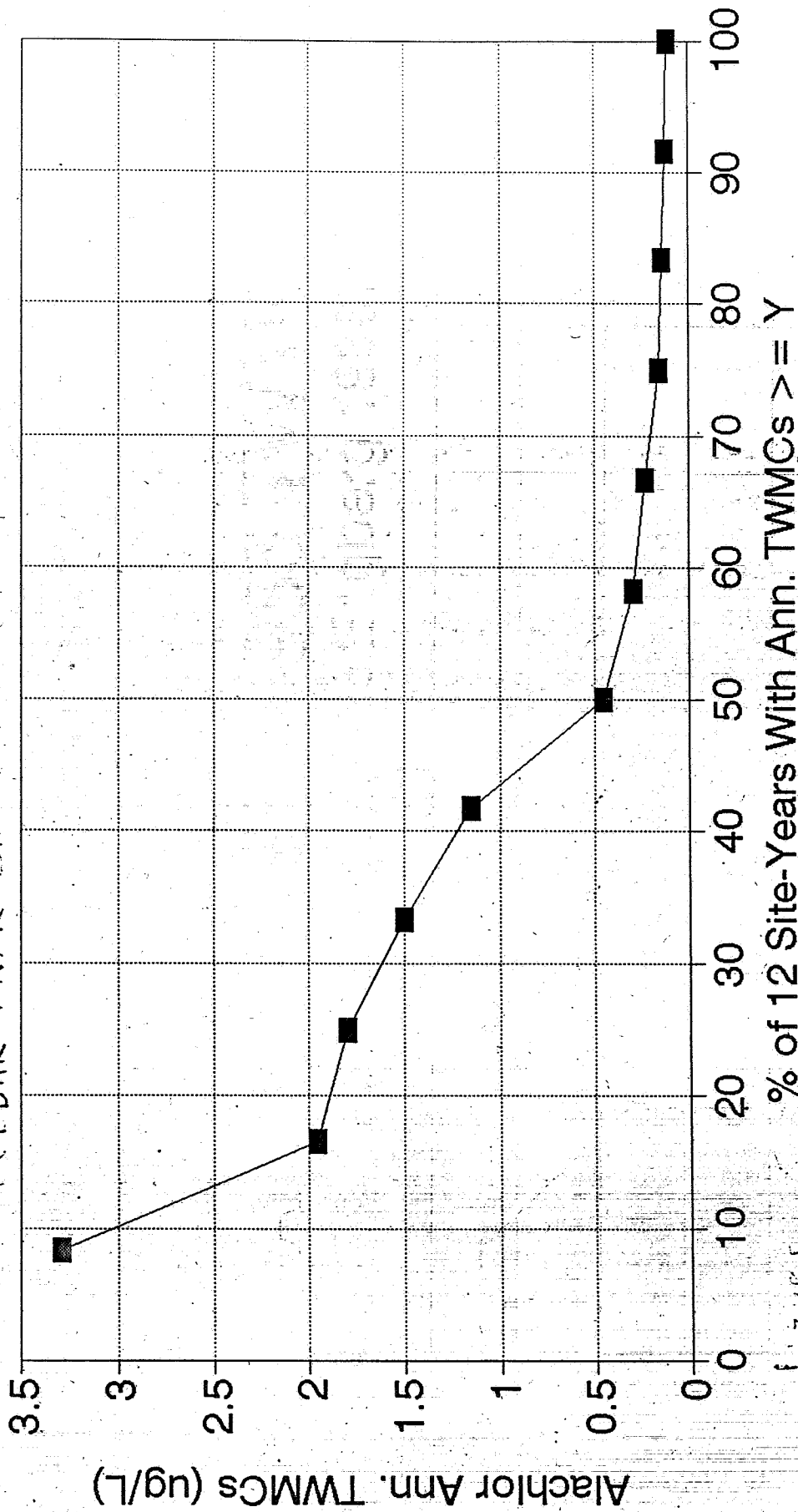


FIGURE 24 % of 12 Site-Years With Peaks \geq Y

Alachlor 1984 & 1985 Annual TWMCs

6 IA Sites (Squillace & Engberg 1988)

(CEDAR RIVER BASIN)



Alachlor 1984-1985 TWMCs

6 IA Sites (Squillace & Engberg 1988)

(CEDAR RIVER BASIN)

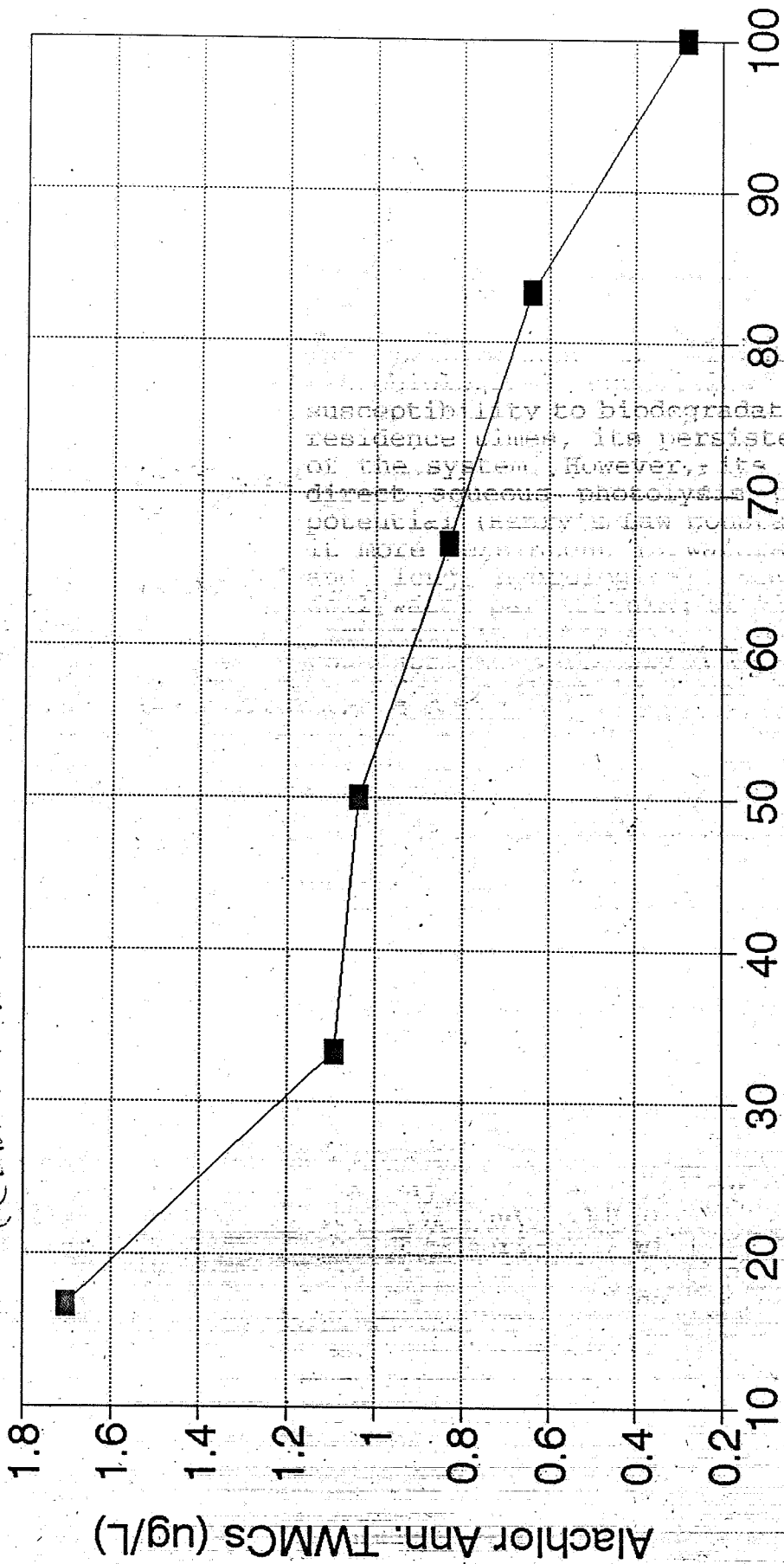


FIGURE 26

■ Alachlor

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Surface Water Assessment of Alachlor (May 28, 1996):

Alachlor can contaminate surface water at application via spray drift. Substantial fractions of applied alachlor could be available for runoff for several weeks post-application (aerobic soil metabolism half-life of 2-3 weeks; terrestrial field dissipation half-life of 11, 15, and 18 days). The relatively low soil/water partitioning of alachlor (SCS/ARS database K_{oc} of 170; K_d values of 3.74, 2.88, and 0.88) indicates that most of alachlor runoff will occur via dissolution in runoff water (as opposed to adsorption to eroding soil).

The persistence of alachlor in surface waters with high microbiological activities should be somewhat limited by its susceptibility to biodegradation. In waters with short hydrological residence times, its persistence will also be limited by flow out of the system. However, its resistance to abiotic hydrolysis and direct aqueous photolysis coupled with its low volatilization potential (Henry's Law constant = 3.2×10^{-8} atm*m³/mol) should make it more persistent in waters with low microbiological activities and long hydrological residence times. The relatively low soil/water partitioning of alachlor indicates that it will readily partition into the water column and that at equilibrium, alachlor concentrations dissolved in sediment pore water will be comparable to or only slightly lower than concentrations on suspended and bottom sediment. Concentrations dissolved in the water column will be somewhat less than concentrations dissolved in sediment pore water.

The major degradates of alachlor in the aerobic soil metabolism study were DM-oxanilic acid, alachlor oxanilic acid, and alachlor sulfonic acid (ESA). The available data are inadequate to fully assess the mobility and persistence of those degradates. However, the results of terrestrial field dissipation studies indicate they are more persistent than alachlor and their anionic properties indicate they are probably more mobile. ESA has frequently been detected in midwestern reservoirs and streams at concentrations much greater than alachlor. That indicates that it is mobile and probably much more persistent than alachlor in surface water. High concentrations of ESA in flowing water even in early Spring before alachlor application may reflect discharges from ground water.

The major degradates may be available for runoff longer than alachlor and will probably runoff primarily by dissolution in runoff water. They will probably readily partition into the water column and in addition to ESA, other degradates may also be more persistent in surface water than alachlor.

The octanol/water partition coefficient of alachlor and the mobility of alachlor and its major degradates suggests that their bioaccumulation potential is low.

Acetochlor Registration Partnership 1995 Data on Alachlor

The most recent and extensive data on alachlor in surface water was supplied to OPP by the Acetochlor Registration Partnership. It has been analyzed and summarized in detail by R. David Jones in a May 24, 1996 memo from him to EEB. Samples were collected at 175 sites in the following 12 states: DE, IL, IN, IA, KS, MD, MN, MO, NE, OH, PA, and WI. Samples were collected once every two weeks from April through September 1995. Two additional samples were collected at each site, one in the Fall and the other in the Winter. Unfiltered samples were analyzed for total alachlor.

Cumulative exceedence curves for peak, annual maximum 96-day time weighted mean, and annual time weighted mean alachlor concentrations over the 175 sites are provided in Figures 1, 2, and 3 (from the Jones memo), respectively. The maximum peak, annual maximum 96-day, and annual time weighted mean acetochlor concentrations were 4, 0.8, and 0.3 ug/L, respectively. The 90th percentile (upper 10th percentile site) peak, annual maximum 96-day, and annual time weighted mean acetochlor concentrations were approximately 0.37, 0.15, and 0.08 ug/L, respectively.

USGS 1989, 1994, and 1995 Midwestern Stream Reconnaissance Studies

Since the data submitted by the Acetochlor Registration Partnership was for samples collected at set intervals once every two weeks, it is probable that the data are generally substantially lower than peak alachlor concentrations associated with post-application runoff events. Such peak alachlor concentrations are probably more closely represented by post-application data collected by the USGS in reconnaissance studies conducted on numerous midwestern streams. The USGS (Goolsby/Thurman 1991; Goolsby 1995; Goolsby 1996) conducted reconnaissance surveys of numerous midwestern streams in 1989, 1994, and 1995 to determine post-application, and in some cases pre-application and Fall concentrations of various herbicides including alachlor. Pre-application samples collected in 1989 and 1994 and Fall samples collected in 1989 had alachlor concentrations much less than 1 ug/L and generally below the detection limit of 0.05 ug/L.

Cumulative frequency curves for post-application alachlor concentrations are given for 129 streams in 1989 and 50 of those streams in 1994 and 1995 in Figures 4, 5, and 6, respectively. Since post-application samples were generally collected during the first major runoff event after application, the concentrations in those samples should generally approximately represent peak alachlor concentrations. The maximum post-application alachlor concentrations for 1989, 1994, and 1995 were 51.3, 10.1, and 19.9 ug/L, respectively. The 90th percentile (upper 10th percentile) post-application alachlor concentrations for 1989, 1994, and 1995 were 12, 6.5, and 2.0 ug/L, respectively. The substantially lower concentrations in 1994/1995 than in 1989 may reflect reported decreases in alachlor use.

In 1989, a pre-application sample, a post-application sample, and a Fall sample were collected from 48 of the sites. A cumulative

frequency curve for annual time weighted mean concentrations (TWMCs) based on 3 samples from each site is given in Figure 7. The maximum and 90th percentile (upper 10th percentile) annual TWMCs were 11.6 and 3.4 ug/L, respectively. Annual TWMCs based on 4 quarterly samples (as specified to determine compliance with the Safe Drinking Water Act) probably would have been somewhat lower but not more than 25% lower.

In 1994 and 1995, samples were analyzed for ESA as well as alachlor. Consequently, ESA is also included on the post-application cumulative frequency curves for alachlor for 1994 (Figure 5) and 1995 (Figure 6). As can be seen, ESA concentrations are much higher than alachlor. That also appears to be true in early Spring even before alachlor application as can be seen from Figure 8. Because of the much greater concentrations in surface water of ESA than alachlor even in samples collected in the early spring prior to alachlor application, EFGWB strongly recommends that both HED and EEB accurately determine the toxicity of ESA so that a risk assessment can be performed for it.

USGS 1991-1992 Study of 8 River Locations Mississippi River Basin

The USGS (Coupe et al 1995) sampled 8 locations on rivers within the Mississippi Basin from April 1991 through March-September 1992 (depending on location) and analyzed the samples for numerous insecticides and herbicides including alachlor. Samples were collected twice per week from May 6 to July 15 1991, once per every two weeks from November 1991 to February 1992, and once per week at other times. The samples were filtered (0.7 u) and analyzed for dissolved alachlor. Alachlor 1991 peaks and 1991 annual time weighted mean concentrations are listed in Table 1 and are plotted as cumulative frequency curves in Figures 9 and 10. The maximum peak and 1991 annual time weighted mean concentrations over the 8 sites were 3.6 ug/L and 0.43 ug/L, respectively (both in the Platte River at Louisville NE).

Concentration versus time plots for the three sites with the highest 1991 alachlor concentrations are provided in Figures 11, 12, and 13. The shapes of the plots are similar to those commonly seen for atrazine and cyanazine, but the peak concentrations are lower. Pre-application concentrations of less than 0.1 ppb in early Spring rapidly increase to several ppb during post-application runoff events in May and June, then rapid decline to background levels by mid-late summer. The White River at Hazelton IN site was the only one of those three sites at which sampling was performed far enough into 1992 to give a second set of alachlor peaks (1992) in addition to the 1991 set. It can be seen from Figure 11 that alachlor concentrations in 1992 were lower than in 1991 at that site.

USGS 1992 Midwestern Reservoir Reconnaissance Study

The USGS (Goolsby et al 1993) sampled each of 76 midwestern reservoirs four times during 1992 and analyzed them for various herbicide degradates and herbicides including alachlor and ESA. Alachlor was detected above a detection limit of 0.05 ug/L in 36%, 48%, 26% and 16% of the samples collected in late April to mid-May, late June to early July, late August to early September and late October to early November, respectively. ESA was detected more frequently (72, 79, 77, and 64%) and at higher concentrations than alachlor. A box plot showing the distributions of alachlor and ESA over the 76 reservoirs is given in Figure 14 which is a copy of Figure 4 in the Goolsby et al 1993 article. The highest alachlor and ESA concentrations were for samples collected in June or July of 1992. The maximum and 95th percentile alachlor concentrations for June-July over the 76 reservoirs appear to be between 5 and 10 ug/L. The maximum and 95th percentile ESA concentrations for June-July appear to be between 10 and 20 ug/L. After June-July, alachlor concentration appear to decrease more substantially than ESA concentrations. We are currently attempting to obtain the raw data necessary to perform further analyses.

Missouri River Public Water Supplies Association 1990 Study

The Missouri River Public Water Supplies Association (MRPWSA) sampled the raw water of 8 surface water supplies within the Missouri River Basin. Samples were collected daily May-July 1990. The peak and mean concentrations are listed in Table 2 and are plotted as cumulative frequency curves in Figures 15 and 16. The maximum peak and May-July mean concentrations were 14.9 and 0.47 ug/L, respectively (both at Kansas City MO). However, the second highest peak and May-July mean concentrations were 2.9 and 0.29 ug/L, respectively. The annual mean concentrations should be greater than 25% of the May-July means.

State of Illinois 1986-1988 Study

The State of Illinois (Moyer and Cross 1990) collected 4-7 samples per year from each of 30 flowing surface water sites during 1986-1988 and analyzed the unfiltered samples for numerous pesticides including alachlor. The peak concentration for each year, the annual TWMC for each year, and the 3 year 1986-1988 TWMC are listed for each of the 30 sites in Table 3. Cumulative exceedence curves for the peak concentrations, annual TWMCs and the three year TWMCs are given in Figures 17, 18, and 19, respectively. The maximum alachlor peaks over the 30 sites were 5.6, 8.5, and 18 ug/L for 1986, 1987, and 1988, respectively. The maximum alachlor annual TWMCs over the 30 sites were 0.65, 0.76, and 2.0 ug/L for 1986, 1987, and 1988, respectively. The maximum three year TWMC over the 30 sites was 0.81 ug/L.

The State of Illinois (Taylor 1994) recently summarized pesticide data for surface water samples collected from 34 stations from 10/1/85 through 2/15/94. Thirty of the stations were the same ones

discussed in the Moyer and Cross 1990 document, but the Taylor summary represents a update to February 1992. A total of 1278 samples were analyzed for alachlor at a detection limit of 0.05 ug/L. Apparently assuming non-detects were equal to the detection limit, Illinois reported maximum, 95th percentile, 90th percentile, and mean total (unfiltered sample) alachlor concentrations over the 34 sites and 9 years of 18 ug/L, 0.90 ug/L, 0.32 ug/L, and 0.065 ug/L, respectively.

Monsanto 1986 Finished Surface Water Supply Study:

In 1986, Monsanto sampled 30 finished surface water supply systems approximately weekly from April through August or September (Smith et al, 1987) and analyzed the samples for 5 herbicides including principally alachlor. The community water systems resampled represented 4 combinations of Lasso (alachlor) use and average soil susceptibility to runoff (high use/high runoff, low use/high runoff, high use/low runoff, low use/low runoff). The susceptibility to runoff was estimated from the weighted average of hydrological classifications (A, B, C, D) of soils within the drainage area. Of the 30 community water systems sampled, 13, 2, and 15 were classified as using sources which drain areas with high, intermediate, and low susceptibility to runoff, respectively.

The total (unfiltered samples) alachlor peak and 1986 annual TWMCs for the 30 systems (along with population served) are listed in Table 4 and are plotted as cumulative exceedence curves in Figures 20 and 21. The maximum and 90th percentile (upper 10th percentile) peak alachlor concentrations over the 30 systems were 9.5 and approximately 6.0 ug/L, respectively. The maximum and 90th percentile (upper 10th percentile) alachlor annual TWMCs over the 30 systems were 1.1 and approximately 0.73 ug/L, respectively.

Monsanto 1985 Finished Surface Water Supply Study:

In 1985, Monsanto had sampled 30 finished surface water supply systems different from the ones sampled in 1986. They also sampled raw water. Samples were collected approximately weekly from April 1995 through August or September 1995 (Lauer et al, 1986) and analyzed only for alachlor. The community water systems sampled represented areas of high, medium and low alachlor use.

The total (unfiltered samples) alachlor peak and 1985 annual TWMCs for the 30 systems (along with population served) are listed in Table 5 and are plotted as cumulative exceedence curves in Figures 22 and 23. The maximum and 90th percentile (upper 10th percentile) peak alachlor concentrations in finished water over the 30 systems were 12 and approximately 4.2 ug/L, respectively. The maximum and 90th percentile (upper 10th percentile) alachlor annual TWMCs over the 30 systems were 1.5 and approximately 0.62 ug/L, respectively.

Due to the low soil/water partitioning of alachlor, the primary treatment processes employed by most surface water supply systems are not expected to be effective in removing it. Figures 22 and 23

support that by showing that the alachlor concentrations in raw water were comparable to those in finished water.

USGS 1984-1985 Study on the Cedar River Basin IA

The USGS (Squillace and Engberg 1988) collected samples at 6 locations within the Cedar River Basin (5 along the Cedar River and one along the Shell Rock River. Samples were collected approximately monthly from May 1984 through September 1985 at the Floyd and Cedar Falls sampling locations, and from May 1984 through November 1985 at the other 4 locations.

Two sets of samples were collected. One set was centrifuged for the determination of the dissolved concentrations of herbicides. "Total recoverable" herbicide concentrations consisting of both extractable adsorbed and dissolved herbicides were determined in the sample set not centrifuged.

Dissolved alachlor peak concentrations and annual TWMCs are plotted as cumulative frequency curves over the 12 site-years (6 sites each over 2 years) in Figures 24 and 25. Two year TWMCs are plotted over the 6 sites in Figure 26. The maximum peak and annual TWMC concentrations over the 12 site-years were 23 and 3.3 ug/L, respectively. The next highest peak and annual TWMCs were 21 and 1.9 ug/L, respectively. The maximum two year TWMC over the 6 sites was 1.7 ug/L.

Baker 1982-1985 Study on Ohio Tributaries to Lake Erie

Baker collected samples at various times including several times per week from mid-April to mid-August from 8 Ohio tributaries to Lake Erie during 1982-1985 and analyzed them for many pesticides including alachlor. Alachlor Peak and 4/15-8/15 TWMCs concentrations were reported. They are listed in Table 6 and plotted as cumulative exceedence curves over 30 site-years (8 sites over 3 years plus six of the sites over another year) in Figure 27 and over 24 site-years (8 sites over 3 years) in Figure 28.

The maximum and 90th percentile (upper 10th percentile) peak alachlor concentrations over the 30 site-years are 76 and 32 ug/L, respectively. The maximum and 90th percentile (upper 10th percentile) 4/15-8/15 TWMCs over the 24 site-years are 3.3 and 2.7 ug/L, respectively. Annual TWMCs should be greater than 33% of the 4/15-8/15 TWMCs.

Possible Concerns Over Alachlor and ESA in Surface Water:

According to EEB, the potential risks to fish and aquatic invertebrates posed by alachlor in surface water are low. Potential risks to aquatic plants posed by alachlor are currently being assessed by EEB. The potential risks of ESA to fish, aquatic invertebrates and aquatic plants has not been well characterized.

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In analyzing surface water concentration data, the EFED considers the frequency that annual averages exceed the drinking water MCL (for alachlor, 2 $\mu\text{g}/\text{l}$), and the frequency that peak concentrations exceed the MCL by a factor of 4 or more. Compliance with the Safe Drinking Water Act is based on comparison of the MCL to an arithmetic average of four quarterly measurements. Consideration of 4 times the MCL (4MCL) is of interest because if one or more of four measurements exceeds 4MCL, then the average of the measurements exceeds the MCL.

Most of our original concern over alachlor in drinking water was due to individual alachlor measurements frequently exceeding 4MCL. The frequency of exceedences of 4MCL was greatest in the 1989 USGS reconnaissance study in which samples were collected during major runoff events following application, and in the study by Baker (1988), in which samples were apparently collected at least 3 times a week and not time composited. They were less frequent in the 1994 and 1995 USGS reconnaissance studies (which were also designed to capture peak concentrations) possibly due to decreases in alachlor use.

With the exception of 2 site-years in the 1984-1984 USGS study of the Cedar River Basin and one site-year in the 1986-1988 Illinois EPA study, none of the annual TWMCs for alachlor exceeded the MCL of 2 ug/L . This includes the 1985-1986 Monsanto studies of drinking water supplies and the recent 1995 Acetochlor Registration Partnership study of 175 sites over 12 states. In that study, the maximum annual TWMC was only 0.26 ug/L . Although the study used set sampling intervals that may often miss peak concentrations associated with runoff events, the once every two weeks sampling from April through September and the Fall and Winter samples (a total of 14/site) is much more than the 4 quarterly samples required under the SDWA. Again, the relatively low alachlor concentrations compared to some earlier studies may reflect substantial decreases in alachlor use.

Alachlor is currently regulated under the Safe Drinking Water Act (SDWA). Water supply systems will be considered out of compliance with respect to alachlor if annual average alachlor concentrations exceed the MCL of 2 ug/L . Since water supply systems are required to sample and analyze for alachlor under the SWDA, EFED is not currently recommending that any monitoring of surface water source drinking water for alachlor be required as a condition for reregistration. However, EFED recommends the following. If the results of the monitoring programs indicate that the annual average concentration of alachlor exceeds the MCL at one or more surface water source supply systems, the following is recommended:

If any community water supply system (that derives its water primarily from surface water) has an annual time weighted mean concentration of alachlor exceeding the MCL of 2 ug/L , then either:

- (1) The registrant will adsorb 100% of treatment and monitoring costs required to restore the system to compliance (if alachlor is

adjacent surface waters with vegetated filter strips, and areas over-laying tile drainage systems that drain to surface water.

RE: ADDITIONAL COMMENTS FOR ACCEPTED PLAN

INTRODUCTION:

The following memo is to update previous document by the Environmental Field and Ground Water Group regarding the proposed plan. The plan includes the following items:

MEMORANDUM

FROM: James K. Wolf, Soil Physicist
Ground Water Technology Section

THRU: Elizabeth Behl, Section Head
Ground Water Technology Section
Environmental Fate and Ground Water Branch

TO: José Luis Meléndez, Chemist
Environmental Chemistry Review Section #2
Environmental Fate and Ground Water Branch

RE: Additional comments for Alachlor RED - Ground Water

JK Wolf 6/5/96
EBehl

INTRODUCTION:

BACKGROUND:

The following memo is to update previous documents (2) completed by the Environmental Fate and Ground Water Branch, Ground Water Technology Section's, Kevin J. Costello as part of the RED process for alachlor. This memo also considers the Sections response to the registrant rebuttal to the "draft" RED chapter.

CONCLUSIONS:

Ground-water monitoring data collected, since 1991, by the USGS and the Acetochlor Registration Partnership (ARP) have found alachlor parent in two to eight percent of ground-water wells sampled. Less than 1.5 percent (0.03 to 1.1%) of these wells were found to have alachlor residues above the MCL of 2.0 $\mu\text{g}/\text{L}$. These recent monitoring data are in agreement with earlier studies (e.g., those reported in Pesticides in Ground Water Data Base, Hoheisel et al., 1992). The maximum and minimum alachlor concentrations were 15.89 $\mu\text{g}/\text{L}$ and 0.05 $\mu\text{g}/\text{L}$, respectively.

Monitoring data collected by the USGS (Kolpin and Goolsby, 1995; Kolpin et al., 1995; Kolpin et al., 1996) also indicates that in addition to alachlor, more than 40 percent of the wells sampled in midcontinental US were contaminated with alachlor-ESA degradate and/or 16 percent were contaminated with the alachlor 2,6-diethylalanine degradate. There is no ground water monitoring data on the other two major degradates (alachlor oxanilic acid and sulfinylacetic acid). These results correspond with the fate data, which indicates that these alachlor degradates are more mobile and persistent than the parent compound.

These recent studies reflect that current alachlor use may still result in ground-water concentrations which exceed the LOCs for alachlor parent as detections have occurred which exceed the MCL of 2.0 $\mu\text{g}/\text{L}$. Since a much greater proportion of ground water wells are impacted by alachlor degradates, if an MCL or cancer

risk level is established for alachlor-ESA at the same level as alachlor parent, levels-of-concern would much greater than for the parent compound only.

Similar chemicals, acetochlor, metolachlor, and propachlor have also found in ground water. Approximately, the same percentage of wells have been found to be contaminated by propachlor (1.2%) as alachlor (1.8%), although many fewer wells have been analyzed for propachlor. Although number of wells sampled for metolachlor and alachlor are similar, there are approximately twice as many wells with detections of alachlor (1.8%) residues than metolachlor (0.96%). Acetochlor, with a maximum of 2.17 $\mu\text{g/L}$, was detected in eight wells (4.6%) of 173 in the registrant's ground-water monitoring study.

BACKGROUND:

Detections of alachlor degradates in ground water are important because ground water may represent an important means of exposure. Four major degradates have been identified for alachlor: alachlor DM oxanilic acid, alachlor sulfinylacetic, alachlor sulfonic acid (ESA), and alachlor oxanilic acid. As noted above, the four degradates are more persistent than the parent compound. The Branch previously requested batch equilibrium studies on the degradates to assess their mobility. The registrant has proposed using adsorption data from two propachlor degradates as surrogate data for the alachlor degradates. The Branch has accepted this for two degradates, but will still require the determination of the mobility for the alachlor-ESA degradate.

CURRENT AND RECENT GROUND WATER MONITORING DATA

Because of their similarity (both chemically and/or use) with alachlor, monitoring results for alachlor and the herbicides acetochlor, atrazine, metolachlor, and propachlor are presented and discussed. These monitoring data are summarized in Tables 2 and 3.

USGS Midcontinent Ground Water Monitoring Studies: In 1991, the USGS sampled 303 wells from a reconnaissance well monitoring network in near-surface aquifers distributed across 12 midwestern states (Kolpin et al., 1995) (Table 1). These wells were distributed geographically and hydrogeologically by state, aquifer class (unconsolidated vs bedrock), and relative depth. At least 25% of the land within a 3.2 km radius of the well was in corn or soybean production during the 1990 growing season. One hundred wells were resampled during 1992 by selecting wells using a stratified random design based upon State and aquifer class.

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The USGS found that five of the six most frequently detected pesticide compounds detected in ground water of 12 midwestern states were pesticide metabolites (Kolpin et al., 1995). Kolpin et al. (1996) also demonstrated that as the analytical reporting limits are decreased, there is an increase in the differences in frequencies of detections. Alachlor-ESA is reported almost 10 times more frequently than parent alachlor at the 0.05 $\mu\text{g/L}$ level.

Alachlor was detected in 6 wells (2%) out of 303 wells in 1991 and 5 wells (5%) out of 100 wells in 1992 in near-surface aquifers in 12 midwestern states (Kolpin et al., 1995). The alachlor reporting limits were 0.05 and 0.002 $\mu\text{g/L}$ for 1991 and 1992, respectively. The degradate alachlor-ESA was the most frequently detected compound detected in 1992, found in 33 wells (45%) of 73 wells for which the degradates were analyzed, with a reporting limit of 0.10 $\mu\text{g/L}$. In the same study, metolachlor was detected in 12 wells (4%) out of 303 in 1991; and, 11 wells (11%) out of 100 in 1992, with the same reporting limits as stated for alachlor. None of the metolachlor detections exceeded existing drinking water standards.

Additional samples were collected in 1993 (110 wells) and 1994 (38 wells) from unconsolidated aquifers (Kolpin et al., 1996). Alachlor was detected in 10 wells (3.3%) out of 303 wells. Alachlor parent was found in 5.9% of the 153 wells for which metabolites were analyzed. The maximum alachlor concentration detected was 4.27 $\mu\text{g/L}$, with a reporting limit of 0.05 $\mu\text{g/L}$. The alachlor degradate ESA was found in 70 wells (45.3%) of 153 wells analyzed for degradates. The maximum concentration of ESA was 8.63 $\mu\text{g/L}$, with a 0.10 $\mu\text{g/L}$ reporting limit. A second alachlor degradate, 2,6-diethylalanine, was also detected in 15 wells (16%) of 94 wells analyzed. The maximum concentration was 0.02 $\mu\text{g/L}$ with a reporting limit of 0.003 $\mu\text{g/L}$.

Atrazine degradates deisopropylatrazine (10% of 303 well; maximum concentration of 1.17 $\mu\text{g/L}$) and deethylatrazine (22.8% of 303 wells; maximum concentration 2.20 $\mu\text{g/L}$) were also detected. Metolachlor was also detected at levels above 0.05 $\mu\text{g/L}$ in 8 wells (2.7%) out of 300 (Goolsby et al., 1995).

Acetochlor State Ground Water Monitoring Program (ARP-GWMP): As a requirement for the registration of acetochlor, the two acetochlor registrants are conducting a ground-water monitoring program in seven major use states. Analytes are parent (no degradates) alachlor, acetochlor, and atrazine, dimethenamid, and metolachlor (only the first three were reported). Ground-water samples are collected monthly from 175 wells located in corn producing areas. The annual report from the first year of monitoring (only for acetochlor, alachlor, and atrazine) has been submitted by the registrants which includes a computer disk with a number of EXCEL data files (DP Barcode D225973). The report

covers the a 13-month period, beginning in December 1994 and ending December 1995. Only parent compounds were reported. The limits of detection and quantification for all analytes are 0.03 $\mu\text{g/L}$ and 0.05 $\mu\text{g/L}$, respectively.

The text of the annual report indicates that alachlor was detected in 45 samples (2.6%) out of 1720 (27 of which were greater than 0.1 $\mu\text{g/L}$). Acetochlor residues were detected in 25 of 1720 samples (15 of which were greater than 0.1 $\mu\text{g/L}$) and atrazine was detected in 651 samples (427 were greater than 0.1 $\mu\text{g/L}$) out of 1720.

The computer disk contained EXCEL files with 13 months (December 1994 to December 1995) worth of data from 180 wells (includes replacement wells as does Tables 16, 17, and 18 in the annual report) was also submitted by the ARP. [The numbers of wells and samples do not correspond exactly to the narrative (e.g., 175 well vs 180 wells, number of samples 1720 vs 2340 as values less than 0.05 $\mu\text{g/L}$ are not differentiated from no data)]. Results for the three pesticides are summarized in Table 2. Fourteen of the wells had alachlor detects greater than limit of quantification (LOQ - 0.05 $\mu\text{g/L}$), six had detections of acetochlor above the LOQ, and 75 had atrazine detections above the LOQ. Twenty-seven wells had alachlor detections above the limit of detection (LOD) of 0.03 $\mu\text{g/L}$, 93 wells had detections of atrazine above the LOD, and eight wells has acetochlor levels above the LOD.

Approximately 36 percent of the alachlor detections exceeded the MCL (2.0 $\mu\text{g/L}$) and 54 percent exceeded a one-in-million cancer risk level of 0.4 $\mu\text{g/L}$. Approximately 75 percent of the detections exceeded 0.11 $\mu\text{g/L}$ for alachlor, acetochlor and atrazine. These current studies should reflect the impact to ground water from the current alachlor use and demonstrates that LOCs are still exceeded for alachlor parent.

Two of the fourteen wells with alachlor detections had detections on more than one sampling date. One of these wells was located in Illinois. The first detection of alachlor for this well (May 1995) was also the greatest (13.05 $\mu\text{g/L}$) concentration. Alachlor concentrations in this well declined with time, reaching 0.42 $\mu\text{g/L}$ by December 1995. The second well with multiple detections occurred in Kansas. The first detection (0.3 $\mu\text{g/L}$) was reported in March 1995. The highest detections for this well occurred in May 1995 (14.17 $\mu\text{g/L}$) and June (15.89 $\mu\text{g/L}$) and generally declined, reaching 3.64 $\mu\text{g/L}$ by December 1995. Seven other wells also had alachlor detections in March 1995.

Alachlor, metolachlor and propachlor in the pesticides in ground water data base: As previously noted (draft EFED RED, 1994), the Pesticides in Ground Water Data Base (PGWDB) (Hoheisel et al., 1992) reports that alachlor was detected in 25 states, in 467 wells of 25933 sampled (1.8%) (Table 3). Of the wells with

detections 99 wells (0.4%) had concentrations above the MCL. The PGWDB (Hoheisel et al., 1992) reported propachlor detections in 33 (1.2%) wells [in five states] out of 2718 wells sampled in eleven states (Table 3). The concentrations ranged from 0.02 to 3.5 $\mu\text{g/L}$, thus the maximum concentration exceeded the MCL of alachlor (2 $\mu\text{g/L}$), but not the Lifetime Health Advisory (HAL) for propachlor (90 $\mu\text{g/L}$) (Table 3).

The PGWDB (Hoheisel et al., 1992) also summarizes a number of studies which included metolachlor (Table 3). Metolachlor has been analyzed for in 29 states and detected in 20 states. Detections occurred in 213 (1%) wells out of 22,255 wells sampled, with concentrations ranging from 0.02 to 157 $\mu\text{g/L}$. Three exceeded the lifetime Health Advisory (LHA) of 70 $\mu\text{g/L}$ for metolachlor, but typically appear to less than 10 $\mu\text{g/L}$.

HEALTH EFFECTS AND DRINKING WATER LEVELS

The cancer grouping of alachlor has been recently redesignated as a known carcinogen, but the specific classification has not been determined. Alachlor was previously classified as a B2 carcinogen, with a one-in-a-million cancer risk level of 0.4 $\mu\text{g/L}$. The MCL has been set as 2.0 $\mu\text{g/L}$, by the Office of Water. There have been no health advisories or cancer risk levels established for any of the degradates.

OTHER CONSIDERATIONS

Since the degradation of alachlor appears to be much slower in aquifers than in the soil root zone and since alachlor-ESA is reported more frequently than alachlor in ground water, Kolpin et al. (1996) concluded that the degradation of alachlor occurs prior to being transported to the aquifer. They theorize that if alachlor degradation occurred after reaching the aquifer, the frequency of detections of alachlor and alachlor-ESA would be more similar. They also report that alachlor-ESA appears to be persistent in shallow aquifers, because 90 percent of the wells having alachlor-ESA concentrations exceeding 0.10 $\mu\text{g/L}$ remained at that level during all subsequent samples (1-year time interval). If an MCL or cancer risk level is established for alachlor-ESA at the same level as alachlor parent and because of the much higher percentages of wells having degradate detections, the concern for the population being exposed to levels of alachlor exceeding levels of concern is much greater than for the parent compound only.

Irrigation appears to increase the probability of contaminating ground water. The frequency of herbicide detection (35%) with irrigation within a radius of 3.2 km was greater than the frequency of herbicide detections (19%) without irrigation (Kolpin and Goolsby, 1995). They also suggest that ground water recharge from streamflow may also be a source of herbicide contamination.

Table 1. Summary of wells with detection of alachlor parent by study.

Study ¹	Number of Wells			Percent			
	Sampled	With Detects			All	<MCL	≥MCL
		All	<MCL	≥MCL			
PGWDB	25933	467	368	99	1.8	1.4	0.4
NPS	1300	1	0	1	<0.1	0	<0.1
NAWWS	1430	28	26	2	2.0	1.8	<0.1
USGS (1991)	303	6	5	1	2.0	1.7	0.3
USGS (1992)	100	5	-	-	5.0	-	-
ARP-GWMP	173	27	25	2	15.6	14.5	1.2

¹ PGWDB - Pesticides in Ground Water Data Base, NPS - National Survey of Pesticides in Drinking Water Wells, NAWWS - National Alachlor Water Well Study, USGS - U.S. Geological Survey Midcontinent Study, ARP-GWMP - Acetochlor Registration Partnership Ground Water Monitoring Program.

Table 2. Detections and concentrations (in $\mu\text{g/L}$) of acetochlor, alachlor, and atrazine in study conducted by the registrants of acetochlor (DP Barcode D225973) and submitted as EXCEL data files.

Statistic	Acetochlor	Alachlor	Atrazine
Number of Samples with Detects ≥ 0.05 $\mu\text{g/L}$ (% of samples)	18 (1.0)	30 (1.7)	539 (31.3)
Number of Wells (% of 173)	8 (4.6%)	14 (8.1%)	75 (43.4%)
Number of Samples ¹	1720	1720	1720
Mean	0.39	3.38	0.75
Standard Deviation	0.52	4.89	5.88
Minimum	0.06	0.05	0.05
1st Quartile	0.11	0.12	0.11
Median	0.25	0.73	0.24
3rd Quartile	0.38	5.06	0.56
Maximum	2.17	15.89	131.53 ²

It was not possible to determine whether data identified as missing were no data or below detection limit.

² The next highest value for atrazine was 30.03 $\mu\text{g/L}$.

Table 3. Summary of alachlor, metolachlor, and propachlor ground water monitoring data from the Pesticides in Ground Water Data Base (Hoheisel et al., 1992).

Detection Information	Alachlor	Metolachlor	Propachlor
	Number of Wells (Percent of Wells)		
MCL or HAL ($\mu\text{g/L}$)	2	70	90
≥ MCL	99 (0.38)	3 (0.01)	0 (0.00)
< MCL	368 (1.42)	210 (0.94)	33 (1.21)
Total Detections	467 (1.80)	213 (0.96)	33 (1.21)
Total Sampled	25993	22255	2718
Number States with detections	25	20	5
Number of States with monitoring	35	29	11
Range of concentrations ($\mu\text{g/L}$)	trace to 3000	0.001 to 157	0.02 to 3.5

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RECOMMENDATIONS:

Because alachlor residues continue to exceed LOCs for ground water, EFGWB recommends the following previous recommendations (as suggested by K. J. Costello) be considered (note some of which have been agreed to by the registrant):

Recommendations

In its response to EFGWB's 1994 draft Reregistration Eligibility Document (RED) for alachlor, Monsanto accepted several ground-water mitigation recommendations:

- a) Monsanto agreed to classify alachlor as a Restricted Use Pesticide (RUP) for ground-water concerns;
- b) Monsanto will change its alachlor labels to include an up-to-date ground-water advisory;
- c) Monsanto has volunteered to add language calling for a 50-foot setback of mixing and loading activities from wells, rivers or lakes unless such activity is protected by an impervious pad, as well as other unspecified language meant to "avoid accidental water contamination."

The draft RED chapter should be edited to reflect Monsanto's agreement to RUP classification for alachlor for ground-water concerns, and to a revised ground-water label advisory, setbacks for mixing and loading areas, and other language meant to help avoid accidental water contamination.

1. The ground-water advisory located on the alachlor label under "Environmental Hazards" must be revised to read:

"This chemical is known to leach through soil into ground water under certain conditions as a result of registered uses. Use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground-water contamination."

2. The recommendation that alachlor be included in State Management Plans should not be removed from the final RED chapter for EFGWB.
3. The registrant must submit to EPA for validation analytical methods for alachlor degradates (including ESA) with minimum detection limits of equal to or less than 0.1 $\mu\text{g/L}$ in water, and make standards available for parent alachlor and its degradates.

- 4 The Registrant should identify mitigation measures to manage the use of alachlor in such a way that ground-water resources will not be contaminated as a result of normal uses. Ground-water monitoring studies should be developed and conducted to determine if these measures are effective at preventing any further contamination of ground-water resources from alachlor use. The Registrant should discuss mitigation measures and study design with EFGWB prior to initiation of these studies.

This could include such things as identifying areas that are vulnerable to ground-water contamination by alachlor, and recommend label restrictions that prevent this from occurring. Such restrictions should address: 1) rate reduction, 2) use restrictions, and 3) soil or geographic restrictions (for example, karst areas). Because the detection of alachlor is related to irrigation, more efficient irrigation methods could be adapted to reduce pesticide leaching. The registrant notes that their have been major alachlor use reductions, but recent monitoring studies still indicate that about the same percentage of wells exceed drinking water criteria as earlier studies.

5. EFGWB believes that it is appropriate to maintain the recommendation for mitigation triggers for alachlor, tied to results of sampling being done in the acetochlor ARP ground water monitoring program or some other monitoring program. Monsanto should enter into negotiations with SRRD to set the details of such triggers, such as number of detections and concentration levels. This recommendation is somewhat dependant upon the outcome of the new cancer risk determination and assessment of the toxicity or cancer potential for the degradates.

REFERENCES

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- Kolpin, D.W., E.M. Thurman, and D.A. Goolsby. 1996. Occurrence of selected pesticides and their metabolites in near-surface aquifers of the Midwestern United States.



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

OFFICE OF
PREVENTION, PESTICIDES,
AND TOXIC SUBSTANCES

MEMORANDUM

May 24, 1996

SUBJECT: Alachlor exposure assessment from acetochlor surface water monitoring study
DP Barcode: NA
DP Type: NA
PC Code: 90501

TO: Brian Montague
Ecological Effects Branch
PM Team 62
Special Review and Reregistration Division

FROM: R. David Jones, Ph.D., Agronomist
Surface Water Section
Environmental Fate and Ground Water Branch

THROUGH: Henry Nelson, Ph.D., Section Chief
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Environmental Fate and Ground Water Branch

Henry Jacoby, Branch Chief
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Environmental Fate and Effects Division

This memo describes an aquatic exposure assessment for alachlor generated from the alachlor data contained in the Acetochlor Registration Partnership's surface water monitoring study for acetochlor. This data is the first year's data (1995) in a five year study at 175 sites in 12 states: Delaware, Illinois, Indiana, Iowa, Kansas, Maryland, Minnesota, Missouri, Nebraska, Ohio, Pennsylvania, and Wisconsin. Samples were collected once every two weeks from April through September at each site. One more sample was collected at each site to represent the Fall and

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Winter. Most sites have fourteen samples. Samples were unfiltered prior to analysis. The samples were analyzed using a GC/MS method.

The three different endpoints, annual peaks, 96 day time-weighted mean concentrations (TWMCs), and annual TWMCs, were calculated in the following manner. For the two TWMCs, two bounding values were calculated. The upper bound was calculated by substituting the detection limit for non-detects and the quantitation limit for values between the detection limit and the quantitation limit. The lower bound was calculated by substituting zero for non-detects and the detection limit for values between the detection limit and the quantitation limit. For the peak values, the detection limit is reported when there were no detects at the site during the year. Because the differences between the upper bound and lower bound estimates were very small, only the upper bound estimates have been reported. The weights for the TWMCs were calculated by taking the length of time from the previous measurement to the following measurement and dividing by 2. For the first and last measurements, the length of time between the first and second, and last and second to last was used as the weight respectively. The 96-day TWMCs were calculated by using a running TWMC through year and selecting the maximum from this running TWMC. Because samples were only taken every two weeks, in most cases, the running mean was calculated on a somewhat shorter time frame, usually 84 days.

The data is summarized in Figures 1-3. Figure 1 shows a site exceedance probability of the peak values at each site. This value should be used for comparison to acute toxicity tests and the 21 day *Daphnia* chronic study. Figure 2 is site exceedance probability of the maximum 96 day TWMCs at each site. A site exceedance probability plot for the annual TWMCs for each site is in Figure 3. This is the most appropriate endpoint for comparison to human lifetime health advisories.

The peak sample as well as the largest 96-day TWMC and largest annual TWMC were found at Defiance, Ohio. The peak concentration was just under 4 ug L⁻¹. Nine of the fourteen samples at Defiance contained detectable amounts of alachlor (detection limit - 0.02 ug L⁻¹). Farina, IL had detectable alachlor in every sample, though at lower levels than Defiance. Thirty-one sites had no detectable residues of alachlor in any sample. Overall, 558 of 2444 total samples had detectable alachlor, or 22.8%. Table 1 has the 90% site exceedance probabilities for the peak, 96 day TWMC, and annual TWMC.

Table 1. 90% site exceedance values for alachlor in the acetochlor surface water monitoring study in 1995		
Peak	96 Day TWMC	Annual TWMC
----- ug L ⁻¹ -----		
0.37	0.17	0.10

This data has several strengths and weaknesses as compared to other monitoring studies. In general, there are more samples collected at each site and more sites than are found in most monitoring studies. Furthermore, the sites were selected to represent a range of agricultural intensities and size in the drainage basins. This is an advantage in a study of this size. This study also has some limitations. All of the data was collected at drinking water facilities and used finished water. Water treatment may reduce the alachlor concentration somewhat, but the amount is not believed to be substantial. Drinking water facilities tend to be on larger streams, rivers, and lakes. Smaller rivers, streams, and lakes are probably have higher peak concentrations of alachlor, and may be somewhat more sensitive ecologically. Another limitation is that the samples were collected once every two weeks. No samples were collected in response to runoff events. This makes it likely that true peak values will be missed at each site. This single sample also is used for the 21 day average which also is not ideal but is the best that can be done with samples collected biweekly. Finally it should be noted that alachlor use has declined substantially from use in the recent past. While these concentrations are an accurate reflection of alachlor surface water concentrations in 1995 (given the limitations mentioned above), the potential market for alachlor is substantially larger, and there is a possibility that alachlor may reclaim some or all of its former share of the market if the conditions in the market were to change.

Alachlor
Annual Means
Acetochlor Surface Water Monitoring, 1995

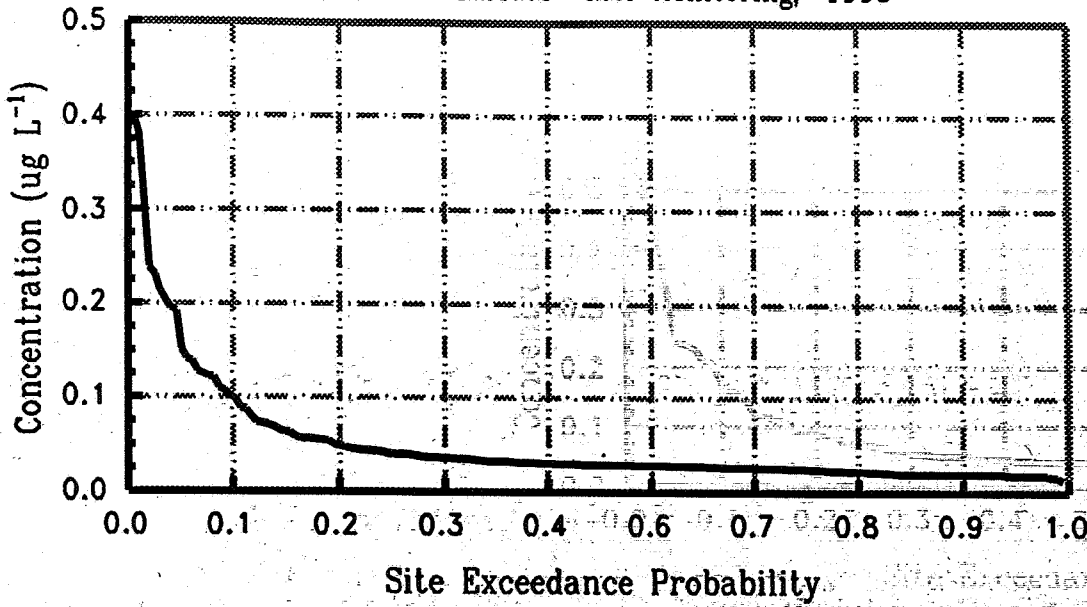


Figure 1.. Site exceedance probability of annual time-weighted concentrations of alachlor in the acetochlor surface water monitoring study in 1995.

Alachlor
Annual Maximum 96 Day Means
Acetochlor Surface Water Monitoring, 1995

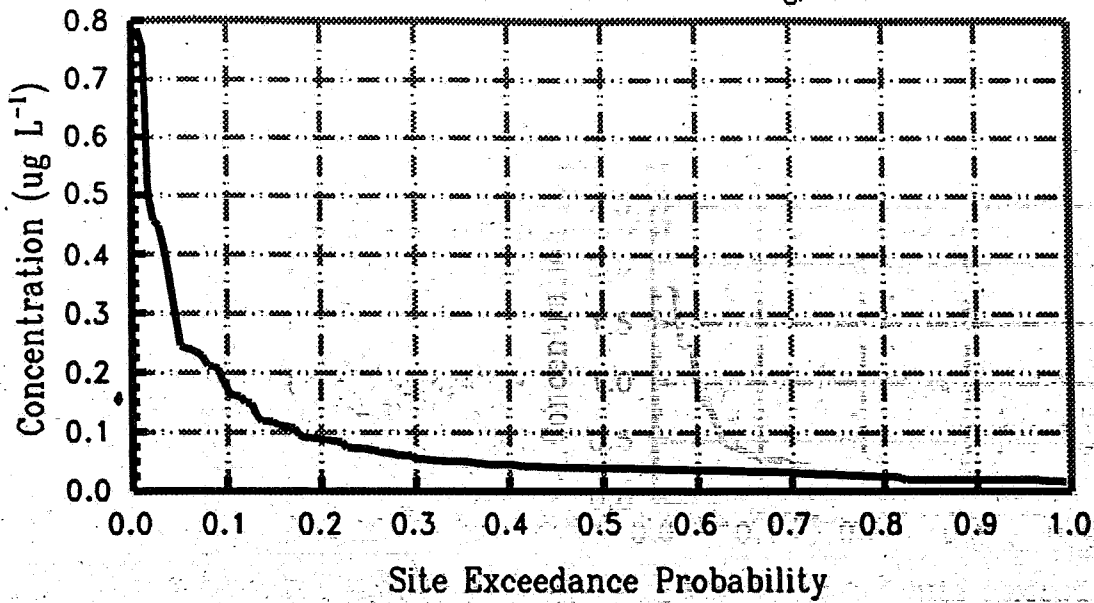


Figure 2.. Site exceedance probability of annual maximum 96 day mean concentrations of alachlor in the acetochlor surface water monitoring study in 1995.

Alachlor
Annual Peak Concentrations
Acetochlor Surface Water Monitoring, 1995

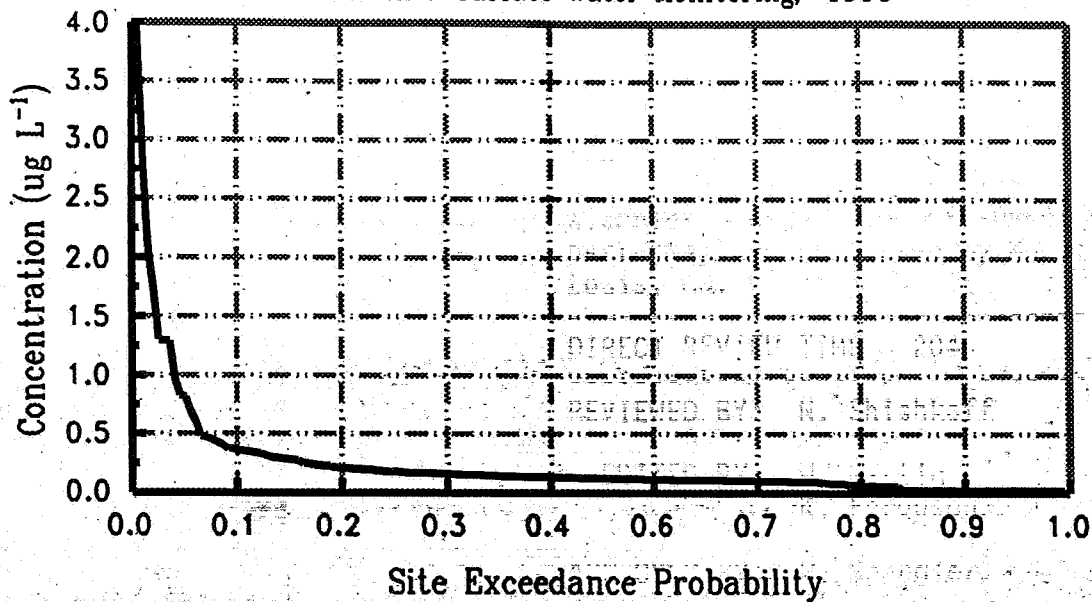


Figure 3.. Site exceedance probability of annual peak concentrations of alachlor in the acetochlor surface water monitoring study in 1995.

cc: Jose Melendez
David Farrar

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DATA EVALUATION RECORD

STUDY 1

CHEM 090501

Alachlor

S161-1,-2,-3;
162-1,-3; 163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 00134327

Suba, L.A., and D.A. Pearson. 1979. The environmental studies of alachlor. Report No. MSL-0860; Project No. 7824. Unpublished study performed and submitted by Monsanto Agricultural Products Company, St. Louis, MO.

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CONCLUSIONS:

Degradation - Hydrolysis

1. This portion of the study can be used to fulfill data requirements.
2. Alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide) was stable in sterile pH 3, 6, and 9 aqueous buffered solutions, sterile lake water, and deionized water that were incubated in the dark at 25°C for up to 30 days.
3. This portion of the study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of carbonyl-labeled [¹⁴C]alachlor in sterile aqueous

buffered solutions (pH 3, 6, and 9). Information on the hydrolysis of pesticides in sterile lake water, nonsterile lake water, and deionized water is not required by Subdivision N guidelines.

4. No additional information on the hydrolysis of alachlor in sterile aqueous buffered solutions is needed at this time.

Degradation - Photodegradation in Water

1. This portion of the study cannot be used to fulfill data requirements.
2. Alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide) degraded with an observed half-life of <24 hours in photosensitized (2% acetone) solutions (composition and pH not reported) that were irradiated with a blacklight for up to 60 hours (temperature not reported). The intensity of the lamp was not reported; a 3-hour exposure to this lamp was reported to be equivalent to 8 hours of California sunlight. The degradates identified were 2',6'-diethylacetanilide (Compound I); 2',6'-diethyl-2-methoxyacetanilide (Compound V); 2',6'-diethyl-N-methoxymethylacetanilide (Compound IX); 2',6'-diethyl-N-methoxymethyl-2-oxoacetanilide (Compound XII); 2',6'-diethyl-2-hydroxy-N-methoxymethylacetanilide (Compound XIII); 2,6-diethylbenzyl alcohol (Compound XX); 2',6'-diethyl-N-hydroxymethyl-2-methoxyacetanilide (Compound XXII); and 8-ethyl-N-methoxymethyl-4-methyl-2-oxotetrahydroquinoline (Compound XXIII).
3. This portion of the study is unacceptable for the following reason:
the methods description was incomplete.

In addition, this portion of the study does not meet Subdivision N guidelines for the following reasons:

the artificial light source used in the study (blacklight) was not comparable to natural sunlight; and

the photodegradation of alachlor in nonsensitized solutions was not addressed (no data were provided, although the preparation of these solutions was described). An additional study is available that provides such information.

4. Since the artificial light source was not comparable to natural sunlight, the problems with this portion of the study cannot be resolved with the submission of additional data.

Degradation - Photodegradation on Soil

1. This portion of the study cannot be used to fulfill data requirements.

2. Alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide) slowly degraded on sterilized silt soil that was irradiated with a "sunlamp" for 72 hours (temperature not reported). The total irradiation intensity of the lamp (wavelengths not reported) was 1500 watts/m². Degradates identified in soil treated at 10 lb ai/A and irradiated for 14 days were 2-chloro-2',6'-diethylacetanilide (Compound II); 2',6'-diethyl-2-hydroxy-N-methoxymethylacetanilide (Compound XIII); 2'-acetyl-2-chloro-6'-ethyl-N-methoxymethylacetanilide (Compound XXIV); and (tentatively) 2'-chloroethyl-6'-ethyl-N-methylacetanilide.

3. This portion of the study is unacceptable for the following reason:
the methods description was incomplete.

In addition, this portion of the study does not meet Subdivision N guidelines for the following reason:

the study was terminated before the half-life of alachlor was established.

4. Since the study was terminated before the half-life of alachlor was established, the problems with this portion of the study cannot be resolved by the submission of additional data. Therefore, a new study must be submitted.

Metabolism - Aerobic Soil

1. This portion of the study is acceptable and can be used to fulfill data requirements.
2. Alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide) degraded with a registrant-estimated half-life of approximately 2-3 weeks in silt, sandy loam, and silt loam/silty clay loam soils that were incubated in the dark at 25 C and 75% of field moisture capacity for 175 days. The degradates identified were 2',6'-diethylacetanilide (Compound I); 2',6'-diethyloxanic acid (Compound III); 2',6'-diethyl-2-sulfoacetanilide (Compound IV); 2',6'-diethyl-2-methylsulfinylacetanilide (Compound VI); 2',6'-diethyl-N-methoxymethylacetanilide (Compound IX); 2',6'-diethyl-N-methoxymethyloxanic acid (Compound X); 2',6'-diethyl-N-methoxymethyl-2-sulfoacetanilide (Compound XI); 2',6'-diethyl-N-methoxymethyl-2-oxoacetanilide (Compound XII); 2',6'-diethyl-2-hydroxy-N-methoxymethylacetanilide (Compound XIII); 2',6'-diethyl-N-methoxymethyl-2-methylthioacetanilide (Compound XV); 2',6'-diethyl-N-methoxymethyl-2-methylsulfinylacetanilide (Compound XVI); 2',6'-diethyl-N-methoxymethyl-2-methylsulfonylacetanilide (Compound XVII); and 2'-acetyl-2-chloro-6'-ethyl-N-methoxymethylacetanilide (Compound XXIV).

Metabolism - Anaerobic Aquatic

1. This portion of the study cannot be used to fulfill data requirements.
2. Alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide) degraded with a half-life of approximately 3-4 days in sandy clay loam sediment:lake water slurries that were anaerobically incubated (nitrogen atmosphere) in the dark at 25°C for 140 days. The degradates identified were 2',6'-diethyloxanic acid (Compound III); 2',6'-diethyl-2-sulfoacetanilide (Compound IV); 2',6'-diethyl-N-methoxymethylacetanilide (Compound IX); 2',6'-diethyl-N-methoxymethyloxanic acid (Compound X); 2',6'-diethyl-N-methoxymethyl-2-sulfoacetanilide (Compound XI); and 2',6'-diethyl-N-methoxymethyl-2-methylthioacetanilide (Compound XV).
The soil was used for longer than one year, but does not meet Subdi
3. This portion of the study is scientifically sound, but does not meet Subdivision N guidelines for the following reason:

[¹⁴C]residues in the floodwater and soil extracts, which totaled up to 16.2% of the applied (0.60 ppm) in individual solutions, were not characterized.
4. Since this portion of the study was conducted approximately 15 years ago (1979), it is unlikely that the extracts are available for further analysis. Therefore, a new study must be submitted.

Mobility - Leaching and Adsorption/Desorption

1. The column leaching experiments using unaged alachlor can be used towards the fulfillment of data requirements. The column leaching experiments using aged alachlor residues and the batch equilibrium experiments using unaged alachlor cannot be used towards the fulfillment of data requirements.
2. Based on column leaching experiments, parent alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide) is very mobile in silt, loamy sand, and sand soils and was somewhat mobile in silt loam soil. In silt, sand, and loamy sand soil columns, 40.9-96.9% of the applied radioactivity was found in the leachate; in the silt loam soil column, 0.5-0.6% was found in leachate. The column leachates contained alachlor; 2-chloro-2',6'-diethylacetanilide (Compound II); 2',6'-diethyl-N-methoxymethylacetanilide (Compound IX); and 2',6'-diethyl-N-methoxymethyl-2-methylthioacetanilide (Compound XV).

Aged (30 days) alachlor residues (uncharacterized) were mobile in sandy loam soil columns (30-cm length) leached with approximately 20 inches of water. The degradates identified in the leachates and soil extracts were 2-chloro-2',6'-diethylacetanilide (Compound II); 2',6'-diethyl-N-methoxymethylacetanilide (Compound IX); 2',6'-diethyl-2-hydroxy-N-methoxymethylacetanilide (Compound XIII); 2',6'-diethyl-N-methoxymethyl-2-methylthioacetanilide (Compound XV); 2',6'-diethyl-N-

methoxymethyl-2-methylsulfinylacetanilide (Compound XVI); and 2',6'-diethyl-N-methoxymethyl-2-methylsulfonylacetanilide (Compound XVII). The degradates 2',6'-diethyloxanilic acid (Compound III); 2',6'-diethyl-2-sulfoacetanilide (Compound IV); 2',6'-diethyl-N-methoxymethyloxanilic acid (Compound X); and 2',6'-diethyl-N-methoxymethyl-2-sulfoacetanilide (Compound XI) were identified only in the leachates. The degradate 2',6'-diethylacetanilide (Compound I) was detected only in the soil extracts.

3. The column leaching experiments using unaged [¹⁴C]alachlor are acceptable and contribute towards the fulfillment of data requirements by providing information on the mobility of [¹⁴C]alachlor in silt, loamy sand, sand, and silt loam soil columns (30-cm length) that were leached with 20 inches of water.

The column leaching experiments using agedalachlor residues are scientifically sound, but do not meet Subdivision N guidelines for the following reasons:

the soil was aged for longer than one half-life so that there may have been insufficient parentalachlor present at the start of leaching; and

the degradates in the soil were not characterized after aging and prior to leaching.

The batch equilibrium experiments using unaged [¹⁴C]alachlor are unacceptable for the following reason:

the soil was oversieved; the soil was sieved through a 500 um mesh, removing a significant portion of the soil sand and possibly reducing the mobility ofalachlor.

4. No additional information is needed on the mobility of unaged [¹⁴C]alachlor in silt, loamy sand, sand, and silt loam soils. Since the degradates in the soil were not characterized after aging and prior to leaching, the problems with the column leaching experiments using agedalachlor residues cannot be resolved by the submission of additional data. Also, since the soil was oversieved, the problems with the batch equilibrium experiments using unagedalachlor cannot be resolved by the submission of additional data. Acceptable information, therefore, is needed on the mobility of agedalachlor residues in one soil.

METHODOLOGY:

Degradation - Hydrolysis

Sterilized solutions: Carbonyl-labeled [¹⁴C]alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; radiochemical purity 98%, specific activity 11.5 mCi/mMol, "prepared by R.C. Freeman") was

dissolved in deionized water; lake water; and commercial pH 3, 6, and 9 aqueous buffer solutions. The solutions were filter-sterilized (pore size not reported) after treatment; the final alachlor concentration was approximately 50 ppm. Aliquots (10 mL) of the test solutions were transferred to sterile centrifuge tubes, which were then capped, and the samples were incubated in the dark at 25°C for up to 30 days. Duplicate tubes of each treated solution were collected for analysis at 0, 8, 14, 23, and 30 days posttreatment.

Duplicate aliquots (0.5 mL) of each solution were analyzed for total radioactivity using LSC. The remaining solution was partitioned with methylene chloride, and aliquots of each phase were analyzed by LSC. The methylene chloride fraction was concentrated (method not reported), and aliquots of the concentrate were analyzed by LSC and GLC with radioactivity detection (GLC/RAD).

Nonsterile lake water: Aliquots (50 mL) of lake water (not characterized) from Missouri were added to 250-mL Erlenmeyer flasks and treated at 2 ppm with carbonyl-labeled [^{14}C]alachlor (previously described) dissolved in ethanol. The flasks were sealed with a foam plug and a two-piece trapping tower (Figure 5). The lower portion of the trapping tower contained Drierite and the upper portion contained Ascarite and Drierite; the layers were separated by glass wool. The samples were incubated in the dark for up to 30 days (temperature not reported). Single flasks were collected for analysis at 0, 7, 15, 21, and 30 days posttreatment; the trapping towers were replaced at each sampling interval.

The water was partitioned with methylene chloride, and aliquots of each phase were analyzed by LSC. The methylene chloride fraction was concentrated, and aliquots of the concentrate were analyzed by GLC/RAD.

The ascarite from the trapping tower was acidified, and the $^{14}\text{CO}_2$ released upon acidification was trapped in scintillation fluid. The scintillation fluid was analyzed by LSC. [^{14}C]Residues in the foam plugs were also quantified (methods not described).

Degradation - Photodegradation in Water

Carbonyl-labeled alachlor (previously described) or phenyl ring-labeled [^{14}C]alachlor (radiochemical purity not reported, specific activity 11.3 mCi/mMol, "prepared by R.C. Freeman") were added at approximately 150 ppm to aqueous "solutions" (composition and pH not reported); a portion of each solution was amended with acetone (2% by volume) as a photosensitizer. Aliquots (250 mL) of test solutions were transferred to the reaction chamber of a Crosby reactor (Figure 4) and irradiated with a blacklight (GE F8T5-BL) for up to 60 hours. The intensity of the lamp was not reported; a 3-hour exposure to this lamp was reported to be equivalent to 8 hours of California sunlight [page 19]. The solutions were aerated with air bubbled into the solutions at <5 mL/minute through sintered glass frits; the air was

vented through a NaOH trapping solution. The temperature of the solutions during incubation was not reported. The test solutions were collected after 6, 24, 48, or 60 hours of irradiation.

Aliquots of the test solution were analyzed for total radioactivity using LSC. The remaining solution was partitioned with methylene chloride, and aliquots of each phase were analyzed by LSC. The methylene chloride fraction was concentrated (evaporated), and aliquots of the concentrate were analyzed by GLC/RAD. "Most of the significant peaks" were analyzed by MS [page 15]. Aliquots of trapping solutions were analyzed for total radioactivity by LSC.

To produce large quantities of photodegradates, a photosensitized (2% acetone) test solution was treated at 300 mg/L with alachlor (not further characterized). The solution was filtered through "filter paper", and aliquots (250 mL) of the filtrate were transferred into four photolysis reactors. The four solutions were simultaneously irradiated with a blacklight for 48-60 hours [page 15]. At the termination of irradiation, the four solutions were combined and partitioned twice with methylene chloride. The methylene chloride fractions were combined and concentrated under vacuum at ambient temperature. The residues in the concentrate were separated by preparative GLC. The individual compounds were mixed with deuterium-labeled chloroform and analyzed using NMR, GLC/MS, FT/IR, and GLC/HRMS (high-resolution MS).

Degradation - Photodegradation on Soil

Aqueous slurries of sieved (0.5 mm) "Ray" silt soil (4.6% sand, 84.2% silt, 10.0% clay, 1.2% organic matter, pH 8.1, CEC meq/100 g) were spread evenly on glass plates (20 x 20 cm) to a thickness of 0.006 inches. The soil plates were air-dried, then irradiated with a sunlamp (GE CG401-E16RS) for 72 hours "in order to eliminate microbial degradation of alachlor [page 16]." The total irradiation intensity of the lamp, measured with a radiometer (wavelengths not reported) was 1500 watts/m²; the intensity and wavelength distribution were not compared to natural sunlight. After the initial irradiation, the plate was divided into four sections (8 x 8 cm), and each section of the plate was treated with carbonyl-labeled [¹⁴C]alachlor (previously described) at a rate equivalent to 3 lbs ai/A. One of the treated sections was covered with aluminum foil to serve as a dark control. The plate was positioned 15 cm below the sunlamp and irradiated for 72 hours. One section of the irradiated soil was scraped from the plate after 24, 48, and 72 hours of irradiation. The temperature of the soil during irradiation was not reported.

The soil was extracted twice with 30% acetonitrile in water; the extracts were pooled and partitioned with methylene chloride. Aliquots of the methylene chloride fractions were analyzed by GLC/RAD.

To produce large quantities of photodegradates, three additional soil plates were prepared and treated with 44.8 mg of carbonyl-labeled [¹⁴C]alachlor (equivalent to 10 lb ai/A). The plates were irradiated for 14 days, then the soil was scraped from each plate and combined. The soil was extracted three times with 30% acetonitrile in water, and the extract was partitioned with methylene chloride. Aliquots of the methylene chloride fraction were analyzed by HPLC using a uBondapak C-18 column eluted with a gradient of acetonitrile:water. The column was equipped with UV detection; also, eluate fractions were collected and analyzed by LSC.

Metabolism - Aerobic Soil

Air-dried, sieved (No. 4 mesh) "Ray" silt, "Spinks" loamy sand, and "Drummer" silt loam soils were weighed (50 g dry weight) into 250-mL Erlenmeyer flasks and treated at 2 ppm with [¹⁴C]alachlor (test substance not characterized) dissolved in ethanol. The soil was then moistened to 75% of field capacity. The flasks were sealed with a foam plug and a two-piece trapping tower (Figure 5). The lower portion of the trapping tower contained Drierite, and the upper portion contained Ascarite and Drierite; the layers were separated by glass wool. The sample flasks were incubated in the dark at 25 °C, and were weighed at weekly intervals; water was added to the flasks as necessary to maintain the soil moisture content. One flask of each soil type was collected at 0, 1, 3, 7, 14, 21, 28, 50, and 175 days posttreatment; the trapping towers were replaced at each sampling interval and at 81, 105, 123, 137, and 155 days posttreatment.

The soil was sequentially extracted four times with 30% acetonitrile in water, once with 0.1 N ammonium hydroxide, and twice with water by stirring for 30 minutes/extraction; after each extraction, the samples were centrifuged and the extracts decanted. Aliquots of each extract were analyzed by LSC. The first three acetonitrile:water extracts were combined and partitioned with methylene chloride; aliquots of both phases were analyzed by LSC. The methylene chloride fraction was concentrated by evaporation, and aliquots were analyzed by GLC/RAD and GLC/MS. The aqueous phase was frozen and lyophilized prior to analysis by HPLC using a uBondapak C-18 column eluted with a gradient of acetonitrile:water; the column was equipped with UV detection, and eluate fractions were collected and analyzed by LSC. Additional portions of the lyophilized aqueous phase were analyzed by high-voltage electrophoresis (HVE) at pH 1.1, 2.1, and 5.9. Subsamples of the extracted soil were analyzed by LSC following combustion.

The ascarite from the trapping tower was acidified, and the ¹⁴CO₂ released upon acidification was trapped in scintillation fluid. The scintillation fluid was analyzed by LSC. [¹⁴C]Residues in the foam plugs were also quantified (methods not described).

To produce large quantities of degradates, 12 kg of "Ray" silt soil was placed in a stainless steel tank (45 x 45 x 15 cm) and treated at 4 ppm with a mixture (55:45) of [¹³C]alachlor (labeled at the C-2 position) and phenyl ring-labeled [¹⁴C]alachlor in water. Sufficient water was added to adjust the soil to 75% of field moisture capacity. The tank was "loosely" covered with cardboard and stored in a greenhouse for 41 days (temperature not reported); the soil was moistened daily with approximately 500 mL of water. After 41 days, portions (5 kg) of the soil were removed for analysis. Soil was extracted five times with 30% acetonitrile in water (methods not further described); aliquots of each extract were analyzed by LSC. The initial extract was partitioned twice with methylene chloride; both phases were analyzed by LSC. The methylene chloride fraction was concentrated under vacuum and analyzed by GLC/RAD. The aqueous phase was lyophilized, and the [¹⁴C]residues were dissolved in acetonitrile and filtered; the acetonitrile filtrate was evaporated to dryness under vacuum. The [¹⁴C]residues were dissolved in deuterium oxide, then the solution was filtered ("Millipore") and analyzed by [¹³C]-NMR. An additional portion (3.5 kg) of the incubated soil was extracted and partitioned as described. Aliquots of the resulting aqueous extract were analyzed by reverse-phase HPLC using a uBondapak C-18 column eluted with a methanol:0.001 M KH₂PO₄ gradient; the column was equipped with UV detection. Eluate fractions were collected and concentrated; the [¹⁴C]residues were dissolved in deuterium oxide and analyzed by [¹³C]-NMR. The [¹⁴C]residues in selected eluate fractions ("C, D, E, and F") were derivatized with diazomethane and analyzed by GLC/RAD and GLC/MS. The [¹⁴C]residues in one fraction ("C") were also derivatized with N,O-bis-(trimethylsilyl)acetamide and analyzed by GLC/RAD and GLC/MS. Additionally, the [¹⁴C]residues in fractions "B" and "F" were derivatized with trimethylorthoformate and analyzed by GLC/RAD and GLC/MS.

Subsamples of untreated "Ray" silt soil, "Ray" silt soil freshly fortified with the alachlor solution used for the large-scale soil experiment, and the soil from the large-scale experiment were incubated for 41 days. The soils were sequentially extracted five times with 80% acetonitrile, three times with 0.1 N ammonium hydroxide, and three times with 1 N ammonium hydroxide by stirring for 30 minutes/extraction; between extractions, the samples were centrifuged and the extracts decanted. Similar extracts from each soil were combined and evaporated to dryness. The residues were refluxed with 1 N sulfuric acid for 25 minutes (Figure 19). The refluxate was cooled for 30 minutes, then treated with 50% sodium hydroxide and refluxed for 2.5 hours. The refluxate was distilled into 12 N sulfuric acid; the distillate was diluted with water, then cooled in an ice bath. The cooled distillate was partitioned with hexane. The aqueous extract was removed and treated with 50% NaOH, cooled in ice water, then held for 15 minutes at room temperature. The aqueous solution was partitioned into methylene chloride. The methylene chloride extract was concentrated by evaporation, then analyzed by GLC/RAD and GLC/FID.

Metabolism - Anaerobic Aquatic

Sandy clay loam sediment (50.0% sand, 26.0% silt, 24.4% clay, 1.4% organic matter, pH 7.3, CEC 7.2 meq/100 g) from a lake in Missouri was weighed (60 g wet weight) into 15 flasks (Figure 6). The soils were flooded with a mixture (90 mL:34.8 mL) of lake water (not characterized) and deionized water, then the flasks were flushed with nitrogen for 1 hour, sealed, and incubated for 30 days. Following the initial incubation, the soil:water systems were treated at 3.7 ppm (with respect to soil dry weight) with carbonyl-labeled [^{14}C]alachlor (previously described) dissolved in ethanol. The flasks were resealed, and the samples were incubated in the dark at 25 C for up to 140 days. Single flasks were collected for analysis at 0, 0.6, 1, 3, 7, 14, 21, 28, 42, 70, 105, and 140 days posttreatment. At each sampling interval, the flasks were flushed with nitrogen; the nitrogen was vented through an Ascarite trap.

The samples were centrifuged and the floodwater was decanted. Aliquots of the floodwater were analyzed for total radioactivity using LSC. The soil was sequentially extracted four times with 30% acetonitrile in water, once with 0.1 N ammonium hydroxide, and twice with water, each time by stirring for 30 minutes/extraction. After each extraction, the samples were centrifuged and the extracts decanted. Aliquots of each extract were analyzed by LSC. The first three acetonitrile:water extracts were combined and partitioned with methylene chloride; aliquots of both phases were analyzed by LSC. The methylene chloride fraction was concentrated by evaporation, and aliquots were analyzed by GLC/RAD and GLC/MS. The aqueous phase was frozen and lyophilized prior to analysis by HPLC using a uBondapak C-18 column eluted with a gradient of acetonitrile:water; the column was equipped with UV detection, and eluate fractions were collected and analyzed by LSC. Additional portions of the lyophilized aqueous phase were analyzed by high-voltage electrophoresis (HVE) at pH 1.1, 2.1, and 5.9. Subsamples of the extracted soil were analyzed by LSC following combustion.

The ascarite from the trapping tower was acidified, and the $^{14}\text{CO}_2$ released upon acidification was trapped in scintillation fluid. The scintillation fluid was analyzed by LSC.

Mobility - Leaching and Adsorption/Desorption

Unaged [^{14}C]alachlor (batch equilibrium): Air-dried, sieved (500 μm) "Ray" silt soil (4.6% sand, 84.2% silt, 10.0% clay, 1.2% organic matter, pH 8.1, CEC meq/100 g) and sandy clay loam sediment (50.0% sand, 26.0% silt, 24% clay, 1.4% organic matter, pH 7.3, CEC 7.2 meq/100 g) were weighed (2.5 g) into glass tubes and treated with carbonyl-labeled [^{14}C]alachlor (previously described) dissolved in water. The volume of the supernatant was adjusted (to 10 mL) with additional water; the finalalachlor concentrations were 0.1, 1.0, 5.0, or 10 ppm. The tubes were sealed with Teflon-lined screw caps, and the soil:solution slurries (2.5 g:10 mL) were vortexed, then

incubated on a mechanical shaker overnight (temperature not reported). After the equilibration period, the slurries were centrifuged and the supernatants decanted. Aliquots of the supernatants were analyzed by LSC.

To study desorption, the supernatants were replaced with an equal volume of pesticide-free water. The soil:solution slurries were equilibrated as described for 4 hours, then centrifuged; the supernatants were decanted, and aliquots were analyzed by LSC. The desorption procedure was repeated five times. Following the final desorption, the soils were air-dried, and subsamples were analyzed by LSC following combustion.

Unaged [¹⁴C]alachlor (soil column-leaching): "Spinks" loamy sand, "Ray" silt, "Lintonia" sand, and "Drummer" silt-loam soils [page 14] were air-dried and sieved (2 mm).

Columns (1.5-inch id x 40-cm length) were constructed by taping together one 10-cm and fifteen 2-cm long glass cylinders; the 10-cm cylinder was the uppermost segment. The columns were packed with soil to a depth of 30 cm using a wooden dowel; two columns were prepared for each soil type. The surface soil was treated with carbonyl-labeled [¹⁴C]alachlor (previously described) dissolved in ethanol at a rate equivalent to 3.5 lb ai/A. The treated columns were allowed to stand 30 minutes, then leached with 540 mL of water (approximately 20 inches). The time required for leaching was not reported; however, the water was "added at a rate slower than the infiltration capacity of the soil [page 17]." Leachate fractions were collected. After leaching was completed, the column was divided into fifteen 2-cm segments, which were then frozen until analysis.

Aliquots of the leachates were analyzed for total radioactivity by LSC. Additional aliquots of the leachates were partitioned with methylene chloride; aliquots of both phases were analyzed by LSC. The methylene chloride fraction was concentrated, and aliquots were analyzed by GLC/RAD.

The frozen soil was lyophilized, and subsamples of each segment were analyzed by LSC following combustion. For each column, the three adjacent soil segments containing the highest concentrations of radioactivity were combined. A subsample was extracted four times with 30% acetonitrile in water (extraction conditions not reported); the extracts were pooled and partitioned with methylene chloride. The methylene chloride fraction was concentrated, and aliquots were analyzed by GLC/RAD. The aqueous extract was stored frozen; no further analyses were reported.

Aged [¹⁴C]alachlor residues (soil column leaching): "Spinks" loamy sand soil (75.1% sand, 17.8% silt, 4.8% clay, 2.4% organic matter, pH 4.7, CEC 11.3 meq/100 g) was air-dried and sieved (2 mm).

Columns (1.5-inch id x 40-cm length) were constructed by taping together one 10-cm and fifteen 2-cm long glass cylinders; the 10-cm cylinder was the uppermost segment. The columns were packed with soil to a depth of 30 cm using a wooden dowel; two columns were prepared for each soil type. The soil columns were moistened (15-20% by volume), and the soil surface was treated with carbonyl-labeled [¹⁴C]alachlor (previously described) dissolved in ethanol at a rate equivalent to 3.5 lb ai/A. A 10-cm long glass cylinder constructed with a side arm was fitted to the top of each column, and an Ascarite trap was connected to the side arm. The treated columns were aged for 30 days (conditions not reported). The columns were then leached over a 45-day period with a total of 540 mL of water (approximately 20 inches) at a rate equivalent to 0.5 inches of rainfall/day twice each week. The Ascarite trap was changed "periodically" [page 18]. Leachate fractions were collected. After leaching was completed, the column was divided into fifteen 2-cm segments, which were then frozen until analysis.

Aliquots of leachate were analyzed for total radioactivity by LSC. Additional aliquots were partitioned with methylene chloride, and aliquots of both phases were analyzed by LSC. The methylene chloride fraction was concentrated, and aliquots were analyzed by GLC/RAD. The aqueous fractions were lyophilized; the resulting residues were redissolved in water and analyzed by HPLC as previously described.

The frozen soil segments were lyophilized, and subsamples of each segment were analyzed by LSC following combustion. The 0- to 2-cm and 16- to 20-cm segments of each column were extracted four times with 30% acetonitrile in water; the extracts were pooled and partitioned with methylene chloride. The methylene chloride fraction was concentrated, and aliquots were analyzed by GLC/RAD. The aqueous extract was stored frozen; no further analyses were reported.

DATA SUMMARY:

Degradation - Hydrolysis

Carbonyl-labeled [¹⁴C]alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; radiochemical purity 98%), at 50 ppm, was relatively stable in sterile commercial pH 3, 6, and 9 buffer solutions (not further characterized), natural lake water (not further characterized), and deionized water that were incubated in the dark at 25°C for 30 days. [¹⁴C]Alachlor comprised 97.5-98.7% of the applied radioactivity in all test solutions; there was no discernible pattern of decline (Tables 1-5).

2',6'-Diethyl-N-methoxymethylacetanilide (Compound IX)

was isolated from the test solutions at 0.75-1.57% of the applied, and uncharacterized [¹⁴C]residues totaled 0.2-1.1%. During the

study, material balances were >98% of the applied (reviewer-calculated from Tables 1-5).

In nonsterile lake water (not characterized), [¹⁴C]alachlor, at 2 ppm, degraded slowly during 30 days of aerobic incubation in the dark; the incubation temperature was not reported. [¹⁴C]Alachlor comprised 98.0% of the applied immediately posttreatment, and declined to 88.8% at 30 days (Table 33). Five nonvolatile [¹⁴C]compounds were identified, each ≤2.7% of the applied:

- 2',6'-diethyl-N-methoxymethylacetanilide (Compound IX);
- 2',6'-diethyl-N-methoxymethyl-2-oxoacetanilide (Compound XII);
- 2',6'-diethyl-N-methoxymethyl-2-methylthioacetanilide (Compound XV);
- 2',6'-diethyl-N-methoxymethyl-2-methylsulfinylacetanilide (Compound XVI); and
- 2',6'-diethyl-methoxymethyl-2-methylsulfonylacetanilide (Compound XVII).

Uncharacterized organosoluble [¹⁴C]residues were a maximum of 1.8% of the applied (0.04 ppm); uncharacterized aqueous-soluble [¹⁴C]residues were a maximum of 2.1% (0.04 ppm; reviewer-calculated from Table 33). At 30 days posttreatment, ¹⁴CO₂ and uncharacterized [¹⁴C]volatiles totaled 0.43 and 2.5% of the applied, respectively. During the study, the material balances were 99.0-100.8% of the applied.

Degradation - Photodegradation in Water

Carbonyl- or phenyl ring-labeled [¹⁴C]alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; radiochemical purities 98% and not reported, respectively), at 150 ppm, degraded with an observed half-life of <24 hours in photosensitized (2% acetone) solutions (not further characterized) that were irradiated with a blacklight (GE F8T5-BL) for up to 60 hours (temperature not reported). The intensity of the lamp was not reported; a 3-hour exposure to this lamp was reported to be equivalent to 8 hours of California sunlight [page 19]. [¹⁴C]Alachlor (Compound XIV) comprised 83.2% of the applied radioactivity at 6 hours posttreatment, 28.1% at 24 hours, and 4.5% at 60 hours (Table 6).

2',6'-Diethyl-2-hydroxy-N-methoxymethylacetanilide (Compound XIII)

was a maximum of 13.1% of the applied at 24 hours posttreatment, and was 6.2% at 60 hours;

2',6'-diethylacetanilide (Compound I),

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2',6'-diethyl-2-methoxyacetanilide (Compound V),
2',6'-diethyl-N-methoxymethylacetanilide (Compound IX),
2',6'-diethyl-N-methoxymethyl-2-oxoacetanilide (Compound XII),
2,6-diethylbenzyl alcohol (Compound XX),
2',6'-diethyl-N-hydroxymethyl-2-methoxyacetanilide (Compound XXII), and
8-ethyl-N-methoxymethyl-4-methyl-2-oxotetrahydroquinoline (Compound XXIII)

were present at maximums of 1.3% to 5.8%. Uncharacterized organosoluble [¹⁴C]residues increased from 1.6% of the applied at 6 hours posttreatment to 26.2-28.0% at 48 through 60 hours (reviewer-calculated from Table 6). Unidentified aqueous-soluble [¹⁴C]residues increased from 7.1% of the applied at 6 hours posttreatment to 39.8% at 60 hours; this radioactivity was comprised of "many components", none of which exceeded >5% of the applied [page 28]. No volatilization was reported. Material balances were not provided.

Degradation - Photodegradation on Soil

Carbonyl-labeled [¹⁴C]alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; radiochemical purity 98%), at an application rate of 3 lbs ai/A, degraded very slowly on "sterilized" silt soil that was irradiated for 72 hours with a "sunlamp" that had a total irradiation intensity of 1500 watts/m² (light source not further characterized; temperature not reported). In the irradiated soil, [¹⁴C]alachlor comprised 91.6% of the applied radioactivity after 24 hours, 90.3% after 48 hours, and 85.4% after 72 hours (Table 8). In the dark control soil, [¹⁴C]alachlor comprised 96.6% of the applied radioactivity at what was assumed to be the final sampling interval.

In the irradiated soil,

2'-acetyl-2-chloro-6'-ethyl-N-methoxymethylacetanilide
(Compound XXIV)

was a maximum of 4.5% of the applied after 72 hours. Uncharacterized aqueous-soluble [¹⁴C]residues totaled a maximum of 5.4% of the applied, and uncharacterized organosoluble [¹⁴C]residues totaled a maximum of 1.7%. Unextracted soil [¹⁴C]residues ranged from 1.6% to 2.9% of the applied at all sampling intervals. Volatilization was not measured. The material balances were 99.9-100% of the applied (reviewer-calculated).

In soil treated at 10 lb ai/A and irradiated with a sunlamp for 14 days (sole sampling interval), [¹⁴C]alachlor comprised 70% of the applied [page 29]; the following degradates were observed:

2-chloro-2',6'-diethylacetanilide (Compound II) was (illegible);

2',6'-diethyl-2-hydroxy-N-methoxymethylacetanilide (Compound XIII) was a maximum of 6.5%;

2'-acetyl-2-chloro-6'-ethyl-N-methoxymethylacetanilide (Compound XXIV) was 3.4%; and

2'-chloroethyl-6'-ethyl-N-methylacetanilide (tentative) was 1.1%.

Two unidentified [¹⁴C]compounds were isolated from the irradiated soil at 0.7 and 1.0% of the applied. The material balance was not provided.

Metabolism - Aerobic Soil

[¹⁴C]Alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; test substance not further characterized), at 2 ppm, degraded with a registrant-estimated half-life of approximately 2-3 weeks in "Ray" silt, "Spinks" loamy sand, and "Drummer" silt loam soils that were incubated in the dark at 25°C and 75% of field moisture capacity for 175 days. Thirteen [¹⁴C]degradates were identified in the soils:

2',6'-diethylacetanilide (Compound I);

2',6'-diethyloxanilic acid (Compound III);

2',6'-diethyl-2-sulfoacetanilide (Compound IV);

2',6'-diethyl-2-methylsulfinylacetanilide (Compound VI);

2',6'-diethyl-N-methoxymethylacetanilide (Compound IX);

2',6'-diethyl-N-methoxymethyloxanilic acid (Compound X);

2',6'-diethyl-N-methoxymethyl-2-sulfoacetanilide (Compound XI);

2',6'-diethyl-N-methoxymethyl-2-oxoacetanilide (Compound XII);

2',6'-diethyl-2-hydroxy-N-methoxymethylacetanilide (Compound XIII);

2',6'-diethyl-N-methoxymethyl-2-methylthioacetanilide (Compound XV);

2',6'-diethyl-N-methoxymethyl-2-methylsulfinylacetanilide
(Compound XVI);

2',6'-diethyl-N-methoxymethyl-2-methylsulfonylacetanilide
(Compound XVII); and

2'-acetyl-2-chloro-6'-ethyl-N-methoxymethylacetanilide
(Compound XXIV).

In the silt loam soil, [¹⁴C]alachlor (Compound XIV) was 87.7% of the applied radioactivity immediately posttreatment, 73.2% at 14 days, 47.4% at 21 days, 14.0% at 50 days, and 1.6% at 175 days (Table 24). The major degradate, Compound XI, was a maximum of 24.9% of the applied at 50 days posttreatment; Compound X was a maximum of 12.7% of the applied; and Compounds III, IV, and XIII were each a maximum of 4.5 to 6.7% (Tables 27 and 30). Compounds I, VI, IX, XII, XV, XVI, XVII, and XXIV were each $\leq 2.8\%$ of the applied at all sampling intervals. Uncharacterized organosoluble and aqueous-soluble [¹⁴C]residues were 0.4-2.6 and 0.2-1.8% of the applied (0.008-0.052 and 0.004-0.036 ppm, reviewer-calculated), respectively. Unextracted [¹⁴C]residues totaled 19.25-20.53% of the applied at 50-175 days posttreatment. At 175 days posttreatment, ¹⁴CO₂ and other [¹⁴C]volatiles totaled 30.33 and 1.15% of the applied, respectively. During the study, the material balances were 94.7-110.2% of the applied.

In the loamy sand soil,alachlor was 98.5% of the applied radioactivity immediately posttreatment, 67.8% at 7 days, 52.4% at 14 days, 11.4% at 50 days, and 2.5% at 175 days (Table 25). The major degradate, Compound X, was a maximum of 19.7% of the applied at 50 days posttreatment; Compounds III and XI were each a maximum of 15.8-16.9%; and Compound XIII was a maximum of 10.2% (Tables 28 and 31). Compounds I, IV, VI, IX, XII, XV, XVI, XVII, and XXIV were each $\leq 2.4\%$ of the applied at all sampling intervals. Uncharacterized organosoluble and aqueous-soluble [¹⁴C]residues were 0.6-2.4 and 0.3-2.9% of the applied (0.012-0.048 and 0.006-0.058 ppm, reviewer-calculated), respectively. At 175 days posttreatment, unextracted [¹⁴C]residues totaled 17.56% of the applied, and ¹⁴CO₂ and other [¹⁴C]volatiles totaled 16.17 and 0.72%, respectively. During the study, the material balances were 92.7-107.0%.

In the silt soil,alachlor was 99.0% of the applied radioactivity immediately posttreatment, 67.0% at 7 days, 40.4% at 14 days, 4.8% at 50 days, and 0.7% at 175 days (Table 26). The major degradate, Compound X, was a maximum of 22.4% of the applied at 28 days posttreatment; Compounds III and XI were each a maximum of 16.0-17.0%; Compound XIII was a maximum of 9.5%; and Compound IV was a maximum of 4.8% (Tables 29 and 32). Compounds I, VI, IX, XII, XV, XVI, XVII, and XXIV were each $\leq 3.7\%$ of the applied at all sampling intervals. Uncharacterized organosoluble and aqueous-soluble [¹⁴C]residues were 0.3-2.1 and 0.4-2.5% of the applied (0.006-0.042 and 0.008-0.050 ppm, reviewer-calculated), respectively. Unextracted

[¹⁴C]residues totaled 19.54-20.76% of the applied at 28-175 days posttreatment. At 175 days posttreatment, ¹⁴CO₂ and other [¹⁴C]volatiles totaled 26.54 and 0.98% of the applied, respectively. During the study, the material balances were 90.8-113.8% of the applied.

Metabolism - Anaerobic Aquatic

Carbonyl-labeled [¹⁴C]alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; radiochemical purity 98%), at 3.7 ppm, degraded with a registrant-estimated half-life of 3-4 days in flooded sandy clay loam sediment that was incubated under nitrogen gas in the dark at 25°C for 140 days. [¹⁴C]Alachlor comprised 90.9% of the applied immediately posttreatment, 55.8% at 3 days, 35.9% at 7 days, 12.8% at 14 days, and 1.3% at 140 days (Table 34). Six

[¹⁴C]degradates were identified:

2',6'-diethyloxanic acid (Compound III);

2',6'-diethyl-2-sulfoacetanilide (Compound IV);

2',6'-diethyl-N-methoxymethylacetanilide (Compound IX);

2',6'-diethyl-N-methoxymethyloxanic acid (Compound X);

2',6'-diethyl-N-methoxymethyl-2-sulfoacetanilide (Compound XI);
and

2',6'-diethyl-N-methoxymethyl-2-methylthioacetanilide (Compound XV; Tables 34-36).

The major degradate, Compound IX, was a maximum of 35.3% of the applied radioactivity at 21 days posttreatment, and was 12.7% at 140 days. Compound XV was a maximum of 9.3% of the applied; Compounds III and IV were each $\leq 1.70\%$; and Compound X plus Compound XI were a maximum of 4.80%. Four [¹⁴C]compounds isolated from the ammonium hydroxide soil extracts at maximums of 0.7-1.8% of the applied (0.03-0.07 ppm) were not identified (Table 36). Uncharacterized [¹⁴C]residues in organic soil extracts totaled a maximum of 16.2% of the applied (0.60 ppm), and uncharacterized [¹⁴C]residues in the floodwater totaled a maximum of 1.84% (0.07 ppm; reviewer-calculated from Tables 34-35). At 140 days posttreatment, ¹⁴CO₂ totaled 0.40% of the applied. Unextracted soil [¹⁴C]residues were a maximum of 40.4-49.0% of the applied at 70 through 140 days posttreatment. During the study, [¹⁴C]residues in the floodwater were a maximum of 4.8% of the applied, and the material balances ranged from 86.5 to 104.9%.

Mobility - leaching and adsorption/desorption

Unaged [¹⁴C]alachlor (batch equilibrium): [¹⁴C]Alachlor was very mobile in silt soil:water slurries and somewhat mobile in sandy clay

loam sediment:water slurries (both 2.5 g:10 mL) containing 0.1, 1.0, 5.0, or 10 ppm of carbonyl-labeled [¹⁴C]alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; radiochemical purity 98%) that were equilibrated overnight at an unspecified temperature. Freundlich K_{ads} values were 1.5 for silt loam soil and 12.8 for the sandy clay loam sediment [page 30]. After six desorptions with water, 84-94% of the radioactivity adsorbed to the silt soil and 19-55% of the radioactivity adsorbed to the sandy clay loam sediment was desorbed. Following desorption, the material balances ranged from 89.8 to 116.8% of the applied (Tables 12 and 14).

Unaged [¹⁴C]alachlor (soil column leaching): [¹⁴C]Alachlor was very mobile in columns (30-cm length) of silt, sand, and loamy sand soil and was mobile in columns of silt loam soil that were treated at 3.5 lb ai/A with carbonyl-labeled [¹⁴C]alachlor (2-chloro-2',6'-diethyl-N-methoxymethylacetanilide; radiochemical purity 98%) and leached with 20 inches of water. The leachate from the silt, sand, and loamy sand soil columns contained 40.9-96.9% of the radioactivity applied to the columns; the leachate from the silt loam soil columns contained 0.5-0.6% (Tables 15-18).

Following leaching of the silt soil ("Ray") columns, the leachate contained 78.2-82.2% of the applied radioactivity; the radioactivity remaining throughout the soil columns increased from 0.5-0.7% in the 0- to 2-cm segment to 2.3-3.8% in the 26- through 30-cm segments (Table 17).

Following leaching of the sand soil ("Lintonia") columns, the leachate contained 86.7-96.9% of applied radioactivity; the radioactivity remaining throughout the soil columns gradually increased from 0.2-0.3% in the 0- to 2-cm segment to 0.4-1.5% in the 28- to 30-cm segment (Table 18).

Following leaching of the loamy sand soil ("Spinks") columns, the leachate contained 40.9-43.4% of the applied radioactivity; the radioactivity remaining throughout the soil columns increased from 0.7-1.6% in the 0- to 2-cm segment to 4.1-5.8% in the 18- through 30-cm segments (Table 15).

Following leaching of silt loam soil ("Drummer") columns, the leachate contained 0.5-0.6% of applied radioactivity. The radioactivity remaining throughout the soil columns increased from 1.9-5.4% in the 0- to 2-cm segment to 10.9-12.9% in the 10- to 14-cm segments and declined to 0.1% in the 28- to 30-cm segment (Table 16).

In the leachates of the sand, silt and loamy sand soil columns,alachlor was the major [¹⁴C]compound;

2',6'-diethyl-N-methoxymethylacetanilide (Compound IX)

was isolated, but was not quantified [page 32]. In the leachate of the silt loam soil columns,alachlor was the major [¹⁴C]compound;

2',6'-diethyl-N-methoxymethylacetanilide (Compound IX),
2-chloro-2',6'-diethylacetanilide (Compound II), and
2',6'-diethyl-N-methoxymethyl-2-methylthioacetanilide (Compound XV)

were isolated at 23, 19, and 5% of the recovered radioactivity, respectively. Uncharacterized [¹⁴C]residues in the leachate totaled 20% of the recovered [page 33]. In the extracts of selected soil segments of all four soils, the radioactivity was "mainly" alachlor [page 33]. The material balances for the columns were 92.1-103.7% of the applied (Tables 15-18).

Aged [¹⁴C]alachlor residues: Based on column-leaching studies, aged (30 days) residues (uncharacterized) of [¹⁴C]alachlor were mobile in columns (30-cm length) of sandy loam soil that were treated at 3.5 lb ai/A with carbonyl-labeled [¹⁴C]alachlor, aged for 30 days under unspecified conditions, and then leached with approximately 20 inches of water over a 45-day period. Radioactivity recovered in the leachate totaled 29.1-31.5% of the applied; the radioactivity in individual biweekly leachate fractions ranged from 0.0 to 3.9% (Table 20).

In the leachates, [¹⁴C]alachlor totaled 8.8% of the applied radioactivity. Also isolated, each at <0.7% of the applied radioactivity, were

2-chloro-2',6'-diethylacetanilide (Compound II),
2',6'-diethyloxanilic acid (Compound III),
2',6'-diethyl-2-sulfoacetanilide (Compound IV),
2',6'-diethyl-N-methoxymethylacetanilide (Compound IX),
2',6'-diethyl-N-methoxymethyloxanilic acid (Compound X),
2',6'-diethyl-N-methoxymethyl-2-sulfoacetanilide (Compound XI),
2',6'-diethyl-2-hydroxy-N-methoxymethylacetanilide (Compound XIII),
2',6'-diethyl-N-methoxymethyl-2-methylthioacetanilide (Compound XV),
2',6'-diethyl-N-methoxymethyl-2-methylsulfinylacetanilide (Compound XVI), and
2',6'-diethyl-N-methoxymethyl-2-methylsulfonylacetanilide (Compound XVII; Table 21 and page 33).

Between 56.7 and 64.9% of the applied [¹⁴C]residues remained associated with the soil following leaching. The radioactivity decreased from 10.5-11.6% of the applied in the 0- to 2-cm segment to 0.9-1.1% in the 28- to 30-cm segment (Table 22). In the extract of the 0- to 2-cm segment, alachlor was 75.4% of the recovered radioactivity, Compound II was 0.6%, Compound IX was 1.1%, and Compound XV was 1.5% (Table 23). In the extract of the combined 12- to 16-cm segments, alachlor was 9.3% of the recovered radioactivity, Compound I was 1.4%, Compound II was 1.3%, Compound VI was 0.8%, Compound IX was 3.7%, Compound XIII was 3.4%, Compound XV was 0.6%, and Compound XVI plus Compound XVII were 1.9%. Uncharacterized residues in the aqueous extracts were 11.7-39.2% of the recovered radioactivity, and unextracted residues were 20.3-34.6% of the recovered. The material balances were 88.2-94.0% of the applied (Table 22).

COMMENTS:

General comments

1. The description of the methods was disorganized and often incomplete. When several related experiments were described simultaneously, the study authors did not clearly distinguish between the methods and results of the individual experiments.
2. The soils used in these studies were consistently misclassified. The study authors had incorrectly included the organic fraction with the mineral fractions to obtain the "100%" textural analyses of the soils. Based on the USDA soil classification system and the soil analyses provided in the document, the soil described as a "Ray silt loam soil" was a silt soil, the soil described as a "Drummer clay loam soil" was a silt loam soil, the soil described as a "Lintonia loamy sand soil" was a sand soil, the soil described as a "Spinks sandy loam soil" was a loamy sand soil, and the sediment was a sandy clay loam. The names of the soils were retained in the review to ease the interpretation of the registrant document; however, since the soil types are specific to texture, the soil types reported by the study author are incorrect.
3. The solubility of alachlor in water at 24°C was reported to be 240 ug/mL. The volatility of alachlor from moist soil was calculated from the vapor pressure (92.2×10^{-5} MM Hg at 24°C) and was 1.1×10^6 ; the volatility from water was 751,500 [units not identified, page 35].
4. The typical agricultural application rate for alachlor was reported to be 2 lb ai/A.

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Hydrolysis

1. The page of the results section containing the text concerning the hydrolysis study [page 24] was missing from the study document. Therefore, the data summary was written only from the pertinent tables (Tables 1-5).
2. The pH and sterility of the buffer solutions apparently was not monitored over the study period. The study authors failed to state the pore size of the Millipore filter used, or if it was sterilized prior to use.
3. The study authors estimated the half-life of alachlor to be >24 months in sterile water. This estimate is of limited value because the calculations involve extrapolation considerably beyond the experimental time limits of the study. Data are often incapable of accurately predicting trends outside of their range because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear.
4. The lake water was not characterized.
5. Information on the hydrolysis of pesticides in sterile lake water, nonsterile lake water, and deionized water is not required by Subdivision N guidelines. The nonsterile lake water experiment was described by the study authors as an aerobic aquatic metabolism study; however, Subdivision N guidelines specify that an aerobic aquatic metabolism study is conducted in a soil:water system, not in water only. The design of the nonsterile lake water system most closely resembles that of hydrolysis.

Photodegradation in Water

1. The page of the results section containing the text concerning the photodegradation in water study [page 24] was missing from the study document.
2. Although the study authors describe the preparation and irradiation of nonsensitized samples, no data from these samples was provided. In the abstract the study authors stated that alachlor was stable in the absence of the photosensitizer [page 6]; this statement cannot be accepted without supporting data.
3. The buffer solutions this study were not adequately described.
4. This study was conducted using a blacklight. Although the light source used in study was neither adequately described nor compared to sunlight, the emission spectrum of what is commonly considered to be a "blacklight" is not sufficiently comparable to sunlight.
5. Although the study authors reported the data for the sensitized solutions in terms of "applied radioactivity", it was uncertain if

this was actually applied radioactivity or recovered radioactivity. Material balances were not provided, and apparently no immediate posttreatment samples were analyzed (see comment 7). The sum of the radioactivity in the water and organic phases presented in Table 6 consistently totaled 100%.

6. Separate dark controls were not prepared. Alachlor was relatively stable in the hydrolysis portion of this study.
7. The temperature of the photolysis solutions was not reported.
8. The study authors reported that an experiment was conducted using [¹³C]-enriched alachlor (labeled at the C-2 position). No data were provided for this experiment.
9. Although test solutions were reportedly prepared using alachlor labeled in different positions, the data presented did not distinguish between the labeling positions. In addition, the alachlor in the large-scale experiment was not characterized.

Photodegradation on soil

1. The study was terminated at 72 hours, which was considerably before the photodegradation half-life for alachlor could be established. Subdivision N guidelines state that at least one sampling interval should be made after one-half of the parent had degraded or at 30 days, whichever occurs first. Based on the data provided, the study authors determined that, "Based on a normal 10 hour day of sunlight, the half-life of alachlor on the soil surface would be approximately 80 days." [page 30].
2. This study was conducted using a "sunlamp". Although the light source used in study was not adequately described and was not compared to sunlight, the emission spectrum of what is commonly considered to be a "sunlamp" is not sufficiently comparable to sunlight.
3. The temperature of the irradiated soil was not reported.
4. It could not be determined if the samples were continuously irradiated.

Aerobic soil metabolism

1. Uncharacterized radioactivity was present in the methylene chloride extracts and aqueous extracts at up to 2.1-2.6% (0.042-0.052 ppm) and 1.8-2.9% (0.036-0.052 ppm) of the applied radioactivity, respectively. Uncharacterized volatiles other than CO₂ were present at up to 0.72-1.15% of the applied (0.014-0.023 ppm). Subdivision N guidelines state that degradates present at ≥0.01 ppm must be identified. However, according to the Environmental Fate

Reregistration Rejection Rate Analysis document (9/93), the Agency now requires identification only of all residues equal to or greater than 10% of the dose rate.

2. The collection and analysis of volatiles other than CO₂ was not clearly described.
3. The large- and small-scale soil incubation experiments were conducted using significantly different procedures. No evidence was provided to demonstrate that the degradates in the small-scale studies were the same as the degradates identified in the large-scale study.
4. The labeling position of alachlor was not reported.
5. The acid hydrolysis experiment (using soil from the large-scale incubation) was conducted to determine if radioactive residues would hydrolyze to diethylaniline. Results "confirmed the fact that the aromatic functionality was not altered [page 41]."

Anaerobic aquatic metabolism

Floodwater samples and ammonium hydroxide extracts containing up to 1.6% of the applied radioactivity (0.06 ppm) and 11.5% (0.42 ppm), respectively, were not analyzed. Additionally, radioactivity present in the floodwater samples and ammonium hydroxide extracts at up to 1.84% of the applied radioactivity (0.07 ppm) and 0.7-1.8% (0.03-0.07 ppm), respectively, was not characterized. Subdivision N guidelines state that degradates present at ≥ 0.01 ppm must be identified.

Batch equilibrium

1. The soil was sieved through a 500-um mesh, removing a significant portion of the soil sand fraction. The removal of the sand fraction can possibly reduce the mobility of alachlor.
2. The study was conducted using water, rather than a 0.01 M calcium solution.
3. The equilibration temperature was not reported.

Column leaching studies (unaged)

1. The study authors stated that when the leachates were analyzed, the results of the GLC/RAD analysis of the methylene chloride extract "showed mainly alachlor with 2',6'-diethyl-N-methoxymethylacetanilide (IX) still present at the same ratio as in the alachlor solution applied to the column [page 32]." Neither the original analysis of test solution, nor the analysis of leachate were provided.
2. The columns were packed with soil to a depth of 30 cm using a wooden dowel. According to the study, the water "was added at a rate slower than the infiltration capacity of the soil." The study authors did

not report if the columns were saturated with water prior to leaching; the columns used for the aged leaching study were specifically described as moistened. These conditions could have decreased the amount of parent observed in the leachates.

3. The study authors stated that the mobility of alachlor was inversely correlated with organic matter content of the soil [pages 31-32].
4. The study authors stated that alachlor was of "intermediate" mobility [page 31]. The mobility determined by the study authors does not correspond to the mobility of the pesticide determined by evaluating the distance the chemical may leach presented in the Federal Register, Vol 44, No. 53 (the system for evaluation of mobility used by the EPA). The mobility of methyl parathion in each soil reported in the data summary section of this review was determined according to the system published in the Federal Register.
5. Even though the amount of radioactivity found in the leachates in the silt loam soil column was only 0.5-0.6% of the applied, substantial movement of the chemical was observed in the column. Most of the radioactivity (53.5-57.7% of the applied) was found in the soil segments corresponding from 9- to 18-cm.

Column leaching studies (aged)

1. In the aerobic metabolism study in this document, the half-life of alachlor was estimated to be 2-3 weeks. In this study, the soil was aged for 30 days, which is considerably beyond the estimated half-life of alachlor. It could not be determined if sufficient parent compound was present since the aged soil was not analyzed prior to leaching. Subdivision N guidelines require that the aged residues be characterized immediately prior to leaching and immediately following leaching.
2. The methods description was incomplete, the aging conditions for the soil were not described.
3. The data presentation of the residues in the soil extracts was unclear (Table 23). The units represented by the numbers were not stated, and the reviewer assumed that the data were presented in terms of "recovered radioactivity". It was uncertain what the information present in the row "¹⁴C-activity found (combustion)" related to, since these figures are different than those presented for the column sections presented in Table 22.

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Page _____ is not included in this copy.

Pages 142 through 240 are not included.

The material not included contains the following type of information:

- Identity of product inert ingredients.
- Identity of product impurities.
- Description of the product manufacturing process.
- Description of quality control procedures.
- Identity of the source of product ingredients.
- Sales or other commercial/financial information.
- A draft product label.
- The product confidential statement of formula.
- Information about a pending registration action.
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