12160l

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

MEMORANDUM: February 14, 1994

SUBJECT: **D198389.** Response to January 14, 1994 memo from A. Maciorowski of EEB to H. Jacoby of EFGWB concerning acetochlor and alachlor.

TO: Anthony Maciorowski, Chief
Ecological Effects Branch
Environmental Fate and Effects Division

FROM: Henry Nelson, Ph.D., Head H Nelson
Surface Water Section
Environmental Fate and Groundwater Branch/EFED

THRU: Henry Jacoby, Chief Henry Jacoby 2/15/94
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division

Question 1: Is monitoring information on alachlor useful in assessing the environmental fate and exposure of acetochlor in surface water?

Answer: Only qualitatively. Compounds that appear to have somewhat comparable fate characteristics and uses such as alachlor and acetochlor would be expected to have somewhat comparable concentrations in the environment, but could still differ by up to an order of magnitude in some places. Such differences may arise because of uncertainty in the fate data, natural variation in fate data due to differing environmental conditions, and because pesticide concentrations in surface water depend upon many factors. Consequently, even small differences in fate and use characteristics between two pesticides can be propagated into much larger differences in surface water concentrations.

Based upon computer inputs of almost identical K_{oc} and aerobic soil metabolism half-lives, but a lower application rate and much lower aerobic aquatic metabolism half-life for acetochlor, Ron Parker reported estimated EECs for acetochlor of 1/10 to 1/2 those for alachlor in the standard farm pond (See attachment A). Based upon those results, EFGWB would expect that average acetochlor concentrations in water bodies with long water residence times such as closed ponds would generally be lower than those for alachlor. However, there is substantial uncertainty in the determination of aerobic soil metabolism half-lives for acetochlor since much longer half-lives have been reported in studies in which exaggerated application rates were used (unfortunately most of the data available is for studies with exaggerated application rates). The lower half-life of 14 days was used because the application rate used (though exaggerated) was less than most other studies. If aerobic soil metabolism half-lives for acetochlor are generally greater for acetochlor than for alachlor, it would to some degree negate the lower aerobic aquatic half-life for acetochlor.

There is also some uncertainty in the aerobic aquatic half-life for alachlor (175 days) since a USGS study on alachlor and other major herbicides in 76 midwestern reservoirs (see below) indicate that alachlor was not very persistent compared to atrazine.

Much of the difference in predicted EECs for alachlor and acetochlor in a closed farm pond appears to be due to the much lower aquatic metabolism half-life reported for and input for acetochlor. However, differences in aquatic metabolism half-lives should not affect average concentrations in rivers and streams nearly as much as in ponds because even if a compound like alachlor is relatively stable to aquatic degradation, it is physically transported away from the sampling points in rivers and streams.

Question 2: Are the results provided in the attached document (cover letter dated January 12, 1994) likely to change the estimated concentrations or loadings of acetochlor provided to EEB December 22, 1993?

Answer: No, because as discussed in the first answer, EFGWB believes that alachlor data can not be substituted for acetochlor data for purposes of risk assessments.

Other attached documents consist of papers by Baker and Richards (Attachment B), Richards and Baker (Attachment C), and Gustafson etal (Attachment D). The Baker and Richards paper presents data on the concentrations of alachlor in 8 tributaries of Lake Erie from 1983 to 1987. The Richards and Baker paper discusses much of the same data, but extends it through 1991. The Gustafson paper is based primarily upon 2 surface water monitoring studies on alachlor performed by Monsanto in 1985 and 1986.

The Monsanto studies' data and some of the earlier (1983-1985) data on alachlor in Lake Erie tributaries were previously summarized by EFGWB in a January 25, 1993 memo to J. Housenger of SRRD from H. Nelson of EFGWB (Attachment E). That memo also summarizes data from 6 other studies including some performed by USGS. The later (1986-1991) data submitted on alachlor in tributaries of Lake Erie (see Table 3 and Figures 6 and 7 of the Richards and Baker report) is consistent with the earlier data, and do not significantly affect the summary of alachlor data in surface water provided in the January 25, 1993 memo.

None of the documents submitted by Monsanto nor the EFGWB January 25, 1993 memo summarizing alachlor data in surface water discuss the USGS study on 76 midwestern reservoirs (Goolsby etal - Attachment F).

In rivers and streams, peak alachlor concentrations after post-application runoff events (May-June) often exceed 4 times the MCL (8 ug/L) and can occasionally exceed 50 ug/L (Table 3 of the Richards and Baker paper, Figure 4 of the Goolsby etal paper). However, concentrations generally decline to less than 1 ug/L by late summer (see time series plots attached in the EFGWB January 23, 1993 memo). Late Spring to early Summer average alachlor concentrations in rivers and streams often exceed the MCL of 2 ug/L, but annual average concentrations appear to be generally less than 1 ug/L. Time weighted mean alachlor concentrations from April to December 1991 for 8 tributaries of Lake Erie ranged from 0.15 ug/L to 0.89 ug/L (Table 3 of the Richards and Baker paper).

Contrary to a reported aquatic metabolism half-life for alachlor of 175 days (used in the modeling), alachlor appears to be much less persistent in reservoirs than atrazine. Consequently, unlike atrazine (whose concentrations in reservoirs often exceed those in rivers and streams for most of the year), alachlor concentrations in reservoirs appear to generally be comparable to those in rivers and streams for most of the year (Figure 4 of the Goolsby report). Although, peak concentrations of alachlor in streams and rivers are generally greater than in reservoirs, the concentration of the major degradate of alachlor (ESA) often exceeded that of alachlor in the reservoirs (Figure 4 of the Goolsby report).

DP BARCODE: D198389

DATA PACKAGE RECORD
BEAN SHEET

* * * FREE STANDING DATA PACKAGE * * *

THERE IS NO CASE OR SUBMISSION DATA

* * * DATA PACKAGE INFORMATION * * *

DP BARCODE: 198389 EXPEDITE: N DATE SENT: 01/14/94 DATE RET.: / /
CHEMICAL: 121601 Acetochlor (ANSI)
DP TYPE: 001 Submission Related Data Package
CSF: Y LABEL: N

ASSIGNED TO	DATE IN	DATE OUT		
DIV : EFED	01/14/94	/ /	ADMIN DUE DATE:	/ /
BRAN: EFGB	/ /	/ /	NEGOT DATE:	/ /
SECT: SWS	/ /	/ /	PROJ DATE:	/ /
REVR :	/ /	/ /		
CONTR:	/ /	/ /		

* * * DATA REVIEW INSTRUCTIONS * * *

Please evaluate the attached alachlor monitoring data and determine if it changes the estimated exposure of acetochlor in surface waters as provided to EEB in December, 1993. Thank you.

* * * DATA PACKAGE EVALUATION * * *

No evaluation is written for this data package

THERE ARE NO ADDITIONAL DATA PACKAGES

Wilson

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

JAN 14 1994

MEMORANDUM

OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

SUBJECT: Request for Review of Alachlor Data for Acetochlor Exposure Assessment

FROM: Anthony F. Maciorowski, Chief
Ecological Effects Branch
Environmental Fate and Effects Division H7507C

Douglas J. Urban 1/14/94

TO: Henry M. Jacoby, Chief
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division H7507C

The EEB has been provided information on the results of surface water monitoring with alachlor. The Acetochlor Registration Partnership believes that this alachlor monitoring information provides useful information to predict the behavior of acetochlor in the environment, and should be considered when estimating how much acetochlor might get into surface water.

Please evaluate this information and determine the following:

1- Is monitoring information on alachlor useful in assessing the environmental fate and exposure of acetochlor in surface water?

2- Are the results provided in the attached document (cover letter dated January 12, 1994) likely to change the estimated concentrations or loadings of acetochlor provided to EEB December 22, 1993?

If it is appropriate to use the results of the alachlor monitoring to predict or characterize the behavior of acetochlor, and if the results change the estimated loading and concentrations in surface water to which fish, aquatic invertebrates and plants may be exposed, please indicate what the new exposure concentrations are. Please provide the estimations based on the same application rates and same scenarios and conditions used in the December, 1993 modeling.

Please provide Dan Rieder with an estimated completion date after you have had a chance to schedule this request. Thank you, and if you have questions, please contact Mike Davy or Dan Rieder.

Acetochlor Registration Partnership
c/o ZENECA Ag Products
P. O. Box 751
Wilmington, DE 19897
302-886-1218

January 12, 1994

HAND DELIVERED

Mr. Robert J. Taylor
Registration Division
Document Processing Desk (H7504C)
U.S. Environmental Protection Agency
Room 266A, Crystal Mall 2
1921 Jefferson Davis Highway
Arlington, Virginia 22202

Dear Mr. Taylor:

RE: Surface Water Monitoring Data

We have been advised that the Ecological Effects Branch has requested copies of the references noted in the Acetochlor Registration Partnership review document on Ecological Effects data submitted to your office on March 30, 1993. Two copies of each of the references are enclosed.

As stated in the review document, it is the Acetochlor Registration Partnership's belief that the surface water monitoring data collected for alachlor provides the best available information to determine the Expected Environmental Concentration for the use of acetochlor on corn.

Please use this information in conjunction with the information provided by the Agency's computerized modeling programs to evaluate the acceptability of our request for registration.

Respectfully submitted,

Robert E Ridsdale

Robert Ridsdale, Ph.D
Managing Agent
Acetochlor Registration Partnership

Attachments

6

ATTACHMENT A

Acetochlor-Alachlor Comparison

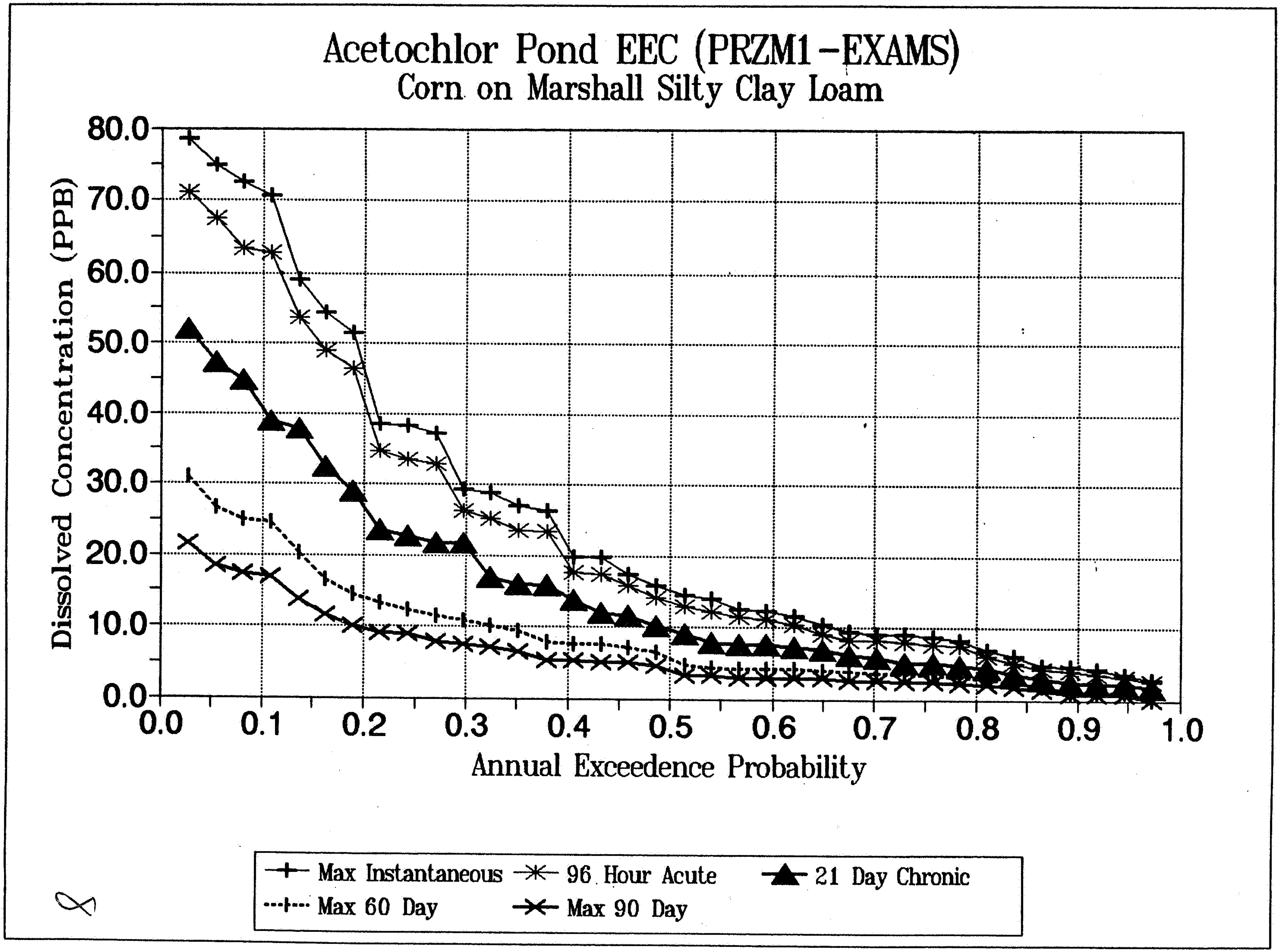
Input Parameters (where different)		
Parameter (Units)	Acetochlor	Alachlor
Application Rate (Kg/Ha)	2.6	3.6
Aerobic Soil Half-life (Days)	14-55* 110-300*	21
Aerobic Aquatic Half-life (Days)	14	175**
Solubility	233	242
Molecular Weight	270	270
Vapor Pressure	4.5e-5	2.2e-5
Soil KOC	200	190

* Function of application rate and possibly texture. Half-life of 14 days used in modelling.

** Extrapolated

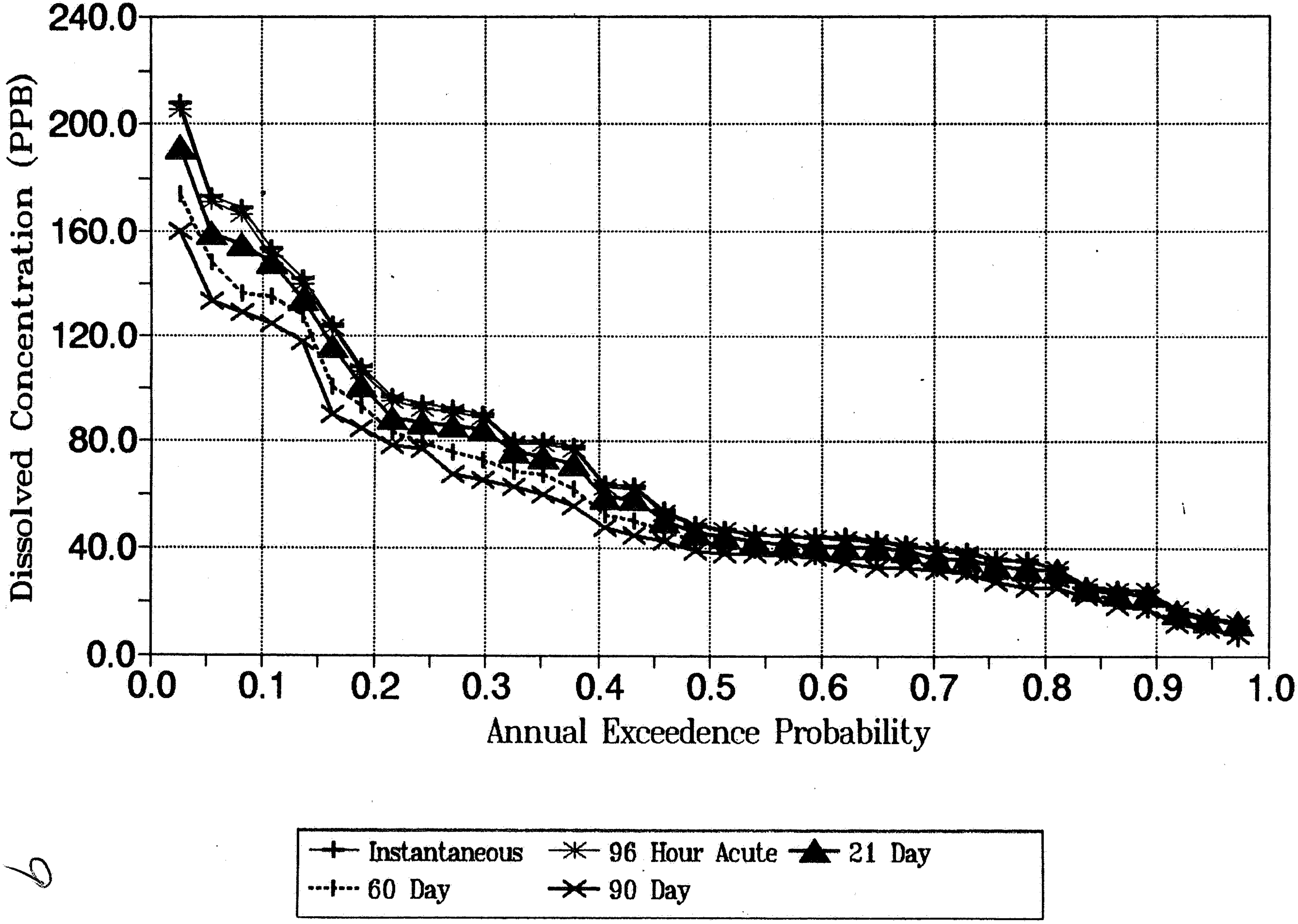
These differences may or may not be real. The one difference known to be real is the application rate. Acetochlor is applied at 2.6 kilograms per hectare and alachlor at 3.6 kilograms per hectare. The aerobic soil half-lives for acetochlor are very different between Zeneca and Monsanto. I have used a Monsanto value. On that basis it is hard to argue that there is a real difference between the two chemicals but these numbers lead to the differences in the attached graphs.

Another big issue is the toxicity of the multiple metabolites. This modelling reflects disappearance of parent only and not necessarily disappearance of toxicity. Levels of metabolites in ground water are much (20x) higher than that of the parent. Is this true in surface water as well. The alachlor monitoring data are likely to shed some light on that.


Acetochlor Pond EEC (PRZM1-EXAMS)
Corn on Marshall Silty Clay Loam
Dissolved Concentration (PPB)
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Annual Exceedence Probability
Max Instantaneous
96 Hour Acute
21 Day Chronic
Max 60 Day
Max 90 Day

8

Alachlor Pond EEC (PRZM1-EXAMS)
Corn on Marshall Silty Clay Loam (IA)



6

ATTACHMENT B
Baker + Richards

The first Baker & Richards paper.

Long Range Transport of Pesticides

David A. Kurtz
Editor

LEWIS PUBLISHERS

10

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11

This book is dedicated to the memory of

DWIGHT E. GLOTFELTY

who passed away in April 1990 following a long and fruitful career in the stu of pesticides: analysis, fate, and transport. He was project leader in the en ronmental chemistry laboratory of the Natural Resources Institute of the Ag cultural Research Service of the U.S. Department of Agriculture Beltsv Agricultural Research Center.

Dr. Glotfelty was instrumental in the use of porous polyurethane foam a sampling medium for measuring the concentration of pesticide vapors in This was a basis for studies of the pesticide movement in the atmosphere. H work on the volatilization of pesticides in the presence of soil moistu advanced the knowledge of transport mechanisms, and his work on the pr ence of pesticides in fog and aerosol particles developed this new field.

The appearance of triazines and other herbicides in groundwater is anoth area in which Dr. Glotfelty did early work. His work on the atmosphe transport of triazines and toxaphene from areas in southern U.S. into t Chesapeake Bay is also noteworthy, and is reported in this text.

Dwight Glotfelty will be severely missed for the contributions he would have made, had he lived longer on this, our only earth. For his research and for his encouragement, I want to dedicate this book.

Hydrocarbon Residues in Adipose Tissue of Canadians," *Bull. Environ. Contam. Toxicol.* 28:97–104 (1982).
18. Mineau, P., G. A. Fox, R. J. Norstrom, D. V. Weseloh, D. J. Hallett, and J. A. Ellenton. "Using the Herring Gull to Monitor Levels and Effects of Organochlorine Contamination in the Canadian Great Lakes," in *Toxic Contaminants in the Great Lakes*, J. O. Nriagu and M. S. Simmons, Eds. (New York, NY: John Wiley and Sons, 1984), pp. 425–52.
19. "1987 Report on Great Lakes Water Quality," International Joint Commission, Great Lakes Water Quality Board, Windsor, Ont. (1987).

12

CHAPTER 17

Transport of Soluble Pesticides Through Drainage Networks in Large Agricultural River Basins

David B. Baker and R. Peter Richards

INTRODUCTION

Most studies on long-range and atmospheric transport of synthetic organic chemicals and pesticides have focused on compounds that are persistent and that tend to bioaccumulate, such as PCBs, DDTs, PAHs, and toxaphene. Such a focus is certainly justified since these two characteristics combine to confer upon such compounds the potential for significant and long-term ecological damage, as well as concern regarding possible human health impacts. Awareness of such damage and concern has led to restrictions and even banning of the use and manufacture of many of these compounds.

Although some pesticides have been banned, total pesticide use in the United States increased by about 170% between 1964 and 1985.[1] Fortunately, most of the newer generation pesticides are much less persistent and have a much lower tendency to bioaccumulate. Much of the increase in pesticide use has been comprised of large increases in the use of herbicides. In the corn and soybean production areas of the Ohio drainage to Lake Erie, herbicides comprised 92% by weight of the total pesticides used in 1986.[2] For many of these compounds, volatilization is a significant pathway leading to their dissipation from application sites.[3] The axiom "what goes up must come down" has again been confirmed in the recent reports of relatively "high" concentrations of many current generation pesticides in dew[4] and in rainfall.[5]

Although the concentrations of current generation pesticides in rainfall are generally high in comparison to concentrations of the persistent organochlorine insecticides in rainfall, by far the highest widely occurring offsite concentrations of current generation pesticides are associated with surface water runoff from edges of fields directly into streams and rivers.[6] Accidental spills or leaks can result in extremely high, localized concentrations, but such incidents are infrequent and localized in comparison with exposures associated with runoff events from fields receiving normal pesticide applications.

Many of the currently used compounds have low affinities for sediments and are transported primarily in the dissolved state rather than through attachment to sediments.[3] Where surface waters containing these soluble compounds are used for public water supplies, conventional water treatment does little to lower pesticide concentrations,[8,9] leading to pesticide exposures through drinking water.

Both the human health risks posed by pesticides in drinking water supplies and the ecological risks posed by pesticides in surface waters are dependent on the interaction of two major sets of factors, the exposure to the pesticides and the toxicity of the pesticides (Figure 1). Given long-standing concerns regarding human health and ecological effects of pesticides, it is rather surprising that there is very little exposure data for current generation pesticides in streams and rivers. In a 1978 review of edge-of-field losses of pesticides, Wauchope noted a paucity of information regarding the fates and effects of pesticides after they left the edge of the field.[10]

This lack of exposure data for current generation pesticides is a consequence of several factors. Most federal and state water quality monitoring programs involve fixed station approaches with sampling frequencies ranging from monthly to annually, depending largely on the cost of the analyses.[11] Such programs provide reasonable information regarding the impacts of point sources of pollution, but they are inappropriate for non-point source pollution studies. A nationwide pesticide monitoring program in rivers, conducted between 1975 and 1980 by the U.S. Geological Survey, involved collection of four samples per year at 160 stations and analysis for 18 insecticides and 4 herbicides.[12] The program focused on studies of the disappearance of banned pesticides rather than the occurrence of current generation compounds. The 22 pesticides together made up less than 33%, by weight, of the pesticides used during that period. Fewer than 10% of the river samples contained reportable

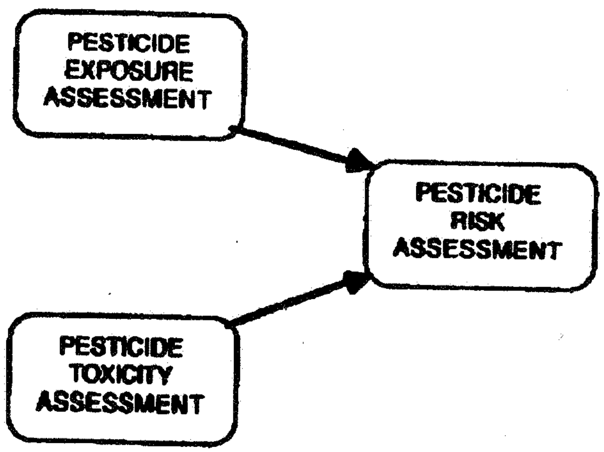

Figure 1. Relationships between exposure assessment, toxicity assessment, and risk assessment for pesticides.

13

pesticide concentrations. More recently, federally mandated pesticide monitoring has been restricted to annual tests in municipal water supplies for six pesticides (endrin, lindane, methoxychlor, toxaphene, 2,4-D, and 2,4,5-TP). Recommended maximum contaminant levels (RMCLs) were set for these six compounds through implementation of the Safe Drinking Water Act, triggering required monitoring for these compounds. These compounds comprise a very small portion of current pesticide use. In Ohio, they make up approximately 1% of the total amount of pesticides applied. They are rarely detected in public water supplies and apparently have never been observed to exceed the RMCLs. In Ohio, as well as in many other states, no mandated pesticide monitoring was in force through 1987 for 99% of the pesticides used in today's agriculture. In 1988, the Ohio EPA required water treatment plants utilizing surface waters to analyze one sample, collected during the May through July period, for alachlor and metolachlor.

Extensive studies of current generation pesticides have been conducted for research plots and individual fields at land grant universities and agricultural research centers.[8] The U.S. EPA's pesticide monitoring strategy is largely based on the use of models to predict in-stream concentrations.[13] Edge-of-field pesticide runoff data are used as input for the models. Although these models have been used to predict pesticide concentrations in streams and rivers, with few exceptions,[14] these predictions have rarely been verified with actual concentration data from detailed monitoring programs.

The streams and rivers draining into Lake Erie have been the focus of detailed studies of nutrient and sediment runoff, beginning in the early 1970s.[15,16] In 1981, pesticide runoff studies were added to the program, in part to assess whether conservation tillage would aggravate pesticide runoff problems. Conservation tillage is viewed as a fundamental component of agricultural nonpoint pollution control programs aimed at reducing phosphorus loading to Lake Erie. It is likely that the resulting pesticide runoff studies in streams and rivers of the Lake Erie Basin are the most detailed of their type in the United States. In the absence of comparable studies in other regions, it is unclear whether the results observed in this region reflect unusually high, normal, or low degrees of pesticide exposure. It is likely, however, that the exposure patterns and characteristics that we have observed in this region will also occur in other streams and rivers draining watersheds with intensive row crop production. In this chapter, we will summarize those exposure patterns and characteristics, using data from the streams and rivers of the Lake Erie Basin as a case study.

METHODS

To characterize pesticide exposure patterns in streams draining agricultural landscapes, we have focused our efforts at a relatively small number of locations; at those locations, however, we collect samples at frequent intervals, especially during runoff events. All of our sampling locations are located at U.S. Geological Survey stream gauging stations in the Lake Erie Drainage Basin (Figure 2). These stations provide continuous discharge data so that both pesticide loadings and concentration patterns can be determined. The drainage areas upstream from the sampling stations range from 11.3 to 16,395 km². Most of the soils have a relatively heavy texture (clays, silty clay loams, and silty loams) and use of subsurface tile drainage is common. The drainage areas and land use upstream from each station are summarized in Table 1.

Corn and soybeans are the major crops grown in the region. Together, they account for 99.7%, by weight, of the herbicides and 90.1%, by weight, of the insecticides used in 1986 in the Ohio portion of the Lake Erie Basin.[2] The 20 pesticides used in the largest quantities in this region are listed in Table 2. The 15 herbicides on the list accounted for 97.3% of the total herbicide use and the 5 listed insecticides accounted for 87.9% of the total insecticide use. The bulk of the pesticide use occurs within the northwestern and north central parts of Ohio, which are drained primarily by the Maumee and Sandusky rivers, respectively. Table 2 also includes a 1982 ranking of pesticides, by amount used, for the entire state of Ohio.[17] Although there have been some changes in

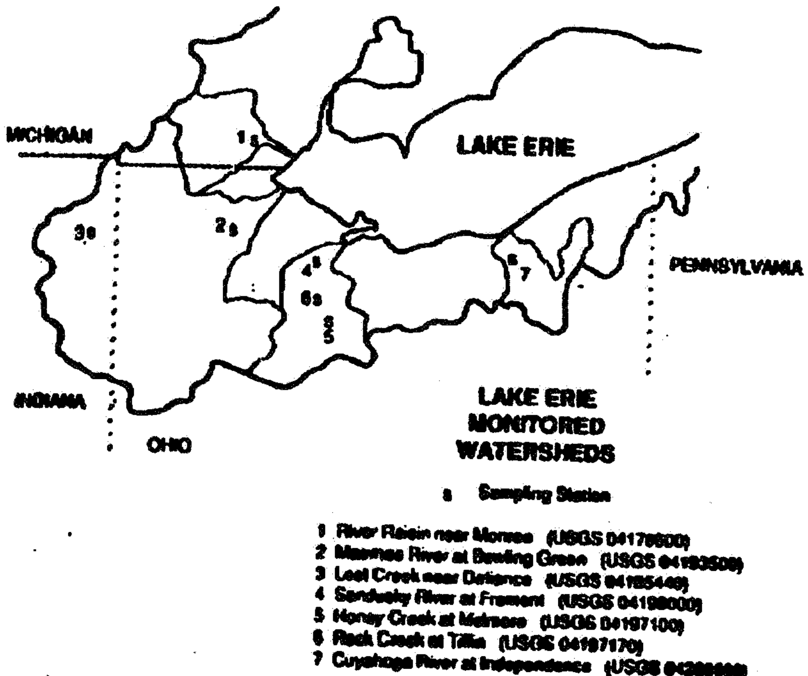

Figure 2. Locations of pesticide monitoring stations for the Lake Erie Basin agricultural runoff studies. The United States Geological Survey stream gauging station identification numbers are listed alongside the name for each of the tributary sampling stations.

14

Table 1. Watershed Areas and Land Use for the Pesticide Monitoring Stations in the Lake Erie Basin

Watershed	Watershed Area (km²)	Cropland (%)	Pasture (%)	Forest (%)	Water (%)	Other (%)
Maumee River at Waterville, OH	16,395	75.6	3.2	8.4	3.5	9.4
Sandusky River at Fremont, OH	3,240	79.9	2.3	8.9	2.0	6.8
River Raisin near Monroe, MI	2,699	67.1	6.8	9.0	3.0	14.1
Cuyahoga River at Independence, OH	1,831	4.2	43.1	29.1	3.0	20.6
Honey Creek at Melmore, OH	386	82.6	0.6	10.0	0.5	6.3
Rock Creek at Tiffin, OH	88.0	80.9	2.3	11.8	0.8	4.2
Lost Creek Trib. near Farmer, OH	11.3	83.0	0	10.6	1.4	5.0

Source: Baker.[18]

the rankings of pesticide use during the course of these studies, the general pattern of pesticide use has changed very little.

For most stations, automatic samplers (ISCO Model 2700 or equivalent) are used to collect from two to four 1-L samples per day during the period from mid-April through mid-August, which encompasses most of the period of high ambient pesticide concentrations and loadings. The automatic samplers are housed in the U.S. Geological Survey stream gauging station shelters. Submersible pumps in the streams deliver water to sampling wells inside the shelters, and the sampler pumps withdraw water from the wells. During periods of runoff events, all of the samples from the automatic samplers are analyzed, while during non-event periods, two-samples per week are analyzed. From mid-August through the winter to mid-April, grab samples are collected twice per month at each station.

Since the frequency of sampling varies in relation to the expected pesticide concentrations, with samples collected more frequently during periods of high concentrations, calculation of average exposures involves weighting of individual samples in relation to the time they are used to characterize the stream systems. These time-weighted mean concentrations (TWMCs) are calculated as follows:

$$\mathrm{TWMC} = \frac{\Sigma c_i t_i}{\Sigma t_i}$$

where c_i are the observed concentrations and t_i are the times represented by each sample.

Table 2. Pesticide Use in the Lake Erie Basin for 1986 and Ranking by Use in the State of Ohio for 1982

Pesticide	Brand	Type[a]	Quantity Used (metric tons)	1986 Rank, by Use	1982 Rank by Ohio Use[b]
Alachlor	Lasso	H	1319	1	1
Metolachlor	Dual	H	887.2	2	3
Atrazine	Aatrex	H	783.9	3	2
Cyanazine	Bladex	H	273.4	4	4
Metribuzin	Lexone, Sencor	H	255.5	5	7
Chloramben	Amiben	H	155.5	6	6
Linuron	Lorox, Linurex	H	133.0	7	8
Terbufos	Counter	I	74.67	8	10
Trifluralin	Treflan	H	65.7	9	12
Butylate	Sutan, Genate plus	H	58.19	10	5
Dicamba	Banvel	H	54.39	11	19
Pendimethalin	Prowl	H	49.49	12	17
Bentazon	Basagran	H	49.36	13	15
Carbofuran	Furadan	I	48.23	14	11
2,4-D	2,4-D	H	44.44	15	14
Chlorpyrifos	Dursban	I	38.33	16	NR
EPTC	Eradicane, Eptam	H	34.67	17	13
Phorate	Thimet	I	31.51	18	NR
Fonofos	Dyfonate	I	25.10	19	9
Simazine	Princep	H	24.82	20	16
Total herbicide use in the Lake Erie Basin. The 15 herbicides listed above make up 97.3% of the total herbicide use in the Lake Erie Basin.			4315.5		
Total insecticide use in Lake Erie Basin. The 5 insecticides listed above make up 87.9% of the total insecticide use in the Lake Erie Basin.			245.8		

Sources: Waldron.[2,17]
[a]H, Herbicide; I, Insecticide.
[b]NR: not in top 20 in 1982.

A multiresidue scan, using gas chromatography, capillary columns, temperature programming, and nitrogen-phosphorus detectors, is used for pesticide analysis. Samples are first extracted with methylene chloride, concentrated with Kuderna-Danish apparatus, and transferred to 2-propanol for subsequent analysis. Simultaneous injection into DB1 and DB5 capillary columns allows separation, identification, and quantification of most of the major pesticides used in this region. A partial list of the pesticides included in the scan, along with detection limits and spike recoveries, is shown in Table 3. All of the data presented in this chapter have been corrected for recoveries less than 100%, using either the average recovery for each compound each year or, where data from several years are combined, using the overall average recovery. The scan provides data for 89% by weight of the herbicides used in this region and for 75% by weight of the insecticides.

Quality control procedures have included the analysis of blanks, replicates, reference standards, and spikes, as well as interlaboratory exchanges with

15

Table 3. Approximate Detection Limits and Lower Limits of Linear Response Ranges

Pesticide	Detection Limit (ng/L)	Lower Limit of Linear Response[a] (ng/L)	Mean Percent Recovery 1984	1985	1986	1987	1988	Used (ACS)
Alachlor (Lasso)	100	500	71	64	76	74	70	71
Metolachlor (Dual)	250	250	67	67	69	77	81	76
Atrazine (Aatrex)	50	500	86	69	76	76	70	75
Cyanazine (Bladex)	250	500	96	79	85	62	51	75
Metribuzin (Lexone, Sencor)	100	2500	54	66	73	70	74	67
Linuron (Lorox, Linurex)	1500	5000	—	80	86	—		83
Terbufos (Counter)	100	nd	76	64	72	73		69
Butylate (Sutan, Genate plus)	50	200	73	70	—	81		66
Pendimethalin (Prowl)	80	nd	80	71	71	71		73
Carbofuran (Furadan)	200	500	89	77	92	100		90
EPTC (Eradicane, Eptam)	50	nd	76	66	86	61		67
Fonofos (Dyfonate)	80	150	80	57	43	62	87	56
Simazine (Princep)	250	2500	86	74	77	89		83

Note: Based on analysis of dilution series of mixed standards; mean percent recoveries of spikes, by year; and mean recoveries used for calculations using the entire data set.
[a]nd: not determined.

Table 4. Comparison of Time-Weighted Mean Concentrations (TWMC) of Five Major Herbicides During the "Winter" and "Summer" Periods

Pesticide	Summer N	Summer TWMC (µg/L)	Winter N	Winter TWMC (µg/L)	Ratio (Summer/Winter)
Maumee River					
Alachlor	267	1.84	78	0.05	40.1
Metolachlor	267	2.80	78	0.22	12.7
Atrazine	267	4.05	78	0.79	5.1
Cyanazine	267	1.17	78	0.07	15.9
Metribuzin	267	0.87	78	0.11	7.6
Sandusky River					
Alachlor	307	2.48	69	0.06	44.1
Metolachlor	307	4.79	69	0.33	14.5
Atrazine	307	5.08	69	0.83	5.9
Cyanazine	307	4.79	69	0.04	31.1
Metribuzin	307	1.07	69	0.10	10.9
Honey Creek					
Alachlor	443	3.32	96	0.22	15.4
Metolachlor	443	5.38	96	0.86	6.3
Atrazine	443	6.72	96	1.55	4.3
Cyanazine	443	1.15	96	0.16	7.3
Metribuzin	443	0.86	96	0.10	4.3

Note: The summer period is defined as April 15 to August 15, the winter period as August 16 to April 14 of the following year. The data represent the period from April 1983 to November 1987.

pesticide manufacturers. Additional details on the sampling procedures have been described by Baker,[18] and the analytical procedures have been described by Kramer and Baker.[20] The analytical method is very similar to the U.S. EPA's Draft Method 507 (nitrogen- and phosphorus-containing pesticides in water by gas chromatography with a nitrogen-phosphorus detector) as revised in 1988 and recommended for use in evaluation study WS023 by U.S. EPA, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

RESULTS AND DISCUSSION

Seasonal Characteristics of Pesticide Exposure

The concentrations of currently used pesticides in rivers of this region are much higher in the late spring through midsummer season, following the major periods of pesticide application, than they are during other times of the year. In Table 4, TWMCs of five major herbicides are shown for three monitoring stations for the April 15-August 15 period ("summer") and the August 16-April 14 period ("winter"). These data were collected between April 1983

16

and November 1987. At these stations, the ratios of the summer to winter TWMCs ranged from 4.3 to 44. The magnitude of the ratio varied among the five herbicides, apparently in relationship to the persistence of the compound. At each site, the ratio of summer to winter concentrations was highest for alachlor, the least persistent of the five herbicides.[19] The ratio of summer to winter concentrations was lowest for atrazine, the most persistent of these herbicides. In the remainder of this chapter, will be referred to as the pesticide runoff season for this region.

Pesticide Concentrations in Relation to Stream Flow

Comparisons of plots of pesticide concentrations as a function of time (chemographs) with plots of stream discharge as a function of time (hydrographs) clearly shows that during the pesticide runoff season, pesticide concentrations increase in association with runoff events.[16] Pesticide chemographs and the discharge hydrograph for Honey Creek at Melmore, Ohio, during the 1985 pesticide runoff season are shown in Figure 3. These data also illustrate that there is no clear relationship between the magnitude of a storm's peak discharge and magnitude of the associated pesticide concentrations. Three successive storm events with greatly differing peak discharges all had similar

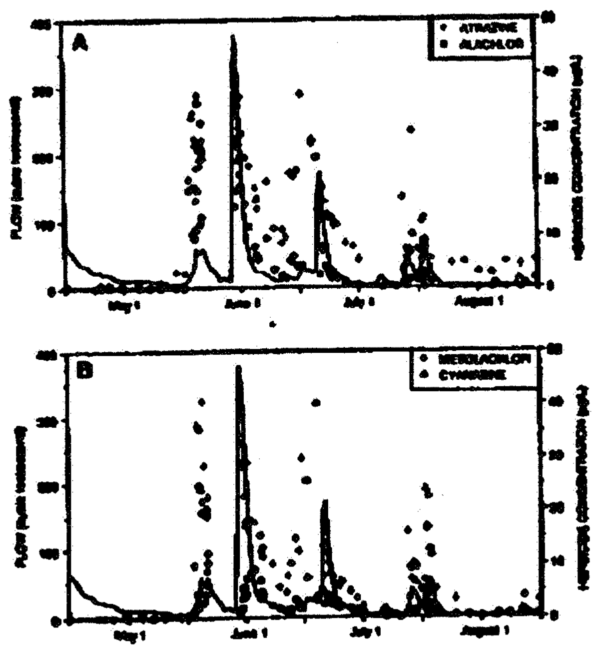

Figure 3. Chemographs for atrazine, alachlor, metolachlor, and cyanazine in relation to the streamflow hydrograph for the Honey Creek sampling station during the April 15-August 15, 1985 pesticide runoff season.

peak pesticide concentrations. However, by mid-July, seasonal aspects of pesticide runoff begin to appear. For example, the mid-July runoff events in Honey Creek (Figure 3) had lower peak concentrations than the May and June runoff events, especially for alachlor. Several factors could account for the lower peak herbicide concentrations of the July storms, including breakdown of the herbicides, depletion of available herbicides at the soil surface by previous runoff, herbicide dissipation through volatilization, herbicide uptake by plants, or herbicide movement into deeper soil layers via leaching.[4]

Plots of herbicide concentration in relation to stream discharge for Honey Creek during the April 15 to August 15 periods illustrate the large amount of variability in the relationships between instantaneous discharge and stream flow (Figure 4). The scattering in Figure 4 occurs because runoff events of greatly differing magnitude can be accompanied by similar pesticide concentrations and runoff events of the same magnitude can have greatly differing

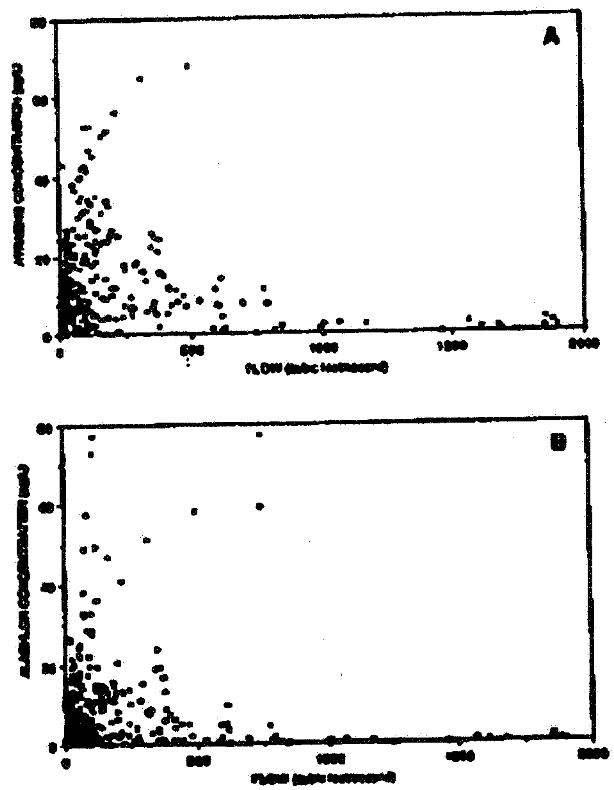

Figure 4. Relationships between herbicide concentrations and stream flow at the Honey Creek sampling stations for samples collected during the April 15-August 15 period for 1983-1987. (A) atrazine; (B) alachlor.

17

pesticide concentrations. Consequently, stream flow is, by itself, not a good predictor of pesticide concentration, even during the pesticide runoff season.

The relationships between pesticide concentrations and runoff events evident in Honey Creek also occur in other watersheds, both larger and smaller.[16] Often storm events are superimposed on one another, so that streams do not return to base flow between storm events. These circumstances lead to complex pesticide concentration patterns in streams and rivers.

Relationships Between Pesticide, Sediment, and Nitrate Transport

The same rainstorms that move pesticides off fields into streams and rivers also move sediments and nitrates into the streams and rivers. During individual storm runoff events, the concentration patterns for pesticides differ from those of sediments and nitrates in a systematic fashion. The timing of the peak concentrations and the chemograph shapes can be used to infer characteristics of the pathways of material movement from fields into streams. A storm in Honey Creek during May 1986 illustrates the typical pattern (Figure 5).

Sediment concentrations usually peak during the rising portion of the hydrograph and are already declining by the time discharges reach their peak values (Figure 5a). Two explanations of the advanced sediment peaks are often proposed. One of these notes that even in runoff studies of individual fields or

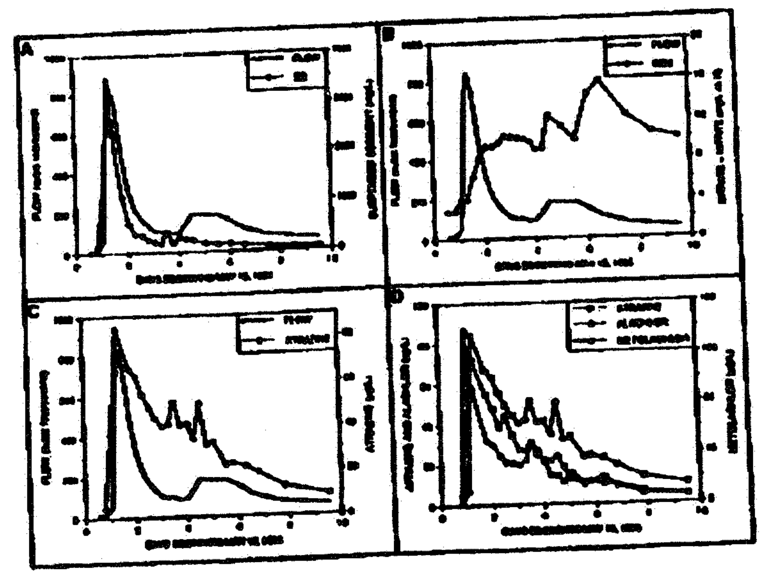

Figure 5. Pollutant chemographs and the storm hydrograph for a runoff event at the Honey Creek station beginning May 15, 1986. (A) suspended solids concentrations in relation to the hydrograph; (B) nitrate concentrations in relation to the hydrograph; (C) atrazine concentration in relation to the hydrograph; (D) comparison between the atrazine, alachlor, and metolachlor chemographs.

plots, the initial surface runoff water has higher sediment concentrations than water leaving the field later during the event.[29] This occurs even in rainfall simulator studies where the rainfall intensity is held constant. Apparently there is a "pool" of readily erodible sediment on the soil surface that comes off with the early runoff water at the beginning of the storm. Advanced sediment peaks in rivers are then thought to be accounted for by the routing of the water from individual fields into and through the stream networks.[30]

An alternative explanation for the advanced sediment peaks involves the role of resuspension and deposition of sediments between the water column and the stream bottom.[31] This explanation considers stream bottom sediment as the major source of sediment observed in a stream during runoff events. A flood creates a wave which propagates down the river, just as a stone thrown into a pond creates ripples (small waves) which propagate across the pond's surface. The time trace of the wave as it passes a given point is what we call the hydrograph. The wave moves independently of the water molecules, which move only in small circles in the pond, but move downstream in the river, more slowly than the wave. As the flood wave moves downstream, it resuspends sediment from the stream bottom into the water column, yielding high sediment concentrations on the rising limb of the hydrograph. Since the flood wave moves downstream more quickly than the water flows downstream, water comprising the rising limb of the hydrograph at an upstream site will comprise part of the falling limb of the hydrograph at a downstream site. Under the channel conditions at the downstream site, much of the sediment originally incorporated into the water column at the upstream site would have settled out of the water column. However, at the downstream site, as the flood wave moved past, it would have picked up sediment during the rising stage of the hydrograph, yielding an advanced sediment peak at the downstream site. According to this hypothesis, the advanced sediment concentration peaks in rivers are a consequence of the movement of the flood front, as a kinematic wave, resuspending sediment as it moves through the drainage network, and redepositing it at downstream sites.

In contrast to sediment, the highest concentrations of nitrate occur during the falling limb of the hydrograph (Figure 5b). Large proportions of the cropland in these watersheds have been systematically tiled. These fields use an array of clay tiles or plastic drainage pipes placed 3–6 ft below the surface, to facilitate drainage. The tiles drain into the tributaries, either directly or via drainage ditches. Plot and field studies indicate that most of the nitrate export from fields in this region occurs through the tile systems.[22] At river sampling stations, the proportion of tile drainage water to surface runoff water increases during the falling limb of the hydrographs, accounting for the observed peak nitrate concentrations during the later portion of the runoff event.

The concentration patterns of those pesticides that are transported primarily in the dissolved state are similar to, but do not coincide with, either the sediment or the nitrate concentration patterns. For atrazine, during storm

18

events the peak concentrations occur near the time of peak discharge, but the concentrations do not decrease nearly as rapidly as the sediment concentrations (Figure 5c). In contrast with sediment, the atrazine apparently is carried into streams throughout the time of surface runoff from the fields. Thus, the atrazine chemograph is much broader than the sediment graph. Also, the peak atrazine concentrations precede the peak nitrate concentrations. Since nitrate serves as a marker for tile effluent, the peak atrazine concentrations cannot be attributed to tile flow. Studies of atrazine concentrations in tile effluent from this region show much lower atrazine concentrations than we observe in the stream systems.[23]

The concentration patterns of other herbicides largely parallel the patterns for atrazine (Figures 3 and 5d). Since peak exposures for multiple herbicides closely coincide, the possibilities of synergistic interactions among pesticides need to be evaluated.

Effects of Pesticide Use Rates on Pesticide Concentrations

In general, the concentration of a particular pesticide in river systems is closely related to the quantity of that pesticide used in watersheds upstream from the monitoring site. In Figure 6, the TWMCs of various pesticides at the Maumee and Sandusky river monitoring stations are plotted in relation to their 1986 use in the Lake Erie Basin. Alachlor, metolachlor, and atrazine are used in the largest quantities in the Lake Erie Basin (Table 2). These three herbicides have the highest TWMCs.

These data also illustrate the importance of factors other than the amount of

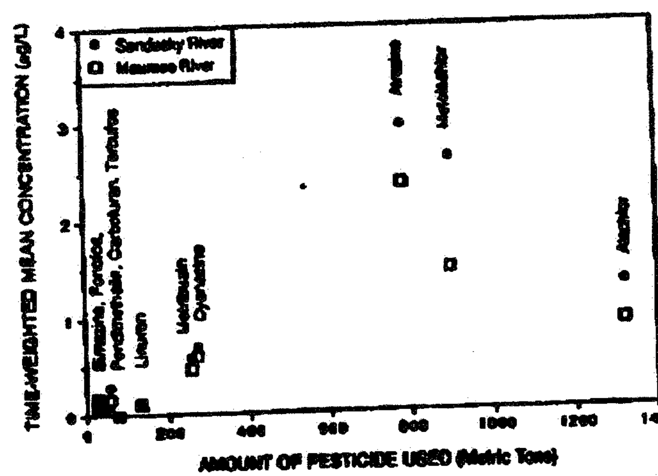

Figure 6. Relationships between the TWMCs for several pesticides at the Maumee and Sandusky river stations and the quantities of pesticide used in the Lake Erie Basin in 1986. The TWMCs were based on all samples collected between April 1983 and November 1987. Source: Quantities of pesticide used from Waldron.[3]

use in affecting environmental exposures. Within this group of three herbicides, the time-weighted mean concentrations are inversely related to the amount of herbicide used. Of the three herbicides, alachlor is the least persistent, and atrazine is the most persistent.[19] One of the pesticides with a very low apparent TWMC relative to the amount applied is terbufos. Terbufos not only breaks down rather quickly in the soil and water, but its application involves incorporation into the soil, thereby greatly reducing its movement in surface runoff water. Furthermore, the sample storage conditions used in these studies (refrigeration for up to three weeks before extraction) are unsatisfactory for terbufos—in the analytical methods for use in the EPA's National Pesticide Survey, terbufos is noted as failing the 14-day sample storage tests.[24] Consequently, we could be underestimating its concentrations.

Efforts are currently underway to develop watershed-specific pesticide use data. Small watersheds are more likely to have significant deviations from regional pesticide use patterns than are larger watersheds, such as those of the Maumee and Sandusky rivers. Such data will allow assessment of the effects of differences in pesticide use patterns among the smaller watersheds on their pesticide concentration patterns. Watershed-specific pesticide use data for the smaller watersheds will also increase the value of these data sets for model development and calibration. It should also be noted that small watersheds are more likely to differ from one another in their deviations from normal regional rainfall patterns.

Annual Variability in Pesticide Runoff

Both the TWMCs and observed peak concentrations of individual pesticides vary considerably from year to year at each station. Examples of annual variability in TWMCs for three major herbicides are shown in Table 5 for the Maumee and Sandusky rivers and for Honey Creek. Two- to fourfold variations in average concentrations during the pesticide runoff season for these herbicides occurred within the six-year period. Annual variability in observed peak concentrations at these same three monitoring stations is shown in Table 6. The variability in observed peak concentrations is even larger than the variability in TWMCs. It should be noted that the actual peak concentrations occurring in the stream systems would probably be higher than the peak concentrations observed from the sampling program. Pesticide concentrations change rapidly during storm events and it is unlikely that the sampler would happen to collect a sample at the precise time when a particular pesticide reaches its peak concentration. It is also unlikely that the peak concentrations of different pesticides would occur precisely at the same time.

The large extent of annual variability in pesticide concentrations underscores the need for long-term studies to characterize pesticide exposure patterns in river systems. Such variability extends to pesticide loading, as well as to concentration patterns. Extensive annual variability is also characteristic of other agricultural contaminants, such as sediments, nitrates, and phos-

19

Table 5. Annual Variations in Time-Weighted Mean Concentrations of Atrazine, Alachlor, and Metolachlor During the Pesticide Runoff Season for the Maumee and Sandusky Rivers and for Honey Creek

	Alachlor (μg/L)			Metolachlor (μg/L)			Atrazine (μg/L)		
Year	Maumee	Sandusky	Honey Cr.	Maumee	Sandusky	Honey Cr.	Maumee	Sandusky	Honey Cr.
1983	1.36	0.69	1.88	1.36	2.78	3.87	2.38	2.22	4.07
1984	2.71	1.90	2.86	2.15	3.44	3.51	3.49	3.01	4.91
1985	0.73	2.63	3.26	1.91	6.65	7.27	2.79	5.98	7.48
1986	2.01	4.10	4.44	3.88	5.98	7.80	4.86	7.81	9.32
1987	1.93	2.20	3.80	4.76	4.04	4.62	5.98	4.74	6.38
1988	0.16	0.08	0.33	0.40	0.36	1.25	1.23	0.90	2.63

Table 6. Annual Variations in Peak Observed Concentrations of Atrazine, Alachlor, and Metolachlor During the Pesticide Runoff Season for the Maumee and Sandusky Rivers and for Honey Creek

Year	Alachlor (µg/L)			Metolachlor (µg/L)			Atrazine (µg/L)		
	Maumee	Sandusky	Honey Cr.	Maumee	Sandusky	Honey Cr.	Maumee	Sandusky	Honey Cr.
1983	10.54	6.94	12.48	9.25	21.97	30.82	7.22	10.63	23.30
1984	17.64	8.76	22.01	13.73	19.45	35.41	13.62	10.15	37.46
1985	6.63	38.82	27.06	8.82	42.38	36.38	9.00	28.20	29.33
1986	8.70	33.82	72.17	31.57	39.00	138.78	13.16	32.38	66.96
1987	7.68	13.18	74.14	13.71	26.12	30.86	13.05	21.64	46.20
1988	0.76	0.40	7.07	1.72	0.73	7.98	3.00	2.19	6.84

20

phorus.[16] This variability greatly complicates the task of assessing the effectiveness of certain types of management practices in reducing agricultural nonpoint pollution.

Watershed Scale Effects

As storm runoff water moves through a watershed's drainage network, it is continually mixing with water from other parts of the watershed. As streams merge, even when they are of similar stream order, they are seldom in the same phase of their hydrographs and chemographs. Thus, they will have differing discharge rates and differing pesticide concentrations. The resulting pesticide concentrations will depend on the discharge rates and the pesticide concentrations of each of the tributaries that merged and will always fall between the concentrations of the two parent streams. The continuous operation of this process within drainage networks gives rise to systematic changes in pesticide concentration patterns in relation to position in the drainage network, even when soil types, land uses, and management practices are similar throughout the entire watershed. These systematic changes in pesticide concentration patterns reflect the operation of what we refer to as "scale effects" within the watershed. Two important aspects of these scale effects are that peak concentrations decrease as drainage area increases and that intermediate concentrations persist for longer durations as drainage area increases.

Concentration exceedency curves provide a convenient way to compare pesticide exposure patterns among various sites. Concentration exceedency curves are constructed by ranking the concentrations in decreasing order and plotting them as a function of the cumulative time the samples represent. The curves allow one to determine the proportion of time any specified concentration is exceeded, or the proportion of time characterized by a specified concentration interval. In Figure 7, atrazine concentration exceedency curves are shown for Lost Creek (11.3 km^2) and the Maumee River (16,395 km^2). Peak concentrations are much higher in Lost Creek than in the Maumee River. However, the concentration exceedency curves cross so that intermediate concentrations persist for a much longer time in the Maumee River than in Lost Creek. Median pesticide concentrations are generally higher in large watersheds than in small watersheds.[56]

In Table 7, peak observed concentrations of several herbicides are shown for various watersheds in relation to watershed size. As watershed size decreases, peak herbicide concentrations increase. This relationship is also evident in the data of Table 6. This trend apparently continues to watersheds much smaller than the smallest we have observed. The peak pesticide concentrations that have been reported for edge-of-field studies[60] are much higher than those that we have observed in our smallest watersheds. Edge-of-field studies can give rise to particularly high concentrations of individual compounds since individual compounds are generally used over the entire field. As watershed size

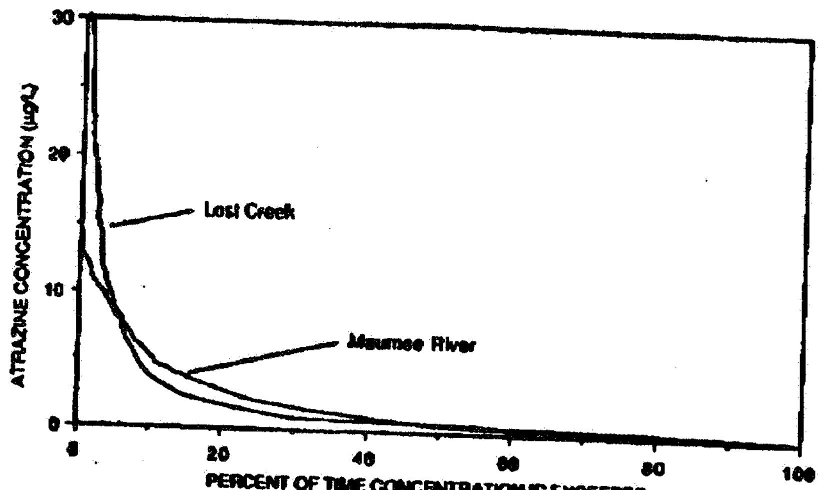

Figure 7. Atrazine concentration exceedency curves at the Maumee River and Lost Creek sampling stations. Curves include the entire period between April 1983 and November 1987.

increases, the percent of area covered by single compounds drops off to the regional averages.

Although scale effects are evident for peak concentrations and median concentrations, they are not readily evident in terms of TWMCs (Table 8). For small watersheds, the short durations of high concentrations coupled with the long durations of low concentrations tend to balance the long durations of intermediate concentrations and the lower peak concentrations of the larger watersheds. The TWMCs of the major herbicides are very similar for the Lost Creek station, the smallest of the study watersheds, and the Maumee River station, which has the largest drainage area.

Effects of Land Use and Soil Texture

In Figure 8, the concentration exceedency pattern for atrazine is compared for the Sandusky River, the River Raisin, and the Cuyahoga River. As a group these rivers are similar in size. The watershed of the Cuyahoga River is dominated by forests and urban/suburban land uses, while the River Raisin and the Sandusky River have similar proportions of cropland. The soils of the River Raisin Basin have a much coarser texture (70% loams and sandy loams) than those of the Sandusky River Basin.[25] The concentration exceedency patterns (Figure 8) show that atrazine concentrations are much higher in the Sandusky River than in the River Raisin, and that the concentrations in the Raisin are much higher than in the Cuyahoga. Concentrations of sediment, nitrate, and phosphorus are also much higher in the Sandusky River than the River Raisin,[18] even though average gross erosion rates are higher in the River Raisin

21

Table 7. Peak Observed Concentrations of Major Herbicides at the Monitoring Stations During the Interval from April 1983 to October 1987

River	N	Alachlor	Metolachlor	Atrazine	Cyanazine	Metribuzin	Linuron
Maumee River	340	25.86	28.66	15.61	13.27	8.61	8.79
Sandusky River	375	35.88	37.34	32.81	26.48	13.82	8.27
Honey Creek	534	77.28	128.98	67.96	21.08	13.31	18.67
Rock Creek	477	32.86	127.53	57.70	33.03	23.81	13.86
Lost Creek	410	91.47	83.74	281.41	30.17	37.54	16.19
Cuyahoga River	94	1.64	7.08	3.80	1.81	1.57	6.08
River Raisin	134	10.59	7.77	16.62	5.00	3.67	2.38

Note: All concentrations are given in µg/L. The first five stations are listed in the order of decreasing watershed size.

Table 8. Time-Weighted Mean Concentrations of Major Herbicides at the Monitoring Stations During the Interval from April 1983 to October 1987

River	N	Alachlor	Metolachlor	Atrazine	Cyanazine	Metribuzin	Linuron
Maumee River	340	0.94	1.51	2.43	0.63	0.50	0.12
Sandusky River	375	1.30	2.61	2.97	0.70	0.60	0.12
Honey Creek	534	1.74	3.05	4.07	0.86	0.49	0.39
Rock Creek	477	0.88	2.29	2.00	0.27	0.37	0.23
Lost Creek	410	1.04	0.96	2.97	0.73	0.28	0.08
Cuyahoga River	94	0.13	0.33	0.55	0.15	0.12	0.23
River Raisin	134	0.70	0.46	1.30	0.38	0.19	0.08

Note: All concentrations are given in µg/L. The first five stations are listed in order of decreasing watershed size (see Table 1).

22

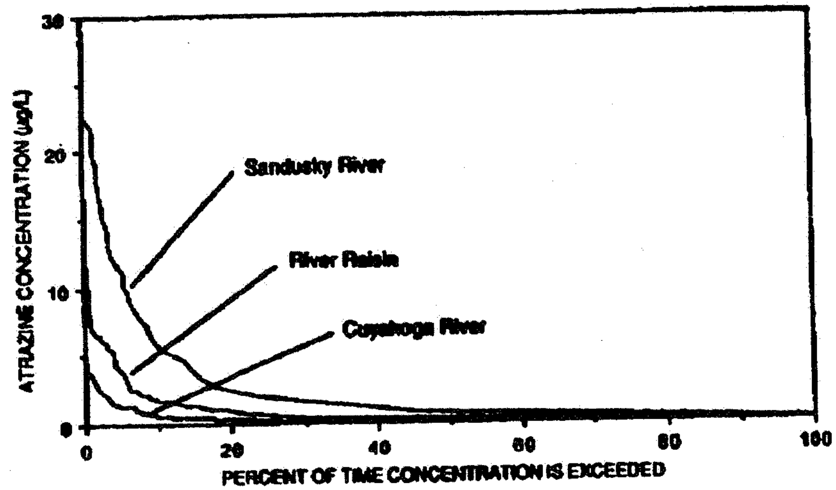

Figure 8. Atrazine concentration exceedency curves for the Sandusky River (agricultural land use, fine textured soils), the River Raisin (agricultural land use, coarser textured soils), and the Cuyahoga River (urban and forested watersheds). Curves include the entire period between April 1983 and November 1987.

Basin (9.75 tons/ha/year) than in the Sandusky River Basin (8.25 tons/ha/year).[26]

Herbicide Exposures in Relation to Proposed Lifetime Health Guidance Levels

The Maumee and Sandusky rivers, as well as Honey Creek, serve directly as raw water sources for 11 community water intakes supplying public drinking water to 124,000 residents of northwestern Ohio.[27] Most of the current generation pesticides pass directly through conventional water treatment plants, giving rise to pesticide exposures through drinking water.[8,9] The occurrence of such exposures generates frequent questions concerning accompanying human health risks. These risks have been discussed in some detail in Chapter 25.

The U.S. EPA has recently published lifetime health guidance levels for several major herbicides.[28] Concentration exceedency curves provide a convenient means of summarizing exposure patterns for comparison with lifetime health guidance levels. In Figure 9, concentration exceedency curves for alachlor, atrazine, and metolachlor at the Sandusky River station are shown. The curves are based on data collected between April 1983 and October 1987. For each herbicide, the proposed lifetime health guidance level, the percentage of time the lifetime health guidance level is exceeded, and the TWMC are indicated. As is evident in Figure 9, the proposed health guidance levels are exceeded about 10% of the time for alachlor, 17% of the time for atrazine, and 5% of the time for metolachlor. The TWMCs for all three herbicides were

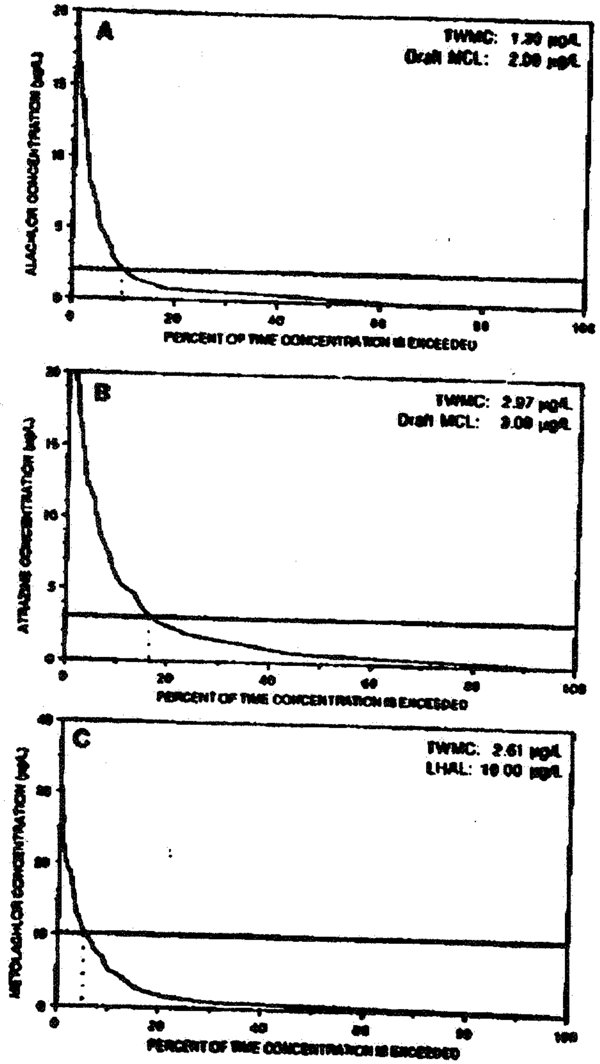

Figure 9. Relationships between lifetime health advisory levels (LHAL) or draft maximum contaminant levels (Draft MCL), and concentration exceedency curves for alachlor (A), atrazine (B), and metolachlor (C) at the Sandusky River station. Curves include the entire period between April 1983 and November 1987.

below the lifetime health advisory levels, although in the case of atrazine, the TWMC and the lifetime health advisory level were very similar.

A very important characteristic of pesticide exposure patterns in rivers is that high concentrations are present for relatively short durations of time. These periods of high concentrations not only can exceed lifetime health guid-

23

ance levels, but they also contribute greatly to the TWMCs of these compounds. Because of these exposure patterns, treatment to remove pesticides at drinking water treatment plants for relatively short periods during high concentrations can simultaneously reduce or prevent the occurrence of concentrations in excess of the standards and efficiently lower the TWMCs. One effective option for pesticide removal would be the use of powdered activated carbon (PAC) during storm runoff events during the late spring and early summer periods.[8] Most treatment plants utilizing rivers for water supplies have experience with and facilities for the addition of PAC, since such treatment is frequently used to deal with periodic taste and odor problems. Other treatment options include granular activated carbon,[8] reverse osmosis, or ozone oxidation.[29]

Ecological Significance of Current Generation Pesticides

Within the Great Lakes Region, there has been great concern over toxic chemicals in aquatic systems, both in terms of human health effects through eating contaminated fish or drinking contaminated water, and in terms of direct impacts on aquatic communities. Although several current generation pesticides have been observed in waters of the Great Lakes, they are notably absent from the lists of toxic compounds of concern in the Great Lakes Region.[30] Persistent organics, such as earlier generation chlorinated insecticides, industrial organics, combustion by-products, and various metals, comprise the lists of toxic substances. Fish consumption advisories in the Great Lakes Region, such as those provided by the Ontario Ministry of the Environment,[31] are based on metals and persistent organics. Current generation pesticides, if detected at all, are not deemed to constitute risks to those eating fish from this region. There is considerable uncertainty regarding the water quality impacts of current generation pesticides and the extent of water quality benefits that would accompany reduced exposures to these compounds.[32]

The major herbicides that occur in rivers of northwestern Ohio have very low acute toxicities to fish.[33] Some representative LC_{50}s for major current generation herbicides and insecticides are shown in Table 9. The peak herbicide concentrations we have observed in small streams are at least an order of magnitude below these acute toxicity values. The acute toxicities of some of the currently used insecticides are much greater (i.e., they have lower LC_{50}s) than those of the herbicides.[33] If stream concentration patterns were strictly proportional to pesticide use, such that the ratios of insecticide concentrations to herbicide concentrations were proportional to their use rates, one could expect rather frequent fish kills in streams due to insecticide runoff. However, the rather rapid breakdown of many of the insecticides, coupled with application techniques that usually involve incorporation into the soil rather than broadcasting on the soil surface, result in ambient insecticide concentrations in streams that are much lower than herbicide concentrations, relative to the quantities applied. We have rarely, if ever, observed insecticide concentrations

Table 9. Acute Toxicities to Fish of Major Herbicides and Insecticides as Represented by Their LC_{50}s in 24 hr and 96 hr Static Bioassays.

Pesticide	Rainbow Trout		Bluegill		Channel Catfish		Fathead Minnows	
	24 hr	96 hr	24 hr	96 hr	24 hr	96 hr	24 hr	96 hr
Herbicides								
Alachlor								
Technical material	—	2,400	11,500	4,300	—	—	—	—
Emulsifiable conc.	4,300	1,400	7,800	3,200	—	—	—	—
Metolachlor								
Technical material	—	—	—	—	—	—	—	8,000
Emulsifiable conc.	—	—	—	—	—	—	—	8,400
Ciba Geigy data	—	2,000	—	15,000	—	4,900	—	11,000
Atrazine 4L								
43% liquid	—	24,000	48,000	42,000	—	—	—	—
Ciba Geigy data	—	4,900	—	6,700	—	—	—	15,000
Cyanazide								
80% wettable powder	12,000	9,000	22,600	20,300	13,400	10,400	19,700	19,400
Metribuzin								
Technical material	—	42,000	—	92,000	>100,000	—	—	—
Linuron								
Technical material	—	—	—	—	—	2,900	—	—
Wettable powder	—	—	—	—	3,200	1,800	—	—
Trifluralin								
Technical material	167	92	120	47	400	210	360	150
Chloramben								
Wettable powder	—	>10,000	—	>10,000	—	—	—	—
Butylate								
Technical material	4,000	2,100	900	470	—	—	—	—

Table 9, continued

Pesticide	Rainbow Trout		Bluegill		Channel Catfish		Fathead Minnows	
	24 hr	96 hr	24 hr	96 hr	24 hr	96 hr	24 hr	96 hr
Insecticides								
Terbufos								
Technical material	24	10	4.8	1.7	—	—	390	380
Granular formation	23	8.8	3.1	1.7	1,800	1,800	210	150
Carbofuran								
Technical material	680	380	101	88	372	248	883	572
Wettable powder	—	—	370	240	—	—	—	—
Chlorpyrifos								
Technical material	53	7.1	—	2.5	410	280	—	—
Phorate								
Technical material	25	13	7.6	2.0	500	280	—	—
Fonofos								
Technical material	109	20	45	6.8	—	—	—	—

Note: All data are from studies at the Columbia National Fisheries Research Laboratory, Columbia, MO,[38] except for additional data for atrazine and metolachlor provided by Ciba Geigy Corporation, Greensboro, NC. Concentrations given in µg/L.

24

in the range of their LC_{50}s. The lower concentrations of the insecticides, coupled with their less frequent occurrence and their lower stabilities during sample storage, combine to make detailed exposure studies for insecticides much more difficult than comparable studies of herbicide exposures.

Although fish kills in farm ponds are often attributed to runoff of current generation insecticides from adjacent fields, actual documentation of the role of insecticides in such incidents is much less common. Reports of fish kills in stream systems, due to runoff of current generation insecticides from fields, are not common. It should be noted that fish kills in farm ponds are much more likely to be observed than fish kills in small streams during runoff events. Impacts of pesticides on fish reproduction in streams and rivers could also be very difficult to observe.

Algal and rooted aquatic plant communities are much more likely to be directly impacted by herbicides than are the fish and invertebrate communities. The herbicide concentrations we have observed in streams and rivers do reach levels that have shown inhibitory or toxic effects on plant communities in both microcosm and mesocosm studies.[34,35] However, within these stream systems, the turbidity associated with sediment transport that co-occurs with the herbicide exposures would likely have a greater effect on the productivity of the plant communities than would the herbicides. Often the effects of herbicide exposures in experimental studies are transitory and the communities quickly recover following the exposures, although the species composition at lower trophic levels may be shifted.[35,36]

The Ohio EPA has made extensive use of both fish indices and macroinvertebrate indices in their assessments of water quality in the streams and rivers of Ohio.[37] For each ecoregion within Ohio, the indices for stream segments are compared to the indices for the "best" streams within that ecoregion. This approach indicates that many of the stream segments within the Huron/Erie Lake Plain ecoregion and the Eastern Cornbelt ecoregion, which encompass the agricultural watersheds discussed in this chapter, have impaired aquatic communities.[37] The five major sets of factors that are thought to interact in determining biological community performance in streams are chemical variables, flow regimes, habitat structure, energy sources, and biotic interactions. Intensive agricultural land use directly affects at least four of the sets of factors (all except for the biological interactions). In addition to pesticide exposures and nutrient enrichment, current agricultural land use in this region results in habitat modification through sedimentation and channelization, extremes in discharge at both the high and low flow ranges, and high light intensities in low-order streams due to a lack of streamside vegetation. While there is no doubt that agricultural land use has had a major impact on the streams and rivers of this region, there is considerable doubt as to whether currently used pesticides have directly resulted in the associated ecological impairments.

25

SUMMARY OF PESTICIDE EXPOSURE PATTERNS IN STREAMS AND RIVERS

The pesticide data sets for Lake Erie tributaries illustrate many characteristics of pesticide transport in river systems. Although many of these characteristics would be expected based on extrapolations from the numerous edge-of-field studies of pesticide behavior or based on modeling programs, actual data sets confirming these expectations and providing quantitative illustrations are rare. These general characteristics are the following:

1. Pesticide concentrations in rivers are much higher during the three months immediately following major spring pesticide applications (May, June, and July) than they are during the remainder of the year.
2. During the three months of "high" concentrations, the pesticide concentrations are highest during periods of storm runoff events and drop to lower concentrations between runoff events.
3. The concentration patterns of soluble pesticides in streams during individual storm runoff events are distinct from both the suspended sediment concentration patterns and the nitrate concentration patterns.
4. The concentration patterns of individual pesticides parallel one another so that the peak concentrations of individual pesticides often coincide.
5. In general, the concentrations of individual pesticides in stream systems are proportional to the amount of their use within the watersheds. Factors such as persistence and mode of application also strongly affect the peak and average concentrations.
6. There is very large year-to-year variability in peak and average pesticide concentrations, and in pesticide loadings, depending on the frequency, duration, and intensity of runoff-generating rainfall events in relation to the timing of pesticide applications.
7. The patterns of pesticide concentrations in streams are greatly affected by watershed size. As watershed size increases, peak pesticide concentrations decrease but the length of time that intermediate concentrations are present becomes extended.
8. For short periods of time, concentrations of major herbicides in streams and associated municipal water supplies do reach levels in excess of the U.S. EPA's proposed lifetime health advisories related to possible chronic effects. However, the TWMCs for herbicide concentrations in streams and public water supplies are usually less than the lifetime health advisory levels, even for those herbicides used in the largest quantities.
9. In public water supplies withdrawn from rivers, TWMCs for pesticides can be efficiently lowered by removal treatment during the rather short durations when high concentrations are present.
10. Although impairment of biological communities is evident in the streams and rivers of this region and is associated with intensive row crop agriculture, it is not clear that pesticides, which are present during runoff events following periods of application, contribute significantly to this impairment.

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27

CHAPTER 18

Studies on the Transport and Fate of Chlordane in the Environment

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INTRODUCTION

Chlordane is a chlorinated hydrocarbon insecticide, which has proven to be quite persistent in the environment. The commonly marketed form of chlordane is a mixture of variously chlorinated products of "chlordene," a Diels-Alder condensate of cyclopentadiene and hexachlorocyclopentadiene.[1] The bulk of technical-grade chlordane is formed by 10 constituents with six to nine chlorine atoms. Due to the nonselective chlorination process and the presence of impurities such as pentachlorocyclopentadiene and tetrachlorocyclopentadiene in hexachlorocyclopentadiene, a larger number of other chlorinated compounds have also been observed in the technical formulation and detected in the environmental samples. A number of studies dealing with the analysis and structure elucidation of chlordane have been published, and typical formulations of technical-grade chlordane have been shown to contain more than 40 different constituents.[2-9]

Chlordane has been used in the United States for approximately 40 years. It is estimated that over ten million kilograms of chlordane were produced and applied for control of a variety of agricultural pests. Chlordane has also been used extensively for control of termites and ants in and around domiciles. However, due to its carcinogenic activity in laboratory animals, its use was suspended as of April 1987 by the U.S. Environmental Protection Agency.

The extensive use and persistent nature of the chlordane constituents have led to the widespread presence of these chemicals in various phases of the environment worldwide. Some of the highly chlorinated constituents and stable metabolites, such as oxychlordane, have been detected by 0.1–19.0 picograms/m³ levels in air from such remote regions as the eastern Indian and Antarctic oceans as well as the arctic areas of Canada.[10,11] These determinations point towards an airborne long-range transport of the pesticide similar to that observed for other chlorinated pesticides. Chlordane constituents have

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ATTACHMENT C

PESTICIDE CONCENTRATION PATTERNS IN AGRICULTURAL DRAINAGE NETWORKS IN THE LAKE ERIE BASIN

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Abstract—This paper presents information on pesticide concentrations in Lake Erie tributaries draining agricultural watersheds, information distilled from data sets spanning nearly a decade and including up to 750 samples per tributary. Pesticide concentrations are strongly skewed and approximately lognormal. Average concentrations in tributaries are correlated with the amount applied in the basin, but with important secondary effects from chemical properties and modes of application of the pesticides. During runoff of storm events following application, concentrations rise rapidly, peak about the time of peak discharge, and decline slowly thereafter. These patterns do not match those for nutrients, major ions, or sediment, indicating a different pathway from the fields for pesticides. On an annual basis, elevated monthly average concentrations are usually observed from May to August, and low concentrations are present during the rest of the year. Monthly average concentrations of atrazine and alachlor generally exceed maximum contaminant levels (MCLs) in at least one month following application, but those of other herbicides do not. Annual averages are below MCLs for all compounds. No long-term trends are apparent. Comparisons of patterns in large and small tributaries show that small tributaries have higher maximum concentrations, more frequent concentrations below detection limit, and fewer intermediate concentrations. Smaller tributaries have more strongly skewed distributions and much greater temporal variability in concentrations than do larger rivers.

Keywords—Pesticides   Agricultural runoff   Nonpoint pollution

INTRODUCTION

In the thinking of the public and even of many environmental scientists, the term *pesticide* carries connotations that are a legacy of DDT and other organochlorine compounds, most of which are no longer used or are of very restricted use in the United States. These connotations include bioconcentration, fat solubility, limited solubility in water, and resistance to degradation, all of which led to substantial and lasting impacts on nontarget organisms, particularly top predators in the food chain. By contrast, most of the pesticides in use today, at least those used on row crops in the Midwest, are transported in aquatic systems primarily in the dissolved state, have much shorter half-lives, are subject to minimal bioaccumulation, and have smaller impacts on nontarget organisms. This is particularly true of herbicides, which are used in much greater quantity than insecticides and other pesticides.

Due to the great chemical differences between current-generation pesticides and the older organochlorine compounds, the pathways of migration through the environment are very different. Detailed information about concentration patterns of current pesticides in different environmental compartments has been largely lacking. Until recently, public water supplies were not required to analyze for these compounds, and current sampling requirements are not very well designed to characterize their concentration patterns, at least in rivers. For various reasons, many other monitoring programs have tended to ignore current-generation pesticides, and agricultural research programs have focused on edge-of-field concentrations, leaving the effects of transportation throughout the drainage network largely unstudied. However, several studies have documented the seasonal presence of herbicides, most commonly atrazine and alachlor, in rivers draining agricultural watersheds in the United States and Canada [1–5]. A few authors have reported pesticide concentrations in relationship to storm runoff [6,7], but the sampling interval of most studies is too long to resolve these patterns very clearly. One recent study provides an excellent analysis of trends in atrazine concentrations and loads in Canadian tributaries to Lake Erie [8].

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28

The Water Quality Laboratory at Heidelberg College (Tiffin, OH) began measuring pesticides in tributaries draining agricultural lands in 1981. With a focus on storm-runoff monitoring inherited from nutrient-runoff studies already underway, we immediately found considerable quantities of several herbicides in storm runoff [9] at a time when many agricultural scientists were proclaiming that pesticides adsorbed to the soil and would rarely show up in rivers at more than trace levels of concentration. Since then, we have developed extensive data on pesticide concentrations in rivers tributary to Lake Erie and draining basins with land uses ranging from 80% agricultural to mostly urban and forested. The purposes of this paper are to describe and illustrate the general patterns of pesticide runoff revealed by these data and to consider some of their implications.

MATERIALS AND METHODS

The Water Quality Laboratory's sampling program for pesticides is operated at U.S. Geological Survey stream-gaging stations and utilizes autosamplers to collect samples. The sampling frequency and pattern have varied somewhat from year to year and from station to station, but at present three samples per day are collected between April 15 and August 15, during which time most of the pesticide export occurs (this period will be referred to as the *pesticide runoff season*, or adjectivally using the term *seasonal*). All samples from runoff events during this period are analyzed, whereas two samples per week are analyzed during low-flow periods. At least two samples per month are collected and analyzed at other times of year (*nonrunoff season* and *nonseasonal*).

At present, pesticide samples are being collected from stations on five tributaries (Table 1). These stations cover a wide range of drainage basin area, and some stations are on tributaries to mainstems that are also monitored. The program has gathered more than 4,000 samples from Lake Erie tributaries since its inception.

Samples are prepared for analysis using liquid–liquid extraction without filtration. In these samples, almost all of the pesticide is present in the dissolved phase. This has been shown directly by analysis of filtered and unfiltered splits of some samples and by comparisons on split samples of our unfiltered results with those of other laboratories that filter their samples. Furthermore, it is consistent with observations that the timing of movement of pesticides and suspended sediment in rivers is different, as is their persistence in the water column when a river enters a lake. Finally, it is consistent with what would be expected, considering the pesticide partitioning coefficients together with the relative volumes of sediment and water present in the sample.

Samples are analyzed on a dual-column GC using nitrogen–phosphorus detectors. Details of the analytical methodology are presented elsewhere [10,11]; the method is very similar to Environmental Protection Agency (EPA) Draft Method 507 [12]. The analytical program quantifies 13 herbicides and insecticides. They are listed together with their quantitation limits in Table 2, ranked by the amount of active ingredient applied to Ohio croplands in 1986 [13]; all 13 were in the top 20 by use in Ohio. Together, these compounds account for approximately 90 weight percent of the active ingredients applied annually in herbicides in the Lake Erie basin of Ohio and 75% of those applied in insecticides, based on the data of Waldron [13]. Table 2 also lists soil half-lives, soil organic matter/water partition coefficients, and lifetime health advisory levels (LHAL) or maximum contaminant

Table 1. Water Quality Laboratory sampling stations for pesticides in the Lake Erie basin

Tributary	Tributary to	Watershed area (km^2)	Land use[a]					Dates of operation	Total no. of samples
			C	P	F	W	O		
R. Raisin	Lake Erie	2,699	67	7	9	3	14	1983–1989	158
Maumee R.	Lake Erie	16,395	76	3	8	4	9	1983–1990	586
Lost Creek	Maumee R.	11.3	83	0	11	1	5	1983–1991	577
Sandusky R.	Lake Erie	3,240	80	2	9	2	7	1983–1991	639
Honey Ck.	Sandusky R.	386	83	1	10	1	6	1983–1991	834
Rock Ck.	Sandusky R.	88	81	2	12	1	4	1983–1991	754
Huron R.	Lake Erie	961	73	4	12	2	8	1988–1991	254
Cuyahoga R.	Lake Erie	1,831	4	43	29	3	21	1983–1990	171

[a]Land-use categories indicate percentage of basin in C, cropland; P, pasture; F, forested; W, water; O, other. Data from [40].

Table

Compound	
Alachlor	Las
Metolachlor	Du:
Atrazine	Aa
Cyanazine	Bla
Metribuzin	Le
Linuron	Lo
Terbufos	Co
Butylate	Sut
Chlorpyrifos	Lo
EPTC	Ep
Phorate	Thi
Fonofos	Dy
Simazine	Pri

[a]H = herbicide; I =
[b]Data from Waldro
[c]Data from Wauco
[d]K_{oc} = Soil organic
[e]LHAL = lifetime h
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Dates of operation	Total no. of samples
1983–1989	158
1983–1990	586
1983–1991	577
1983–1991	639
1983–1991	834
1983–1991	754
1988–1991	254
1983–1990	171

: W, water; O, other. Data

Table 2. Pesticides quantified in the Water Quality Laboratory monitoring program

Compound	Common name	Type[a]	Quantitation limit (μg/L)	Rank by amount used in Ohio, 1986[b]	Half-life (d)[c]	Soil K_{oc}[c,d]	LHAL or MCL[e]
Alachlor	Lasso®	H	0.05	1	15	170	2.0
Metolachlor	Dual®	H	0.05	2	90	200	100.0
Atrazine	Aatrex®	H	0.05	3	60	100	3.0
Cyanazine	Bladex®	H	0.05	4	14	190	10.0
Metribuzin	Lexone®, Sencor®	H	0.1	5	30	41	200.0
Linuron	Lorox®	H	0.2	7	60	370	none
Terbufos	Counter®	I	0.01	8	5	1,000	0.9
Butylate	Sutan®	H	0.05	10	13	400	360.0
Chlorpyrifos	Lorsban®	I	0.02	16	30	6,070	20.0
EPTC	Eptam®	H	0.05	17	6	200	none
Phorate	Thimet®	I	0.01	18	90	2,000	none
Fonofos	Dyfonate®	I	0.01	19	40	870	10.0
Simazine	Princep®	H	0.05	20	60	130	4.0

[a] H = herbicide; I = insecticide.
[b] Data from Waldron [13].
[c] Data from Waucope et al. [41].
[d] K_{oc} = Soil organic matter/water partition coefficient at 20 to 25°C.
[e] LHAL = lifetime health advisory level established by the EPA; MCL = maximum contaminant level established by the EPA. For many compounds, the LHAL and the MCL are the same. Units expressed as μg/L.

levels (MCL), properties that reflect the expected behavior of these compounds in the environment and their relative potential for human health effects.

Unless otherwise specified, results are based on concentration data that have not been corrected for recovery, which typically falls between 75 and 85% for the six compounds seen in largest concentrations. The results discussed below are based on samples collected between the beginning of 1983 and the end of 1991.

All analytical results are retained for statistical purposes, regardless of whether they are higher than the quantitation limits listed in Table 2. Analytical results that fall below the quantitation limit are considered unreliable as measurements of concentrations in individual samples; nonetheless, they are the best available estimates of the actual concentrations for use in studies such as ours, which seek to characterize populations of measurements. Several papers in recent years [14–17] have pointed out the biases that can enter statistical summaries, such as estimates of mean and median concentrations, when low-level data are censored; these papers have argued for the use of uncensored data whenever possible. We have followed that practice in this paper, and for the same reasons we report summary statistics at their calculated values, regardless of where they fall relative to quantitation limits.

Pesticide concentrations for specified intervals of time are calculated either as time-weighted average concentrations (TWMCs) or as flow-weighted average concentrations (FWMCs), defined by

$$\text{TWMC} = \frac{\sum_i c_i t_i}{\sum_i t_i} \quad \text{and} \quad \text{FWMC} = \frac{\sum_i c_i q_i t_i}{\sum_i q_i t_i}$$

where c_i is the concentration for the ith time period, q_i is the instantaneous flow at the time the sample was taken, and t_i is the time characterized by that concentration. We generally assign each sample a time equal to half that between it and the preceding sample, plus half that between it and the following sample, except that neither time interval may exceed 7 d. The great majority of these intervals do not exceed 2 d, and most longer intervals are during low-flow periods at times of year when pesticide concentrations are low. Use of time weighting is necessitated by our seasonally and flow-stratified sampling strategy and by occasional gaps in the record, to avoid biasing the mean toward concentrations from high-flow periods and to avoid giving samples adjacent to gaps undue influence. If sampling were at a fixed frequency, the TWMC would be equivalent to the simple mean. Time weighting is appropriate for many purposes, because the potential impacts of pesticides on instream organisms, or on human populations who rely on these rivers for drinking water, are basically

30

independent of flow. However, for estimating loading rates the flow-weighted average is more appropriate [18].

A useful way to display and compare concentration patterns is to represent them as concentration exceedency curves. In this paper, they have been created by sorting the data by decreasing concentration, allotting a time to each sample as above, and then plotting concentration on the vertical axis against cumulative time, expressed as a percentage of total time, on the horizontal axis. These plots are analogous to cumulative frequency distributions, but with the axes switched and with the observations weighted by time. They are particularly convenient for determining the percentage of time a given concentration is exceeded, and for otherwise comparing concentration distributions to standards for the protection of health or aquatic life, when the time sequence of the concentrations is not important.

BASIC ATTRIBUTES OF PESTICIDE CONCENTRATIONS

The raw concentration data for all parameters and all tributaries are strongly right skewed. The example in Figure 1A shows two parameters, representing the extremes of skewness among the six most commonly detected pesticides. The data are from the Maumee River, which has the least skewed distributions. Because the sampling program is designed to emphasize the higher concentrations that occur during runoff events, the sample distributions are less skewed than the parent distributions from which they are drawn. To more nearly reflect the parent distributions of in-stream concentrations, time-weighted distributions for the same parameters are shown in Figure 1B. Experiments with the family of power transformations [19]

$$\phi_p(x) = \begin{cases} \dfrac{x^p - 1}{p} & p \neq 0 \\ \ln x & p = 0 \end{cases}$$

show that these data are approximately lognormal. If p is confined to integers, $p = 0$ is the best transformation for normality. For some parameters, a fractional exponent may be more satisfactory; the fourth-root transform ($p = 1/4$) was optimal for the alachlor data, although it was only slightly better than the log transform.

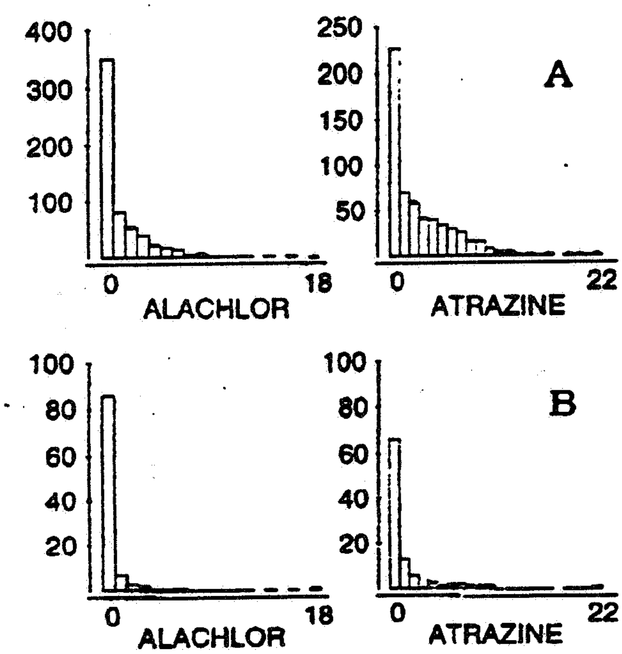

Fig. 1. Distributions of atrazine and alachlor in samples from the Maumee River. Histogram bar width is 1 µg/L. (A) Sample distributions; vertical axis gives numbers of samples. (B) Approximately unbiased distributions; vertical axis gives percentage of time concentration is present.

Concentrations of six major pesticides at seven monitoring stations are summarized in Table 3. The six listed pesticides are the most heavily used in Ohio among those quantified by our methods; they are also the ones most frequently detected, and in the highest concentrations, at the monitoring stations. In this table, many medians and means are lower than the quantitation limit for individual samples, and quite a few medians are zero (at least to two decimal places), reflecting the extreme skewness of the distributions. For the purposes of this paper, it is not very important whether a particular mean or median is really 0.0002 or 0.005 or 0.011. What is more important is that these values are very small, both in comparison to health standards and in comparison to the concentrations that define the patterns we will discuss below.

Occurrences of the remaining seven pesticides are summarized in Table 4. Because they occur infrequently at concentrations above their quantitation limits and are typically not detected, we do not attempt to estimate means or medians for these compounds but only report the percentage of analyses above quantitation limit, the maximum observed concentration, and the 95th percentile concentration (time-weighted).

Table 3. Concentrations (μg/L) of major herbicides at the monitoring stations, April 1983 to December 1991

River basin area (km^2)	Parameter[a]	Atrazine	Alachlor	Metolachlor	Metribuzin	Cyanazine	Linuron
Maumee (16,395)	Max	21.45	18.35	26.20	5.77	9.96	7.29
	95	7.47	3.00	5.32	1.83	1.97	0.00
	50	0.58	0.00	0.28	0.01	0.03	0.00
	TWMC	1.61	0.54	1.16	0.29	0.38	0.05
	FWMC	1.77	0.84	1.14	0.39	0.46	0.02
Sandusky (3,240)	Max	24.61	36.13	36.76	9.26	19.87	6.86
	95	8.84	3.76	8.59	1.68	1.73	0.29
	50	0.53	0.00	0.35	0.00	0.00	0.00
	TWMC	1.78	0.66	1.65	0.28	0.35	0.05
	FWMC	1.69	0.65	1.49	0.23	0.21	0.03
Honey Ck. (386)	Max	54.04	54.87	95.75	10.52	17.47	15.50
	95	10.85	4.44	9.08	1.28	2.07	0.68
	50	0.66	0.11	0.35	0.00	0.03	0.00
	TWMC	2.33	0.89	1.80	0.24	0.40	0.17
	FWMC	2.47	1.13	1.57	0.25	0.38	0.20
Rock Ck. (88)	Max	48.63	23.40	96.92	15.95	24.77	12.01
	95	6.61	2.16	8.15	1.20	0.71	0.68
	50	0.21	0.00	0.17	0.00	0.00	0.00
	TWMC	1.34	0.39	1.62	0.23	0.18	0.15
	FWMC	1.69	0.48	1.47	0.19	0.25	0.16
Lost Ck. (11.3)	Max	68.40	64.94	63.64	25.15	22.62	13.44
	95	5.67	1.07	3.08	0.80	1.64	0.00
	50	0.27	0.00	0.00	0.00	0.00	0.00
	TWMC	1.30	0.48	0.62	0.20	0.50	0.05
	FWMC	2.44	1.26	1.17	0.29	0.90	0.08
Cuyahoga (1,831)	Max	6.80	1.16	5.39	1.49	1.36	5.04
	95	0.99	0.24	0.63	0.28	0.27	0.06
	50	0.09	0.00	0.00	0.00	0.00	0.00
	TWMC	0.31	0.04	0.15	0.07	0.05	0.08
	FWMC	0.23	0.03	0.03	0.09	0.01	0.00
Raisin (2,699)	Max	12.46	7.52	5.91	2.46	3.75	1.92
	95	3.91	2.02	1.50	0.37	1.11	0.18
	50	0.30	0.00	0.00	0.00	0.00	0.00
	TWMC	0.76	0.37	0.32	0.11	0.21	0.04
	FWMC	1.30	0.75	0.44	0.20	0.33	0.08

[a]Listed in each block, from top to bottom, are the maximum observed concentration, the 95th and 50th percentiles (time weighted), the time-weighted average concentration (TWMC), and the flow-weighted average concentration (FWMC). Concentrations have not been adjusted for recovery. Analyses are of unfiltered samples.

32

Table 4. Occurrences of minor pesticides at the monitoring stations, April 1983 to December 1991

River	Parameter[a]	Terbufos	Butylate[b]	Chlorpyrifos	EPTC[b]	Phorate[b]	Fonofos	Simazine
Maumee	Max	1.165	0.271	0.482	3.990	0.090	2.490	2.374
	95	0.005	0.049	0.011	0.065	0.000	0.065	0.486
	% > QL	6.89	12.69	0.33	19.60	4.48	18.22	57.50
Sandusky	Max	1.120	5.727	3.836	14.186	0.863	2.503	6.006
	95	0.006	0.044	0.020	0.045	0.004	0.026	0.270
	% > QL	11.38	22.27	1.06	24.09	5.00	18.82	48.41
Honey Ck.	Max	0.302	0.728	0.178	5.696	0.226	5.665	6.493
	95	0.002	0.022	0.009	0.054	0.000	0.022	0.228
	% > QL	4.32	11.11	0.00	15.67	3.87	13.54	45.86
Rock Ck.	Max	0.644	0.613	0.792	7.639	0.090	3.343	3.683
	95	0.002	0.019	0.027	0.062	0.000	0.004[c]	0.137
	% > QL	5.43	10.20	0.52	18.53	2.79	10.61	29.92
Lost Ck.	Max	0.483	0.823	0.161	21.065	0.202	11.858	6.991
	95	0.002	0.000	0.000	0.000	0.000	0.011	0.124
	% > QL	5.56	3.71	0.00	6.19	3.22	15.48	34.43
Cuyahoga	Max	1.057	0.493	0.500	0.865	0.944	3.750	2.530
	95	0.007	0.030	0.037	0.021	0.000	0.041	0.688
	% > QL	10.00	15.46	0.57	6.19	3.09	27.65	54.97
Raisin	Max	0.341	0.237	0.251	0.119	0.004	0.959	1.033
	95	0.000	0.000	0.000	0.000	0.000	0.015	0.216
	% > QL	6.96	7.69	0.63	5.77	0.00	14.01	33.54

[a]Listed in each block, from top to bottom, are the maximum, the 95th percentile of concentration (time weighted), and the percentage of samples in which the pesticide exceeded the quantitation limit. Concentrations are reported as µg/L and have not been adjusted for recovery. Analyses are of unfiltered samples.
[b]Not quantified in samples analyzed before 1986.

An overall direct relationship between the amount of pesticide used and the TWMCs observed in river samples is shown by Figure 2. Given the great range of the quantities used, this relationship is hardly surprising. There is also an inverse relationship between TWMCs and amount used for the three most extensively used pesticides—alachlor, metolachlor, and atrazine. This pattern is related to the ease of mobilization of the three compounds and to their relative half-lives: Atrazine has a more sustained chemograph during storms than alachlor and occurs longer in runoff after the period of application; metolachlor is intermediate.

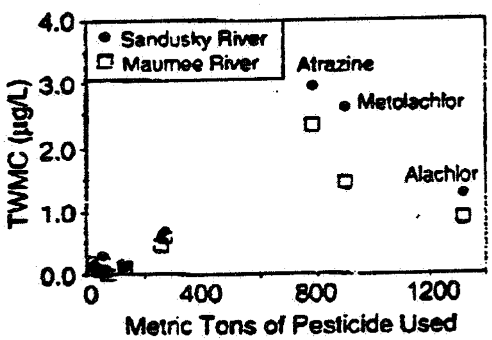

Fig. 2. Relationship between pesticide use and average instream concentrations. See Table 1 to identify less used pesticides.

TEMPORAL PATTERNS OF PESTICIDE CONCENTRATIONS

Pesticide concentrations are highly variable over time in these rivers, and several scales of temporal variability can be identified, including at least an annual cycle and storm event signatures, as well as interactions between the two, and longer term patterns involving year-to-year variation and perhaps persistent trends related to amount of compound in use, weather cycles, and so forth. The illustrations of these patterns, which follow, draw on data for the most extensively used herbicides. Patterns for compounds used in smaller quantities appear to be similar, although they are less clearly defined because the in-stream concentrations are lower and consequently their patterns tend to be noisier. In particular, the insecticides listed in Table 2 occur in very low concentrations, because the amounts used

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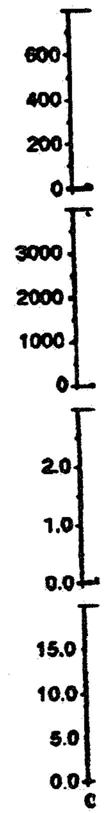

Fig. 3. Storm runoff
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83 to December 1991

rate[b]	Fonofos	Simazine
090	2.490	2.374
000	0.065	0.486
48	18.22	57.50
963	2.503	6.006
004	0.026	0.270
00	18.82	48.41
226	5.665	4.493
000	0.022	0.228
87	13.54	45.86
390	3.343	3.683
000	0.004	0.137
79	10.61	29.92
202	11.858	6.991
000	0.011	0.124
22	15.48	34.43
944	3.750	2.530
000	0.041	0.688
39	27.65	54.97
004	0.959	1.033
000	0.015	0.216
30	14.01	33.54

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PATTERNS OF NCENTRATIONS

ns are highly variable over several scales of temporal fied, including at least an vent signatures, as well as two, and longer term pat- ear variation and perhaps to amount of compound and so forth. The illustra- which follow, draw on data used herbicides. Patterns maller quantities appear to are less clearly defined be- centrations are lower and rns tend to be noisier. In es listed in Table 2 occur in because the amounts used

are roughly an order of magnitude less than those for herbicides and because breakdown is more rapid, application is more likely to involve incorporation into the soil, and binding to the soil is stronger.

Storm event signature

Most of the land in the Lake Erie drainage basin in Ohio has heavy soils with high clay content, which seal quickly during rainfall, producing overland flow that creates a strong storm runoff response in the tributary. The discharge pattern observed over time is called the hydrograph; similarly, the concentration pattern of a chemical constituent in transport is called a chemograph. A typical storm hydrograph is shown in Figure 3A. The chemographs of most constituents are related to the storm runoff shown by the hydrograph, in ways that reflect their mechanisms of movement from the land into and downstream along the tributary.

Suspended sediment concentrations rise sharply and rapidly, often peaking before the peak flow (Fig. 3B). This advanced peak has been explained both as a consequence of resuspension of channel sediments [20] and as a result of routing of water from individual fields into and through the tributary system [21].

Constituents that are carried mostly or entirely adsorbed onto the sediment show similar chemographs, notably total phosphorus (Fig. 3C). Its chemograph peaks early but declines more slowly than suspended sediment because some of the phosphorus is transported in solution. Increasing particulate phosphorus-to-sediment ratios with decreasing sediment grain size may also play a role because the

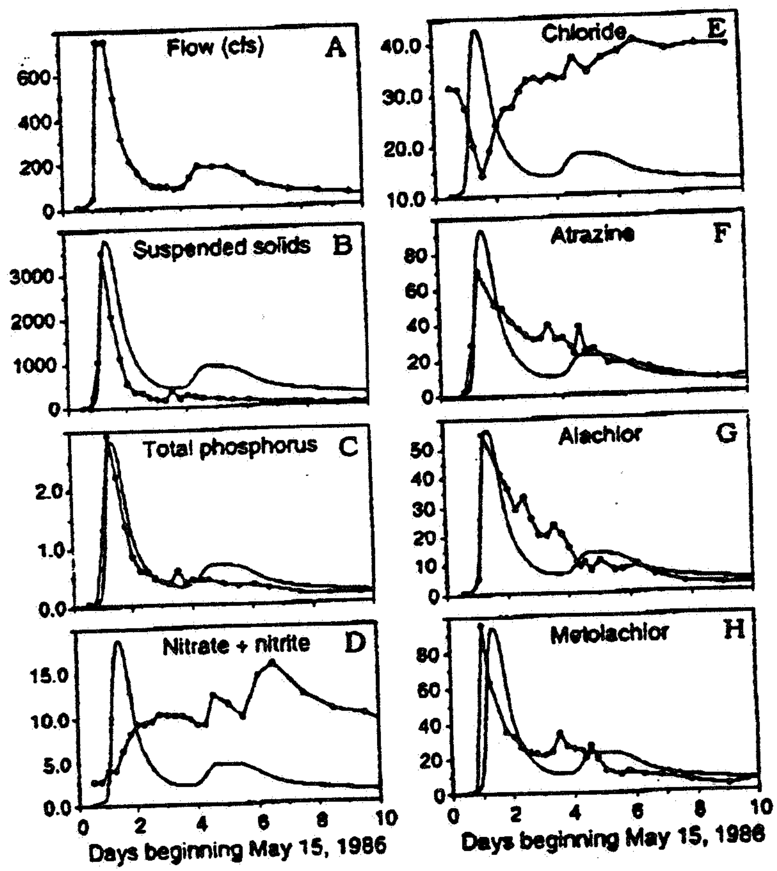

Fig. 3. Storm runoff patterns for Honey Creek for the period from May 15 to 24, 1986. Concentration units for herbicides are micrograms per liter; units for other parameters except flow are milligrams per liter.

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coarser sediment tends to drop out of suspension first.

Nitrate (Fig. 3D) reaches the tributaries primarily through tile systems draining the fields [22]. Its short passage through the ground into the tile system slows its delivery to the stream and causes its chemograph to peak as the hydrograph is declining.

Compounds that are essentially missing from and not rapidly mobilized by the rainfall, such as calcium, magnesium, bicarbonate, sulfate, and chloride, are present primarily in base-flow river water and groundwater contributions to the runoff hydrograph. They are diluted by the rainfall and consequently often have chemographs that are nearly mirror images of the hydrograph (Fig. 3E).

Chemographs for pesticides are quite similar to each other but different from any mentioned above. Pesticide chemographs (Fig. 3F–H) match the hydrograph more nearly than they do the other chemographs. Concentrations rise and fall more slowly than suspended sediment and total phosphorus, but more rapidly than nitrate. This indicates that the pesticides are not being carried primarily adsorbed onto sediment, a fact that is borne out by comparison of concentrations in filtered and unfiltered samples, by the similarity of concentrations in raw and finished drinking water when carbon filtration is not employed [23,24], and by the dissimilar patterns of concentration change when river plumes enter a bay [25]. Because nitrate serves as a marker for tile effluent, the peak pesticide concentrations cannot be attributed to tile flow either. Studies of atrazine concentrations in tile effluent from this region show much lower atrazine concentrations than those generally found in the stream systems [26,27]. The pesticide chemograph appears to reflect solution from surface and near-surface soils, operating continuously throughout the rainfall event.

Although these qualitative relationships are quite consistent, they cannot easily be raised to a quantitative level that would allow the chemograph to be predicted from the hydrograph. The relationship involves at least the following factors [28,29]: duration and intensity of the rainfall event, recent rainfall history, time since application, soil type, crop condition, water and soil temperature, pesticide use history, and chemical characteristics of the pesticide.

Annual cycle

The annual cycle of pesticide concentrations in these rivers is essentially one of storm event chemographs modified by an annual pattern of availability of pesticides. Half-lives mostly shorter than three months, seasonal application, seasonally variable rainfall, and frozen soils in the winter contribute to a broad pattern of declining availability of pesticides from the time of application one year until the same time the next year. Herbicide chemographs for the Maumee and Sandusky rivers and Honey Creek for the pesticide runoff season for each of the years 1982 through 1985 were presented by Baker [18]. Figure 4 shows a representative annual hydrograph and chemograph for atrazine. The first runoff following application is characterized by high pesticide concentrations, often the highest for the year. Thereafter, succeeding storm runoff events tend to have lower concentrations. The period from July 15 to September 30 is normally quite dry. The occasional rainfall events during this period may produce virtually no increase in runoff but may be marked by concentration peaks. The fall and winter typically have higher stream flow and more runoff events, but pesticide concentrations are declining, reach very low levels by winter, and remain so until the following application season.

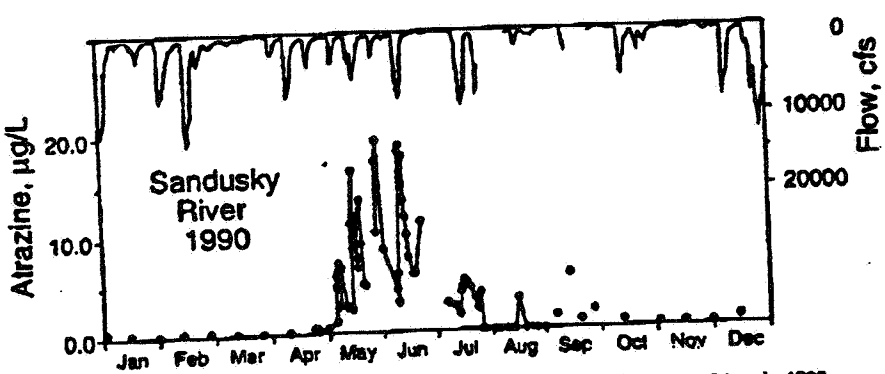

Fig. 4. Annual hydrograph and atrazine chemograph for the Sandusky River in 1990.

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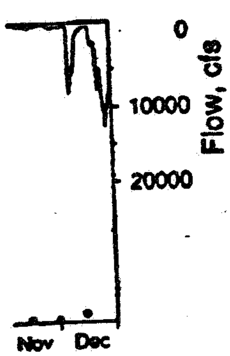
f pesticide concentrations in ly one of storm event chemo- annual pattern of availabil- ives mostly shorter than three lication, seasonally variable ils in the winter contribute to ining availability of pesticides cation one year until the same rbicide chemographs for the y rivers and Honey Creek for son for each of the years 1982 esented by Baker [18]. Fig- tative annual hydrograph and ine. The first runoff follow- racterized by high pesticide n the highest for the year. g storm runoff events tend to tions. The period from July normally quite dry. The oc- s during this period may pro- crease in runoff but may ntration peaks. The fall and higher stream flow and more sticide concentrations are de- v levels by winter, and remain g application season.



sky River in 1990.

The annual pattern of pesticide concentrations is summarized by monthly TWMCs in Figure 5. These TWMCs represent the average exposures to in-stream biota or (for most quantified compounds) to the human population using the river as a public water supply, if carbon filtration is not employed [23,24,30]. Although much of this pattern is due to the high concentrations of pesticides in rainfall runoff during the pesticide runoff season, low-flow periods are also characterized by higher concentrations at this time of year [30]. Indeed, these low-flow concentrations are higher than winter runoff concentrations for many pesticides.

Systematic differences exist in the rate of disappearance of pesticides from the rivers over the course of the year. As a result, certain pesticides are found almost entirely during the pesticide runoff season, whereas others continue to be present at reduced concentrations for much or all of the year. Seasonal and nonseasonal average TWMCs are shown in Figure 6. Atrazine and metolachlor have higher nonseasonal TWMCs than alachlor, cyanazine, and metribuzin, consistent with their half-lives in soils (Table 1).

Long-term patterns

Year-to-year variability in peak concentrations and in TWMCs is considerable, due to variations in rainfall amount and time relative to the time of application and various other weather- and crop-related factors. This variability is illustrated in Figure 7 for monthly TWMCs; peak concentrations would be even more variable.

Long-term trends in concentrations that might result from climatic cycles or from changes in the crops and pesticides of preference are difficult to detect in data as noisy as even the monthly TWMCs. A full analysis of possible trends in pesticide concentrations is beyond the scope of this paper. However, Figure 8 presents the data of Figure 7, deseasonalized and smoothed using the LOWESS procedure [31] with a window size of 50% of the data. Deseasonalization was accomplished by subtracting from each monthly TWMC the difference between the mean of that month's TWMCs and the overall mean of the TWMCs; this procedure was also followed using the medians rather than the means. The results do not suggest any sustained trends in concentration during the period of record.

SPATIAL PATTERNS OF PESTICIDE CONCENTRATIONS

Two kinds of patterns discernible in the data can be related to the spatial distribution of the sampling

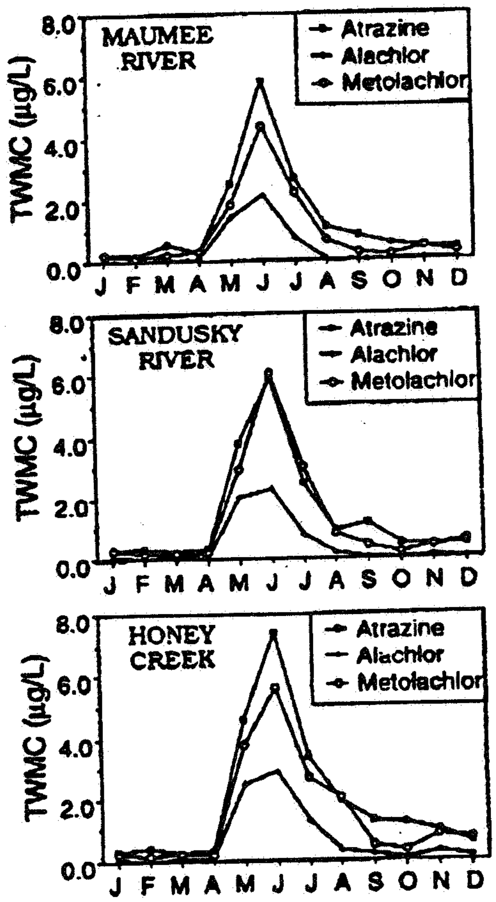


Fig. 5. Monthly time-weighted mean concentrations of atrazine, alachor, and metolachlor in the Maumee River, Sandusky River, and Honey Creek.

sites. The most important are scale effects—the effects of watershed size on the properties of the data derived from a site. The other spatial patterns are due to differences in land use and soil types in different drainage basins.

Scale effects

Scale effects appear in the pesticide data in several ways, and these effects can be expected to be present all the way down to the plot scale. Table 3 lists the peak observed concentrations of six pesticides. In general, they increase as watershed size decreases. The probability of sampling at or very near the time of peak concentration decreases as the stream size decreases, given a fixed frequency sampling program, due to the shorter duration of the

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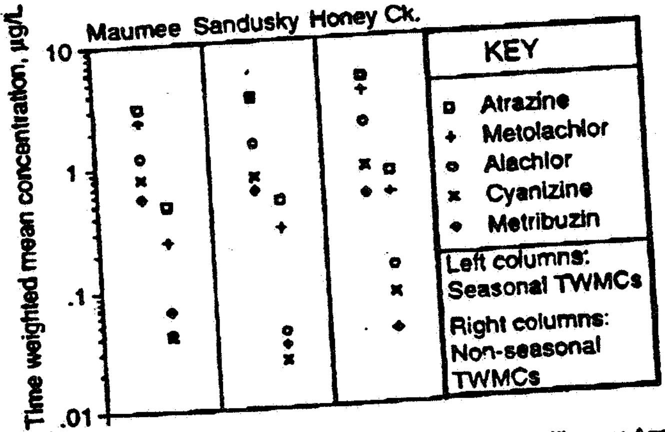


Fig. 6. Seasonal and nonseasonal time-weighted mean concentrations. "Seasonal" means April 15 to August 15.

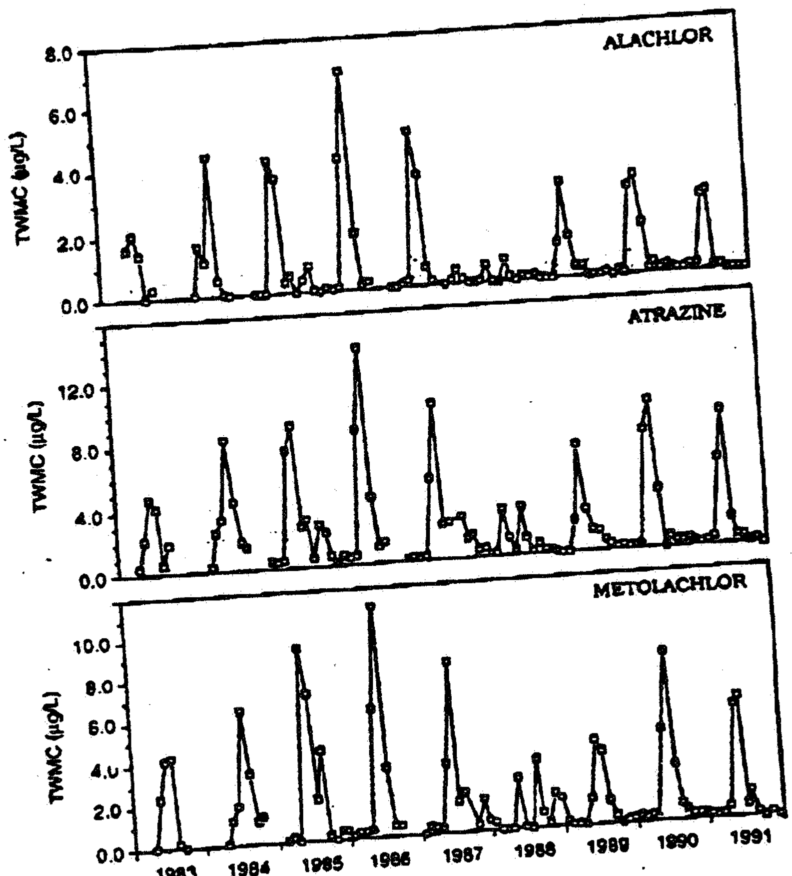
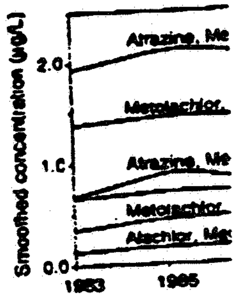


Fig. 7. Annual variation in monthly and annual time-weighted mean concentrations, Honey Creek.



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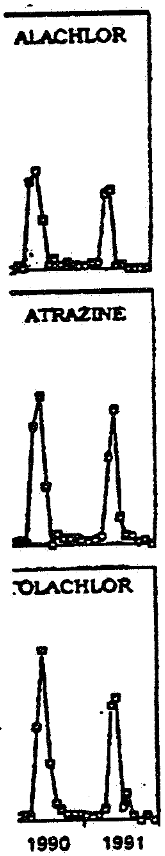

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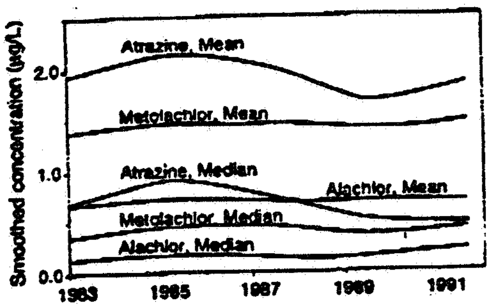

Fig. 8. LOWESS trends for deseasonalized monthly time-weighted mean concentrations, Honey Creek.

runoff chemograph. Thus it must be assumed that measured peak concentrations are biased low with respect to true peak concentrations and are increasingly so biased with decreasing stream size. In spite of this, the effect of stream size on peak concentration is apparent in these data. Although the peak concentrations decrease with watershed size, the average duration of periods in which moderate pesticide concentrations are continuously exceeded is likely to increase with watershed size, as a result of the longer duration of the runoff chemographs during which such concentrations usually occur.

Both scale effects are reflected in concentration exceedency curves such as those in Figure 9. The crossing points in the figures separate regions in which the smaller tributary has the higher concentrations from those in which the larger tributary has higher concentrations. The transition between these two regions occurs quite near the extremes of the concentration distributions, usually around the 99th percentile. The concentration exceedency curve for Honey Creek does not cross that for the Sandusky River, but they diverge at about the same point where other pairs cross.

Larger watersheds are generally characterized by less variable conditions than their component tributaries. In part, this is due to the timing of delivery of water to the mainstem from the tributaries. Because the downstream movement of a runoff event takes different lengths of time in different tributar-

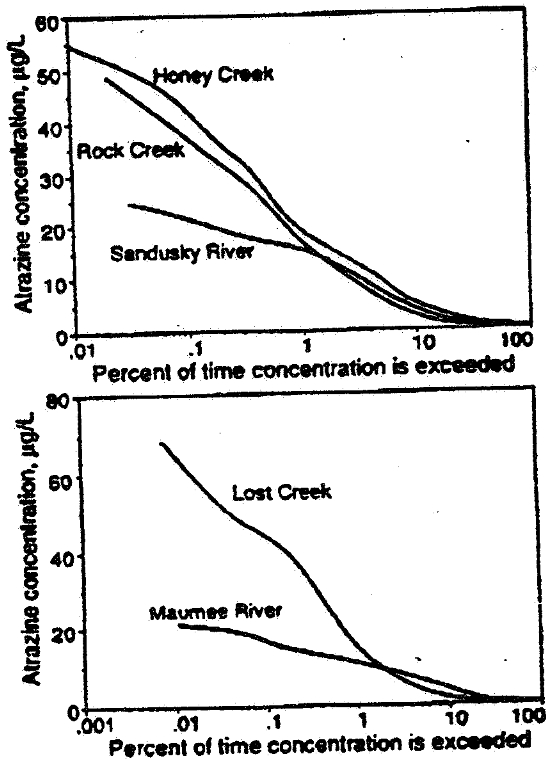

Fig. 9. Effects of river size on concentration exceedency.

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ies, the parcel of water from one tributary that carries maximum runoff concentrations is very likely to mix with water from another tributary at a different stage of the chemograph when the two meet. Every merging tends to mix waters at different stages of their storm runoff pattern, thereby reducing peaks (and minima) and increasing the percentage of the water mass characterized by intermediate concentrations. As a result, small streams have more rapid fluctuations in concentration than larger rivers, and these fluctuations cover a wider range with fewer intermediate values, resulting in more strongly skewed distributions.

Other spatial patterns

The effect of differences in land use on pesticide concentrations is shown by the peak concentration data for the Cuyahoga River, which is comparable in drainage basin area to the Sandusky but dominated by forest and urban land uses (Table 1). Concentration exceedency curves (Fig. 10) show that this difference characterizes the entire data distribution, not just the peak concentrations.

The effects of soil type can be seen by comparing the River Raisin and the Sandusky River. Both have similar basin size and similar land-use patterns. However, the soil in the River Raisin basin is much coarser on average, with better infiltration and less surface runoff. More of the pesticide is apparently retained in the soil column, resulting in lower concentrations in the river. This relationship is also seen in concentration exceedency curves and loading rates of nutrients and sediment from these two rivers.

IMPLICATIONS OF THE PATTERNS

Assessment of pesticide best-management practices

Practices designed to reduce the off-site impacts of agricultural land use are usually evaluated initially in plot- and field-level studies. Due to uncertainty about how to translate edge-of-field results to even a small watershed scale, demonstration projects are often contemplated in which the goal is to implement a practice as extensively in a watershed as possible and then monitor the watershed to measure the impact. Because it is much easier to achieve implementation in a small basin than a larger one, such demonstration projects are usually targeted to small watersheds. The great temporal variability in concentrations that characterizes small watersheds makes the detection of change more difficult [32,33]. As a result of this characteristic of small watersheds, monitoring must be frequent and often of long duration in order to detect trends that

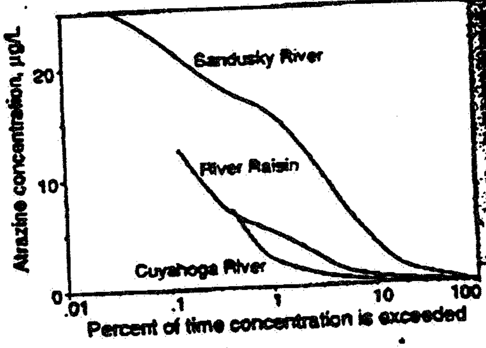

Fig. 10. Soil type and land use effects on concentration exceedency.

result from changed management practices. The information presented in this paper indicates that this is likely to be true for evaluating the effectiveness of pesticide management practices as well.

Effects of pesticides on stream biota

The herbicides described in this paper must be present in high concentrations to be acutely toxic to animal species [34–37]. However, some herbicide concentrations do reach levels that can adversely affect aquatic plants, at least temporarily [34–36], and insecticide concentrations reach levels that might adversely affect aquatic fish and invertebrates. For example, the bluegill 96-h LC50 for chlorpyrifos is in the range of 2 to 5 µg/L and that for mature *Gammarus lacustris* is 0.11 µg/L [36]; stream concentrations of nearly 1 µg/L have been observed in our studies, although the duration of these concentrations is unknown (but probably less than 96 h).

More subtle effects of herbicides on aquatic plants, as a result of chronic exposures at lower concentrations, have been demonstrated in some studies but not in others [35]. Other pollutants present in the river water may have more substantial effects on aquatic biota than the pesticides [36], including the effect of suspended sediment on light penetration to periphyton on the river bottom.

Although the actual extent of biotic effects is poorly known, scale effects of watershed size on concentration distributions have implications for the kinds of effects that might be expected as a result of typical runoff-related pesticide concentrations. Small tributaries are characterized by higher peak concentrations but shorter durations of intermediate concentrations. In effect, as one moves downstream from first-order tributaries to the mainstem, the concentration exposure patterns change from more acute to more chronic.

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Thus direct toxic effects due to short exposures at high concentrations would be more likely to occur in small tributaries. These effects could include fish and aquatic insect kills due to insecticides, and aquatic macrophyte and algal kills due to herbicides. On the other hand, more subtle biotic and ecosystem effects that result from intermediate to long-term exposures to moderate concentrations would be more likely in larger rivers and associated wetlands.

Drinking water monitoring

Beginning in 1993, most public water systems using river water vulnerable to pesticide contamination will be required to monitor quarterly for pesticides for which an MCL has been established [38,39]. If the running average of the last four quarterly sampling periods exceeds the MCL, the water system is declared out of compliance and various remedial actions and public notification are mandated [38,39].

Our data (Table 3) show that the annual time-weighted average concentrations for the Maumee and Sandusky rivers do not exceed the MCL for any of the pesticides we monitor. However, during storm events in the pesticide runoff season, individual samples commonly exceed four times the MCL for alachlor and atrazine. In the Sandusky River during May and June, atrazine concentrations exceed 12 μg/L (four times the MCL) about 13% of the time. Thus a sample for the spring quarter, taken at a random time during May or June, would have better than one chance in 10 of exceeding four times the MCL. If this happened, the four-quarter running average would of necessity exceed the MCL and the system would be declared out of compliance, regardless of the values in the previous three samples [38,39].

The goal of the legislation is to ensure that the true annual average exposures do not exceed the MCL. Given the short-term variability that characterizes pesticide concentrations in the rivers we have studied, four samples provide a very imprecise estimate of the annual average concentration. The law allows for compositing of samples from different points in the treatment plant to reduce monitoring costs [38] but apparently does not permit compositing over time to reduce the impact of short-term concentration fluctuations. The goal of the legislation would be better served if composite sampling over time were permitted at those systems that utilize rivers as a water source, or some other means were used to assure a more reliable estimate of the annual exposure concentration.

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40

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41

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TITLE: **OCCURRENCE AND MAGNITUDE OF PESTICIDE RESIDUES IN SURFACE WATERS OF THE UNITED STATES**

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ABSTRACT:

A variety of studies have shown that pesticide residues are occasionally present in the surface waters of intensively farmed watersheds of the United States. While suggestive, none of the previous studies has been sufficiently broad in terms of geographical extent, temporal coverage, or number of pesticides examined to allow a complete description of the occurrence and magnitude of these residues. We seek to remedy the situation in this paper by reporting the results of a two-year, 52-watershed monitoring program in which weekly composites of daily grab samples from across the most intensively farmed areas of the United States were analyzed for the presence of several heavily used pesticides. We also present two useful methods for analyzing the available surface water data. The first is a graphical approach for determining what types of pesticides, in terms of mobility and persistence, tend to occur at detectable levels. The second technique is a regression equation for predicting the annualized mean concentration of pesticides in a specific watershed based on chemical-specific properties, environmental factors, and the nature of the watershed itself.

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42

OCCURRENCE AND MAGNITUDE OF PESTICIDE RESIDUES IN SURFACE WATERS OF THE UNITED STATES

Introduction

Runoff of water, sediment, and nutrients from agricultural fields has long been recognized as a major conservation and environmental issue. The loss of topsoil and nutrients is a serious economic problem to the grower, and the negative impacts of sediment, phosphorous, and nitrogen loadings on estuaries, wetlands, and other sensitive environments have been well-documented(*US EPA, 1988*). Recently, the occurrence of dissolved and sorbed pesticide residues in these runoff waters has been reported(*USGS, 1989*). If transported from the edge of the field to surface water bodies of the watershed, the presence of these materials raises several issues, including potential effects on human health, toxicity to fish or other aquatic species, and phytotoxocity to beneficial aquatic plant-life.

In order to provide better data on the actual levels of alachlor and other pesticides in surface water, Monsanto conducted a pair of large-scale montioring programs in 1985 and 1986(*Klein et al., 1987*). Surface water from a variety of sources, including the Great Lakes, the major rivers of the Midwest (Mississippi, Missouri, and Ohio), and smaller watersheds were sampled in 1985. Because such low levels were found in the major Midwestern rivers and the Great Lakes, the 1986 sampling was confined to smaller watersheds and designed to determine the relative importance of soil-type, alachlor use, and other factors in determining the observed levels. In addition to the data collected in our studies, we used the results of other detailed monitoring programs to further define the combinations of physical properties most important in establishing the likelihood that a pesticide occurs at detectable levels in surface water(*Gustafson, 1987*).

As described more fully in the sections that follow, what has been derived from this work is a basic understanding of the occurrence and magnitude of pesticide residues in surface water. A simple graph of the physical properties (persistence and mobility) of the pesticides that have been detected in surface water shows essentially all soil-applied pesticides with K_{oc} less than about 500 mL/g can occur in surface water. K_{oc} is the soil-water partition coefficient divided by soil organic carbon, and thus represents a soil-independent measure of mobility. On the basis of Monsanto's extensive monitoring program for pesticides with such properties, a regression equation was developed to predict the annualized mean concentration in surface water. The regression is based on both watershed properties and the physical properties of the pesticide. Peak concentrations defy prediction because of the complex nature of the hydrology and chemical transport processes that define them, nevertheless long-term averages are generally more important from an environmental health perspective.

Previous Studies

With few exceptions, the public concern expressed about the possible dangers of pesticide residues in surface water has far out-stripped the scientific efforts to determine the actual levels present. Computer-based models of the runoff process have been used in attempts to predict what concentrations might occur, e.g. HSPF (*Donigian et al., 1987*) and CREAMS (*Knisel, 1980*). These programs attempt to model very complicated physical processes --- such as soil particle disintegration by impinging raindrops and precipitation interception by growing crops. Such processes have been modeled despite the absence of significant data for calibration, and without any experimental evidence that such complicated processes are even required in order to adequately model observed behavior.

Until the Monsanto study, the most comprehensive surface water monitoring programs were the significant monitoring efforts of David Baker in northwestern Ohio(*Baker, 1983 and 1985*) and the more limited (temporally) set of data collected by the Iowa Department of Natural Resources(*Iowa DNR, 1988*). Each of these studies have involved the analysis of surface water samples for pesticides spanning a wide range of physical properties (see Table I). In general, the same pesticides were detected in surface water in both studies.

In order to see whether there is any pattern to the types of pesticides that tend to occur in surface water, a graphical strategy analogous to that previously used to describe well water contaminants was employed(*Gustafson, 1989*). Figure 1 plots a measure of mobility in soil, K_{OC}, against a measure of persistence in soil, DT_{50}. DT_{50} is simply the time required for 50% of the applied chemical to dissipate. It is equivalent to the "half-life" when linear, first-order kinetics are obeyed in the dissipation process. The physical properties of the compounds are taken from the data base currently under development by Don Wauchope of the USDA Agricultural Research Service in Tifton, GA(*Wauchope, 1989*). The target compounds are shown in Figure 1, in which the closed circles represent the contaminants, and the non-contaminants are given as open circles. The contaminants appear to be confined to those chemicals with K_{OC} values below about 500 mL/g. Less mobile compounds apparently have a lower chance of generating detectable runoff quantities.

Models of the runoff process predict the occurence of a maximum in solution phase runoff at a particular range of K_{OC} and a continuing increase in sediment-phase runoff as K_{OC} increases(*Leonard and Knisel, 1988*). The data in Figure 1 therefore suggest that the sediment-phase runoff is a less important contributor to the residues observed in surface water. Edge-of-field losses may be high with high K_{OC}, relatively immobile compounds, but such losses do not translate into detectable concentrations in surface water. Exactly what physical processes are involved in this attenuation phenomenon has not been shown, but sedimentation is undoutedly one of the key factors.

This graphical approach gives a simple and intuitive assessment of an agrochemical's threat to surface water, once its persistence and mobility properties have been obtained. Armed with such a graphical procedure, the pesticide registrant or regulator can make an early informed judgment regarding the runoff potential of a chemical, without ever having to resort to one of the multitude of available computer models.

The graph also suggests which types of chemicals deserve the most attention in more detailed monitoring studies, such as was conducted by Monsanto in 1985 and 1986. Efforts should be focussed primarily on those high-use pesticides with K_{OC} values below about 500 mL/g.

The Monsanto Surface Water Monitoring Studies -- Methods

Alachlor, 2-chloro-N-(methoxymethyl)-N-(2,6-diethylphenyl)acetamide, is the active ingredient in Lasso® and other herbicides by Monsanto. Alachlor products have been used since 1969 for the control of annual grasses and certain broadleaf weeds in corn, soybeans, peanuts and other crops. The EPA issued a guidance document for the alachlor registration standard in November of 1984(*US EPA, 1988*). The registration standard required Monsanto to conduct a monitoring study to evaluate the manner and extent of contamination of surface water with alachlor. Subsequently, EPA issued Position Document 1 (PD-1),(*US EPA, 1984*) initiating a Special Review of alachlor. The Special Review was concluded in 1987 with alachlor registration maintained(*US EPA, 1987*). The concentrations found in surface water were judged by EPA not to present an unreasonable health risk given the socio-economic benefits of the compound(*US EPA, 1987*).

The Monsanto surface water monitoring data come from two separate studies -- one started in the spring of 1985 and the other in the spring of 1986. In the 1985 study raw and finished water from 24 locations were examined. In addition to alachlor, eight other herbicides were also measured. The 1986 study focussed on finished water and only five herbicides, and was targeted for completion by September, based on the data collected in 1985 showing the decline of alachlor to unmeasurable levels (< 0.2 µg/L) by that time of year. In North America, alachlor is generally applied once per year coinciding with planting in the spring. All sites sampled are shown in Figure 2, with the numbers serving as a key to Table II.

Briefly, daily samples were collected at each location and composited into weekly samples for chemical analysis. Each composited sample was analyzed by either capillary GC with electron capture detection (ECD) and thermionic specific detection (TSD) in the nitrogen mode or combined gas chromatography - mass spectrometry (GC-MS) with selected ion monitoring. The analytical methods were validated over a concentration range of 0.20 to 25 µg/L using raw and finished water.

Site Selection in 1985: Monsanto sales data (1984) were used to enumerate US counties where more than 80,000 lb of alachlor were sold. These 418 counties accounted for 75% of Lasso sales in that year. This information was cross-matched with data obtained from the US Environmental Protection Agency on community water systems (CWS). Only the CWS satisfying the following additional criteria were included in the target population:

- The CWS used only surface water.
- The CWS used surface water year round.
- The CWS treated surface water.

Eighty-five CWS satisfied these criteria; however, the plants were clustered in relatively small geographic areas (e.g., 39 were located in Illinois). Thus, a simple random sample of all eighty five plants would be heavily weighted with Illinois locations. In order to obtain a wider geographic distribution of plants, the hydrologic unit region, subregion and accounting unit of each CWS in the target population was identified by inspection of United States Geological Survey Hydrologic Unit maps(*USGS, 1975*). The 85 CWS were contained in 29 such hydrologic units, most located in the midwest with two in North Carolina. A random sample of 24 of the 29 hydrologic units was selected. One CWS was then randomly chosen from each of these sampled units.

Site Selection in 1986: The most recent information on CWS available was obtained directly from each of the 22 states accounting for 99% of Lasso sales in 1985. Besides using exclusively surface water year-round, the following criteria had to be satisfied by each CWS:

- The CWS was located in a hydrologic unit where >0.1 lb/acre of alachlor was used in 1985 (the denominator of this use rate refers to the total area of the watershed).
- The CWS did not use surface water from the Great Lakes, the Mississippi, Missouri, or Ohio Rivers.

Inclusion of the last criterion was justified on the basis of the results of the 1985 monitoring study in which no detectable alachlor was found in the three CWS using water from the Great Lakes and very small, barely detectable concentrations were found in the four CWS located on continental rivers. Using these selection criteria, 457 CWS in 22 states constituted the target population. The target population was then divided or stratified into nine subpopulations using high, medium and low soil runoff vulnerability (see the definition of the *soil index* in the *Regression* section below) crossed with high, medium and low alachlor sales. Seven CWS were randomly selected for sampling from each subpopulation on the extremes of the resulting 3 x 3 matrix, i.e. from the high-high, high-low, low-high, and low-low domains. In addition to these 28, two additional sites were sampled that had initially been miscategorized according to soil-vulnerability or alachlor use.

<u>Sample Collection:</u> Before sampling, visits were made to the managers and operators of cooperating CWS. The program's objectives, and proper sample handling and storage procedures to be used at the CWS were discussed. Particular emphasis was placed on sample integrity.

Specially cleaned amber glass bottles with polytetrafluoroethylene (PTFE) lined caps were used for sample collection, transport, storage and compositing. Insulated, corrugated shipping containers were used for shipping. Sample bottles and shipping containers were purchased by Monsanto and shipped to the CWS.

In the 1985 study, separate 500 mL raw and finished water daily grab samples were taken at the individual CWS by their personnel. Approximately every two weeks, samples were collected from each CWS by Monsanto personnel. All samples were refrigerated at the water plants and upon arrival at Monsanto. Separate raw and finished water weekly composites were made in 4 L specially cleaned bottles from the raw and finished water daily grab samples; samples for analysis were taken from these composites.

For the 1986 study, finished water daily grab samples were taken at the 30 CWS from April, 1986 through at least August, 1986. As discussed further below, raw water was not collected in 1986 because no significant differences had been seen in 1985 between raw and treated surface water. Collection continued at one CWS through April, 1987. The daily grab samples were composited into weekly (7 day) samples by the CWS operators, giving 3.5 L weekly composite samples. The completed 4 L composite bottle was taped around the cap and packed in a special corrugated shipping container insulated with polyurethane foam. The weekly samples were then shipped from the CWS to Monsanto, St. Louis by a commercial overnight delivery service and stored for analysis. Samples were stored refrigerated at the water plants and upon arrival at Monsanto.

Sample chain-of-custody was maintained throughout the study. Sample information chain-of-custody sheets were supplied to each plant. The top section of the sheet was completed by CWS sampling personnel. A completed sheet was shipped with each one-week set of daily samples (1985 study) or with each weekly composite sample (1986 study).

Sample collection at Breese, IL, (a 1985 study CWS) was continued for an additional 15 weeks in 1986. Daily grab samples were collected according to the 1985 protocol. A comparison between daily grab samples and weekly composite samples from Breese, IL, showed that the use of weekly composites did not have a material impact on the results of the study.

In order to demonstrate that there was no in-transit contamination, quality control samples (deionized water) were routinely sent to each CWS and returned to Monsanto using the same mode of shipping as was used with the regular weekly samples. In addition, to show that samples had not degraded in-transit, fortified samples (0.2 to 10.0 μg/L) of deionized water accompanied the quality control samples.

Materials: Reference grade alachlor was purified in-house to >99% purity (as determined by GC-FID). Reference grade atrazine, cyanazine, and metolachlor were obtained from Chem Service (West Chester, PA) and were used as received. Deuterium labeled alachlor was prepared in-house from deuterium labeled 2,6-diethylaniline obtained from MSD Isotopes (Pointe Claire-Dorval, Quebec) and the labeled alachlor was recrystallized to >98% purity (as determined by GC-FID). Deuterium labeled atrazine (D_5-ethyl) was obtained from Cambridge Isotope Laboratories (Woburn, MA). Deuterium labeled cyanazine (D_6- gem-dimethyl) was prepared in-house and purified to >98% purity (as determined by GC-MS). Deuterium labeled metolachlor (D_3-ethyl) was prepared in-house and chromatographed to >95% purity (as determined by GC-MS).

All solvents were HPLC grade unless otherwise stated. Distilled, deionized water was obtained by passing distilled water through a commercially available cartridge water purification system. High purity nitrogen or helium were used as carrier gases.

<u>Raw Water Extraction for GC & GC-MS Analyses:</u> The herbicides were liquid/liquid extracted from 500 mL of the raw surface water with 100 X 2 mL of methylene chloride. The organic solvent was evaporated and solvent exchanged into 5% ethyl acetate/isooctane. The extract was made up to a precise volume and quantified by GC with ECD and TSD, using GC conditions and procedures described below for finished water extracts. For GC-MS analyses, the procedure was the same except that sample size was 1 L and 1 mL of a 3.0 μg/mL internal standard solution (deuterium labeled alachlor, atrazine, cyanazine, and metolachlor in ethanol) was added to each sample.

<u>Finished Water Extraction for GC Analyses:</u> The herbicides were extracted from 500 mL of the finished water by pulling the sample through a prerinsed (75 mL methanol) 6 mL Baker C_{18} solid phase extraction (SPE) column. A drying column was prepared by filling to 25 mm with anhydrous Na_2SO_4 a prerinsed (75 mL methanol) 6 mL Baker filtration column and coupled to the end of the C_{18} column. The herbicides were eluted from the C_{18} column with 2 X 2 mL 10% ethyl acetate/iso-octane. The sample was diluted to 10 mL with iso-octane.

<u>Finished Water Extraction for GC-MS Analyses:</u> The herbicides were extracted from 1 L of the finished water by pulling the sample through a 6 mL Baker C18 SPE column. Before the solid phase extraction, one mL of a 3.0 μg/mL internal standard

solution (deuterium labeled alachlor, atrazine, cyanazine, and metolachlor in ethanol) was added to each sample. The four herbicides were eluted by passing 3 mL of 5% ethyl acetate/45% iso-octane/50% methylene chloride (v/v/v) through the column and subsequently through a column containing 3 mL of anhydrous sodium sulfate. The eluent was collected and concentrated to 1.5 mL under a dry nitrogen stream.

GC Quantification: A Varian capillary gas chromatograph equipped with an automatic sampler and ^{63}Ni electron capture (alachlor and metolachlor) and thermionic specific (atrazine and cyanazine) detectors was used. A J&W DB-5 bonded phase capillary column, 30 m length, 0.322 mm internal diameter, 0.1 μ film thickness was used for the ECD determinations. A 5 μL split injection (split ratio 20:1) was performed. High purity nitrogen carrier gas was used at 3 mL per minute. For TSD determinations, a Varian fused silica wide bore BP-1 column, 25 m length, 0.33 mm internal diameter and 0.5 μm film thickness was chosen. High purity gases and a 5 μL injection (no split) were used. Both columns were simultaneously programmed to hold at 150°C for 7 minutes, ramp linearly from 150°C to 220°C at 8°C per minute, and hold at 220°C for 10 minutes. An injector temperature of 250°C and a detector temperature of 300°C were used.

Linear calibration curves from 0.005 μg/mL to 0.05 μg/mL for each acetanilide (ECD) and 0.010 μg/mL to 0.20 μg/mL each triazine (TSD) were generated for every set of samples run. Results were reported as μg/L or ppb of the pesticides in water.

GC-MS Quantification: A Finnigan Model 4535 capillary gas chromatograph mass spectrometer-data system with a Varian Model 8000 autosampler was used. The electron ionization mode was used with electron energy maintained at 70 eV. The herbicides were detected by selected ion monitoring at m/z 160 and 188 (alachlor), 200 and 215 (atrazine), 225 and 240 (cyanazine), and 162 and 238 (metolachlor). The corresponding ions used for monitoring the deuterium labeled herbicides used as internal standards were at m/z 171 and 199 (D_{13}-alachlor), 205 and 220 (D_5- atrazine), 228 and 246 (D_6-cyanazine), and 165 and 241 (D_3-metolachlor). The fused-silica bonded-phase capillary column (J&W DB-5) was 15 m X 0.322 mm i.d., with a 0.25 µ film thickness.

Quality Assurance: The methods were validated by fortification of finished and raw water from each of the CWS sampled in the study. Fortification levels ranged from 0.20 to 25.0 µg/L. The recoveries of these fortification samples were background-corrected and censored when background exceeded 50% of the fortification level. The overall recoveries (Std. Dev.) are 99.3% (9.6) for alachlor, 97.3% (7.0) for atrazine, 89.1% (27.5) for cyanazine, and 98.0% (8.2) for metolachlor.

A side-by-side comparison of the solid phase extraction procedure and the conventional methylene chloride partitioning procedure was performed in order to guarantee equivalent extractability for the two procedures. No statistically significant differences between the extractabilities of the two methods were found.

The identities of the four herbicide peaks were confirmed by retention times relative to deuterated standards and comparison of the levels determined at the two m/z values being monitored for each compound. Only concentrations determined at the most intense m/z value above 100 for each herbicide were reported, i.e., m/z 160 for alachlor, m/z 200 for atrazine, m/z 225 for cyanazine, and m/z 162 for metolachlor.

Storage stability was demonstrated for both raw and finsihed water samples for the 8 week period within which the weekly composite samples were analyzed.

The Monsanto Surface Water Monitoring Studies -- Results

Table II contains a summary of the results for alachlor, atrazine, cyanazine, and metolachlor. For each site two concentrations are given: the maximum weekly and the annualized mean concentration. The annualized mean concentration (AMC) is the time weighted average for the entire year. In the 1985 studies, calculation of an annualized mean concentration (AMC) was performed by taking a simple average of all 52 weekly concentrations measured during the year (trace levels giving negative concentrations were treated as zero in these calculations). In the 1986 studies, alachlor levels were below 0.20 µg/L at the start of the study and sampling continued until alachlor was below 0.20 µg/L for four consecutive weeks. Therefore, for the remaining weeks of the year for which no sampling was performed, alachlor concentrations were assumed equal to 0 µg/L, and thus represent a lower bound. The 1985 results suggest that actual alachlor AMC's in 1986 could have been, at most, as much as 0.2 µg/L higher than the values shown in Table II.

Sampling was terminated in 1986 at most of the CWS before atrazine, cyanazine, and metolachlor returned to undetectable levels. AMCs for atrazine, cyanazine, metolachlor, and simazine at each CWS were calculated based on the apparent relationship between Seasonal Mean Concentration (SMC) and AMC. The SMC was defined as the average weekly concentration from May 1 to September 1. These herbicides were monitored for the entire year during 1985, thus both the SMC's and AMC's could be calculated. A linear regression model was fit to these 1985 data of the following form:

$$\log_{10} AMC = A + B(\log_{10} SMC)$$

The equations determined for the three herbicides were:

Atrazine:	$\log_{10} AMC = -0.26318 + 0.94909(\log_{10} SMC)$	$(r^2=0.974)$
Cyanazine:	$\log_{10} AMC = -0.37458 + 0.99050(\log_{10} SMC)$	$(r^2=0.986)$
Metolachlor:	$\log_{10} AMC = -0.33394 + 0.81763(\log_{10} SMC)$	$(r^2=0.983)$

SMC's of the three herbicides were determined for all CWS in the 1986 study. The AMC's were then calculated for the three herbicides at each CWS using the above regression equations.

Herbicide occurrence was seasonal, i.e., the maximum weekly concentration occurred in May or June, during the peak herbicide use season, followed by a general decline. Shown in Figure 3 is an example from one of the watersheds sampled during both the 1985 and the 1986 surveys. Alachlor, cyanazine, and metolachlor were never detected in any of the plants using the Great Lakes (Michigan City, Monroe and Toledo). Atrazine was detected at low levels in the plants using Lake Erie. Very low alachlor AMCs (0.01 to 0.06 µg/L) were determined for those systems using major Midwestern rivers (Davenport, Lexington, Mount Vernon and Quincy). Little, if any, difference was seen between corresponding raw and finished water from all plants sampled. This was the rationale for monitoring only finsihed water in the 1986 study.

Two pairs of CWS in the 1986 study had their surface water intakes within one mile of each other on the same river. Iowa City and University of Iowa both have their surface water intakes on the Iowa River while Bowling Green and Waterville have their intakes on the Maumee River. As shown in Table II, the excellent agreement between CWS pairs shows the precision of the sampling methodology.

Frequency distributions of AMC across the alachlor use area for the four herbicides are shown in Figure 4. The chance of the AMC in a particular CWS exceeding a given value, A, is computed as follows:

$$\text{Chance (AMC} > \text{A)} = \sum_{i=1}^{9} \frac{\text{N(i) \{\# AMC's in Subpopulation i} > \text{A\}}}{\text{N(.) \{\# AMC's in Subpopulation i\}}}$$

where N(i) is the number of CWS in subpopulation i, and N(.) is the total number of CWS in the alachlor use area, i.e. 457. This chance may be computed at every desired value of A in order to generate the frequency plots given in Figure 4.

Regression Analysis of the Monsanto Study Results

As shown in Figure 3, the concentrations typically form a complicated time series determined by the timing and intensity of rainfall events near the peak application period of early May to mid June. At this particular location, concentrations were considerably higher in 1986 than in 1985, even though overall use patterns were known to be quite similar during the two years. Meteorological data indicate that the watershed was much drier in 1985 than in 1986, apparently contributing to the year-to-year variability. It would be desirable to have a more quantitative understanding (i.e. a model) of the physical phenomena which act in concert to determine the concentrations of these crop chemicals in surface water.

Rather than using an extensive simulation to model the results, a simple multiple linear regression model was developed for predicting the annualized mean concentrations (AMC's) of alachlor, atrazine, cyanazine, and metolachlor. Factors used as independent variables included the following:

- Susceptibility of the watershed soils to runoff
- Physical properties of the chemical
- Total application rate of each chemical within the watershed
- Monthly precipitation totals in the watershed
- Residence times of reservoirs (if any) in the watershed

The methods used to collect each of the independent variables are described below.

<u>Soil Vulnerability to Runoff:</u> The United States Soil Conservation Service (SCS) has identified the runoff vulnerability of various agricultural soils.(*USDA, 1972*) Four hydrologic soil groups have been identified for the purpose of determining runoff susceptibility, A, B, C, and D, with A being the least and D the most vulnerable. A simple ordinal scheme was used as follows: A=1, B=2, C=3, and D=4. State SCS (soil) maps were compared with hydrologic unit (drainage) maps and an average soil type was calculated for each watershed. This average watershed value is referred to as the *soil index* in the subsequent discussion. The *soil index* was used to define sampling domains in the 1986 study.

Chemical Parameters: As mentioned above, most models of chemical runoff assume that K_{OC} and DT_{50} are the measures of mobility and persistence which explain observed differences between chemicals.(*Mills and Leonard, 1984*) Values for the four chemicals were taken from the USDA/ARS data set quoted previously. The mobilities of all four are quite similar, but the average soil half-lives are quite different, ranging from 14 days for cyanazine up to 69 days for atrazine.

Another chemical specific parameter is the dissipation rate in water. Reservoirs were present in several of the water systems sampled, and the concentrations of the four chemicals dissipated at different rates in such systems.(*Gustafson, 1990*) A surface-water dissipation rate constant for each compound was calculated by analysis of several time series in the survey data in which simple first-order decay was apparently taking place (i.e. in reservoirs under very low flow conditions). The half-lives which appeared to fit the data are listed in Table III. In general these half-lives are quite similar to the values reported for soil, and they ranged from 23 days for alachlor up to 69 days for the two triazine herbicides.

Finally, it was necessary to estimate the amount of chemical used in the watershed. For alachlor, proprietary county sales data were available that allowed such an estimate to be made.(*Monsanto, 1986*) Total sales in each county were divided by county area to determine a lumped use rate (lb/A) for the county. The lumped use rate in the watershed was then calculated through the use of digitized hydrologic unit file(*USGS, 1975*) that gives the area of each county intersecting with each hydrologic unit.

For the other chemicals, such detailed sales data were not available to Monsanto. Instead, national scale marketshare information, again available from proprietary sources,(*Monsanto, 1986*) was used to estimate use rates of the other chemicals as a constant multiple of the alachlor use rate (see Table III). These national figures, though not strictly applicable to individual watersheds, provided the best available estimate of overall use patterns.

Weather Data: Weather station locations and data were obtained from the National Climatic Data Center (Asheville, NC) in computer tape form. The problem which remained was to select the proper weather stations with which to represent the rainfall in the watershed. It was decided to characterize each portion of the watershed with data from the closest recording weather station. This involved digitization of the watershed and comparison of the discretized (1 square mile parcels) map with the locations of the weather stations. Average precipitation in each watershed was then determined by giving each weather station's data a weighting factor equal to the area of the watershed to which it was the nearest. Totals were thereby calculated for April, May, and June rainfall.

Reservoir Capacity: The concentration time series were qualitatively different when reservoirs were present in the watershed. In rivers, the concentrations peaked and fell very erratically, whereas in reservoirs the changes were damped considerably, resulting in much smoother curves. The larger the mean residence time of the reservoir, the greater this dampening effect should be. The residence time is equal to the volume divided by the input flowrate, and the flowrate is proportional to the area of the watershed.

Thus, a measure of residence time is reservoir volume divided by total watershed area, both of which were available from water system personnel. The resulting parameter, with units of length, was defined as the reservoir capacity and included as a regressor variable. If no reservoir was present, the parameter was set to 0.

Evaluation of the Regression Coefficients: The regression itself was performed on the logarithm of the measured AMC's. This transformation is reasonable because of the compensatory weighting it provides for the common proportional increase of standard deviation with chemical concentration. These transformed concentrations were then regressed against the other variables using SAS® software (version 5.18) implemented on a VAX 8650. The all-subsets regression procedure RSQUARE(*SAS Institute, 1985a*) was first utilized to determine combinations of regression variables which best explained the observed variance, and the procedure REG(*SAS Institute, 1985b*) was used to estimate the multiple regression coefficients and their significance. The selected regression equation was chosen by picking the linear model with the highest R^2 value and having only significant ($p<0.05$) regressor variables.

The selected regression model is summarized in Table IV, and its predictions are compared with the observed values in Figure 5. Herbicide use, as measured by alachlor sales and relative marketshare, was the most significant variable. Following closely behind were the half-life in water, reservoir capacity, May rainfall, and K_{OC}. These five parameters were all highly significant in explaining the observed variation in AMC ($p < 0.0001$). Marginally less significant was soil vulnerability to runoff as measured by the soil index ($p = 0.0076$). April and June rainfall were not significant, nor was the half-life of the pesticide in soil.

The median absolute error of prediction with this regression is 0.0068 ppb. In other words, half the predicted AMC's are within 0.0068 of the observed value. The relative importance of the various monthly rainfall totals is closely coupled to the time of application, most of which occurs in May. The relative importance of the pesticide physical properties suggested by the regression equation may not be widely applicable because of the rather narrow range of values spanned by the four pesticides.

A considerably more complex model of surface water contamination, HSPF, had been used by the US EPA to predict a typical AMC range of 2-5 ppb for alachlor in the corn belt, which now appears to be much too high given the available monitoring data.(*25*) HSPF requires a dedicated mainframe and several months of calibration, whereas the regression equation requires the estimation of a few parameters and a hand calculator. Clearly, the regression modeling approach has significant advantages over the more complex model.

Conclusions

Examination of previous monitoring studies suggests that only those pesticides with K_{OC} less than 500 mL/g are found at detectable levels in the surface water. Examination of the Monsanto's surface water studies shows that the occurrence of pesticides is seasonal with peak concentrations occurring, as expected, immediately following the application season. Levels observed later in the year are principally a function of soil half life, with the less persistent materials (cyanazine, alachlor) occurring at low or undetectable levels. The appearance and disappearance of the pesticides in a particular watershed is a complex function of chemical, meteorological, and hydrological factors.

In order to estimate the average magnitude of such residues, the regression model has proved useful in revealing the relative importance of the various chemical and watershed parameters which determine the observed concentrations. For chemicals with K_{OC} near 100 mL/g, the half-life in water is the most important of the physical-chemical properties, whereas overall chemical use, reservoir volume, and May rainfall are the most important watershed properties. These important observations could not have come from the comparison of a highly complex model with the data, because such fine differences in input parameter importance become indiscernible during the involved calibration/validation process.

Acknowledgments

Outstanding computerized data base support was provided by L. D. Cheung. Fred Rupel oversaw the considerable logistic support required for sample shipment and tracking. Numerous other members of Monsanto Agricultural Company's Environmental Science Department helped in the analysis of the samples and contributed their time by visiting community water systems during the 1985-1986 studies.

Table I. **Physical Properties* for Several Pesticides Included in Surface Water Monitoring Programs in Iowa and Ohio**

Key	Compound	Koc (mL/g)	Half-life (days)	Found§ in Iowa?	Found¶ in Ohio?
1	2,4-D ACID	20	10	Yes	
2	ALACHLOR	170	15	Yes	Yes
3	ALDRIN†	14000	120	No	
4	ATRAZINE	100	60	Yes	Yes
5	BUTYLATE	126	12	No	No
6	CARBOFURAN	22	50	Yes	
7	CHLORAMBEN	15	14	No	
8	CHLORDANE†	33600	54	No	
9	CHLORPYRIFOS	6070	30	No	No
10	CYANAZINE	190	14	Yes	Yes
11	DDT†	160000	3800	No	
12	DIAZINON	500	40	No	No
13	DICAMBA	2	14	No	
14	DIELDRIN†	7100	1000	No	
15	ENDRIN‡	11188	2240	No	
16	EPTC	280	30		No
17	ETHOPROP	70	50	No	No
18	FONOFOS	532	45	No	No
19	HEPTACHLOR†	16000	2000	No	
20	LINDANE†	2500	790	No	
21	LINURON	370	60		Yes
22	MALATHION	1800	1	No	
23	METOLACHLOR	200	20	Yes	Yes
24	METRIBUZIN	41	30	Yes	Yes
25	PENDIMETHALIN	24300	90	No	No
26	PHORATE	2000	85	No	No
27	PROMETON	300	120	Yes	
28	PROPACHLOR	80	6	No	
29	SILVEX†	ND	16	No	
30	SIMAZINE	138	75		Yes
31	SULPROFOS	550	14	No	
32	TERBUFOS	3000	5	No	No
33	TOXAPHENE‡	95816	9	No	
34	TRIFLURALIN	7000	60	No	No

* All properties are taken from the USDA/ARS data base as the first source (*Wauchope, 1989*) with the exception of any compound marker by a † (*Johnson, 1988*) or a ‡ (*Wilkerson and Kim, 1986*) No data on the *Koc* of silvex could be found in any of the three sources.

§ Detected in one of the state's surface water-based community water systems during the 1987 DNR survey (*Iowa DNR, 1988*).

¶ Detected during 1982 in either the Honey Cr., Sandusky R., or Maumee R. watersheds at runoff loads in excess of 0.5 g/ha (*Baker, 1983*).

64

Table II. Maximum Weekly and Annualized Mean Concencentrations§ (ppb) of Four Herbicides in the Finished Drinking Water of Several US Community Water Systems During 1985 and 1986

Map Key	Community Water System		Year	Alachlor MWC	Alachlor AMC	Atrazine MWC	Atrazine AMC	Cyanazine MWC	Cyanazine AMC	Metolachlor MWC	Metolachlor AMC
1	Appleton	WI	1986	<0.20	0.00	<0.20	0.02	<0.20	0.03	<0.20	0.01
2	Bethany	MO	1985	<0.20	0.00	0.88	0.58	1.02	0.69	<0.20	0.00
3	Blanchester	OH	1985	1.10	0.15	22.20	5.96	8.78	2.22	0.52	0.08
4	Bowling Green	OH	1986	5.21	0.52	9.37	2.08	4.11	0.50	5.91	1.01
5	Breese	IL	1985	4.40	0.29	19.10	2.04	2.68	0.38	2.72	0.22
6	Caledonia	OH	1986	9.48	0.57	12.33	1.85	2.75	0.20	17.80	1.28
7	Carlinville	IL	1986	<0.20	0.00	1.97	0.84	0.44	0.09	0.25	0.10
8	Charleston	IL	1985	<0.20	0.00	0.37	0.23	0.23	0.00	<0.20	0.00
9	Clarinda	IA	1985	<0.20	0.00	2.15	0.62	1.30	0.33	0.82	0.11
10	Columbus	OH	1985	10.90	1.30	18.50	4.29	4.04	0.58	9.15	2.07
	Columbus	OH	1986	3.45	0.44	11.96	3.11	4.95	0.68	6.59	1.27
11	Creston	IA	1986	<0.20	0.00	1.22	0.35	0.66	0.13	0.34	0.11
12	Crewe	VA	1986	<0.20	0.00	<0.20	0.03	<0.20	0.04	<0.20	0.03
13	Davenport	IA	1985	0.32	0.01	0.56	0.11	0.25	0.03	0.23	0.00
14	Dearborn	MO	1986	1.12	0.09	2.74	0.82	0.24	0.05	0.28	0.03
15	Decatur	IL	1985	0.28	0.03	1.27	0.53	0.36	0.10	0.74	0.26
16	Delta	OH	1986	<0.20	0.00	0.34	0.12	0.23	0.05	<0.20	0.04
17	Eskridge	KS	1986	<0.20	0.00	<0.20	0.03	0.27	0.04	<0.20	0.02
18	Fort Wayne	IN	1986	5.03	0.52	13.04	2.31	3.46	0.33	7.58	0.90
19	Greenville	NC	1985	0.27	0.01	0.37	0.02	0.21	0.00	<0.20	0.00
20	Hettick	IL	1986	<0.20	0.00	1.45	0.61	0.24	0.06	<0.20	0.06
21	Iowa City	IA	1986	5.07	0.42	7.31	1.68	6.14	0.69	3.85	0.60
22	Jacksonville†	IL	1986	6.12	0.85	22.51	4.52	3.48	0.53	20.40	2.10
23	Jarratt	VA	1986	<0.20	0.00	0.96	0.14	0.93	0.06	<0.20	0.03
24	Jefferson County	KS	1986	0.29	0.02	4.23	1.59	0.22	0.04	1.02	0.37
25	Kankakee	IL	1985	0.77	0.08	1.64	0.37	0.34	0.06	0.68	0.12
26	Lexington	MO	1985	0.59	0.03	3.11	0.60	0.59	0.07	0.42	0.02
27	Macomb	IL	1986	1.42	0.09	3.72	0.90	1.88	0.31	1.53	0.26
28	Marion	IL	1985	<0.20	0.00	1.59	0.48	0.29	0.01	0.43	0.11
29	Maysville	OH	1986	<0.20	0.00	0.34	0.07	<0.20	0.04	<0.20	0.03
30	Michigan City	IN	1985	<0.20	0.00	<0.20	0.00	<0.20	0.00	<0.20	0.00
31	Monroe	MI	1985	<0.20	0.00	0.26	0.00	<0.20	0.00	<0.20	0.00
32	Mount Vernon	IN	1985	1.00	0.05	4.62	0.60	0.91	0.13	0.56	0.06
33	Muncie	IN	1985	2.80	0.25	7.31	0.70	1.36	0.05	2.53	0.21
34	Olathe	KS	1986	0.51	0.06	2.82	1.13	0.27	0.04	0.48	0.16
35	Ottawa	KS	1986	<0.20	0.00	3.60	1.22	0.22	0.04	0.28	0.10
36	Piqua	OH	1985	0.63	0.03	1.73	0.38	0.44	0.09	0.34	0.01
37	Plattsburg	MO	1986	<0.20	0.00	1.91	0.68	0.26	0.06	0.35	0.10
38	Pomona Lake	KS	1986	0.45	0.06	10.75	2.90	<0.20	0.04	1.68	0.48
39	Quincy	IL	1985	0.70	0.06	1.31	0.44	0.52	0.10	0.31	0.02
40	Richmond	IN	1985	3.60	0.57	10.30	2.05	3.67	0.65	1.25	0.26

§ Weekly composites with measured concentrations less than 0.2 ppb are indicated by < 0.20. Annualized mean concentrations are calculated by summing all non-negative estimated concentrations and dividing by 52, with the exception of the 1986 AMC's for atrazine,

65

Table II. Maximum Weekly and Annualized Mean Concencentrations (ppb) of Four Herbicides in the Finished Drinking Water of Several US Community Water Systems During 1985 and 1986 (continued)

Map Key	Community Water System		Year	Alachlor MWC	Alachlor AMC	Atrazine MWC	Atrazine AMC	Cyanazine MWC	Cyanazine AMC	Metolachlor MWC	Metolachlor AMC
41	Roanoke Rapids	NC	1985	<0.20	0.00	<0.20	0.00	0.23	0.00	<0.20	0.00
42	Sabetha	KS	1986	0.91	0.16	9.95	2.00	0.59	0.04	3.16	0.54
43	Shelbina	MO	1986	0.30	0.01	3.19	1.17	0.98	0.17	0.50	0.05
44	Shipman	IL	1986	7.44	0.89	16.33	6.04	1.96	0.63	9.32	2.08
45	Swanton	OH	1986	0.33	0.02	1.07	0.33	0.29	0.06	0.27	0.06
46	Toledo	OH	1985	<0.20	0.00	0.24	0.02	<0.20	0.00	<0.20	0.00
47	University of Iowa	IA	1985	1.80	0.11	2.95	0.62	1.54	0.21	0.87	0.11
	University of Iowa	IA	1986	5.29	0.48	7.97	1.91	5.61	0.78	4.87	0.69
48	Waterville	OH	1986	5.25	0.42	8.65	1.78	3.73	0.44	6.17	0.92
49	Westerville	OH	1986	1.25	0.03	5.43	0.71	1.47	0.13	1.86	0.18
50	White House	TN	1986	<0.20	0.00	0.52	0.07	0.45	0.04	<0.20	0.02
51	Wyaconda	MO	1985	<0.20	0.00	1.42	0.63	0.28	0.01	<0.20	0.00
52	Ypsilanti	MI	1985	<0.20	0.00	<0.20	0.00	<0.20	0.00	<0.20	0.00

cyanazine, and metolachlor, which were calculated using the relationship between SMC and AMC given in Table II.

Table III. Compounds Included in Surface Water Regression Model

Common Name	Trade Name	Chemical Name	Relative US Sales (lb)	Half-life in Water (days)
Alachlor	Lasso®	2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide	1.00	23
Atrazine	Aatrex®	6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-trizine-2,4-diamine	0.59	69
Cyanazine	Bladex®	2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-amino]-2-methylpropanenitrile	0.41	69
Metolachlor	Dual®	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methyoxy-1-methylethyl)acetamide	0.69	55

® Registered trademarks of the various polluting entities.

Table IV. Statistical Summary of a Regression Model for Predicting Annualized Mean Concentrations (AMC's) of Four Herbicides

Variable (units)	Coefficient	Standard Error	Observed Significance Level*
Intercept	-3.38789	0.37337	<0.0001
Herbicide Use (lb/A)	3.39377	0.35103	<0.0001
Half-Life in Water (days)	0.02264	0.00242	<0.0001
Reservoir Capacity (cm)	0.14943	0.02548	<0.0001
May Rainfall (cm)	0.05566	0.00972	<0.0001
Mobility in Soil, Koc (mL/g)	-0.00542	0.00100	<0.0001
Soil Index (1.0-4.0, A-D)	0.23612	0.08742	0.0076

* For a 2-tailed test of the coefficient = 0.

Median Absolute Error 0.0068 ppb (half the predicted AMC's are within 0.0068 ppb of the observed value)

Model: $\log_{10}(AMC)$ = Intercept + Σ(Coefficient*Variable) with AMC is given in (ppb)

Overall $R^2 = 0.5904$ (N=192)

Concentrations are AMC's measured in surface water for alachlor, atrazine, cyanazine and metolachlor during 1985 and 1986.

68

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Figure Captions.

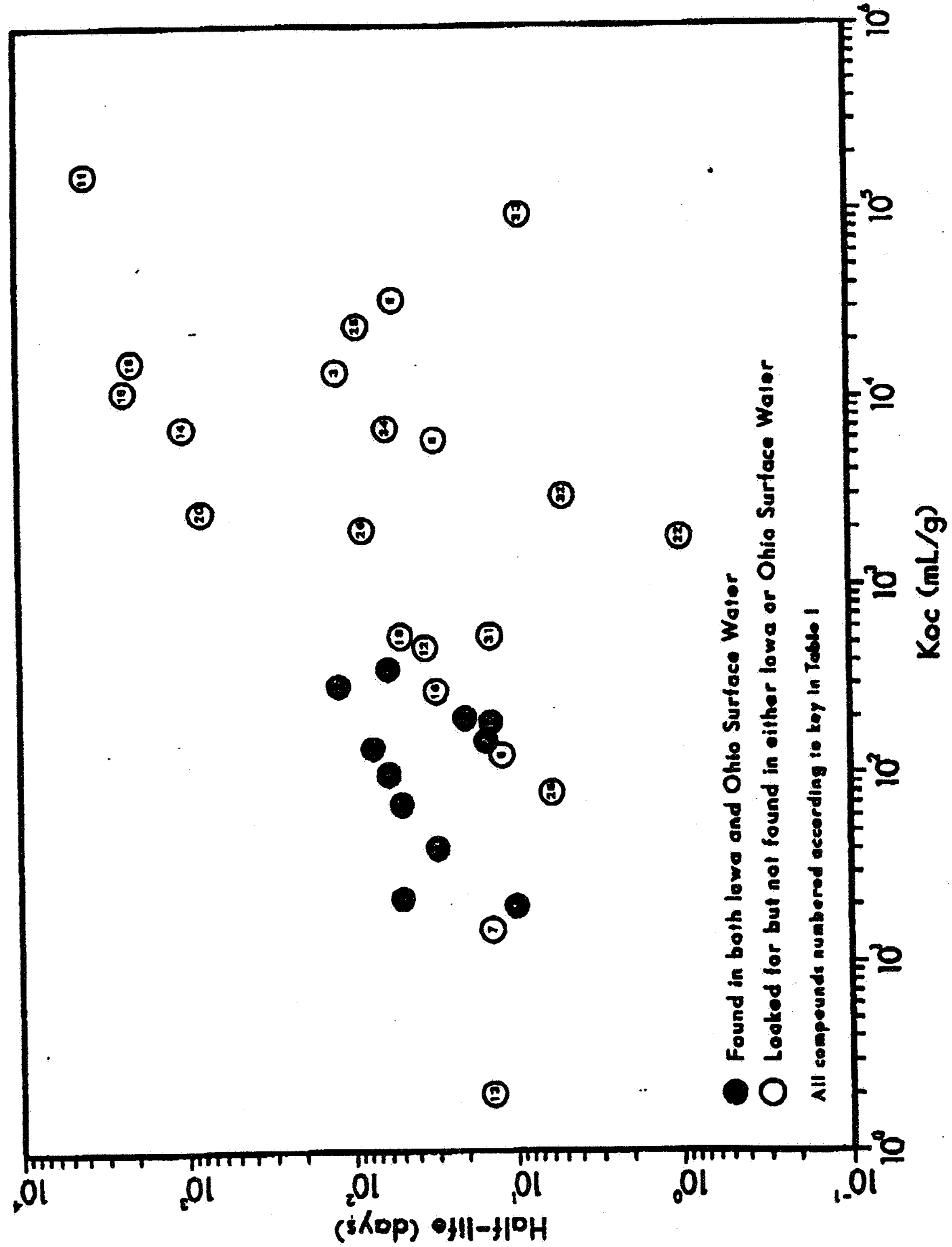
1. Illustration of the influence of pesticide physical properties (mobility and persistence in soil) on the propensity for occurrence at detectable levels in surface water.

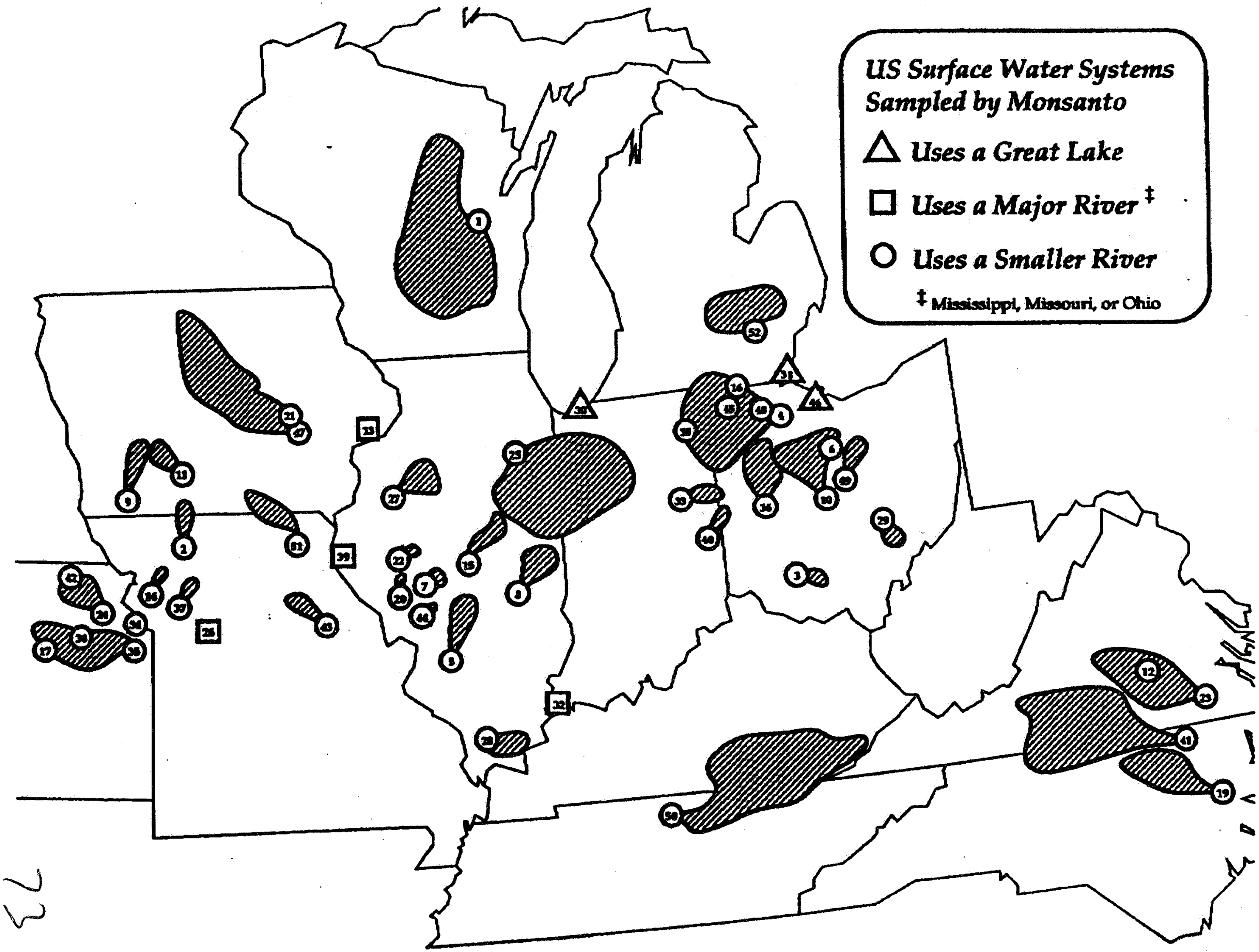
2. United States community water systems sampled by Monsanto during 1985 and 1986. The watersheds of the smaller rivers are indicated by the shaded areas.

3. Measured concentrations in the Iowa River at the University of Iowa in Iowa City during the 1985-1986 monitoring study.

4. Frequency distribution of AMC's in the alachlor use area during 1985-6 for alachlor, atrazine, cyanazine, and metolachlor.

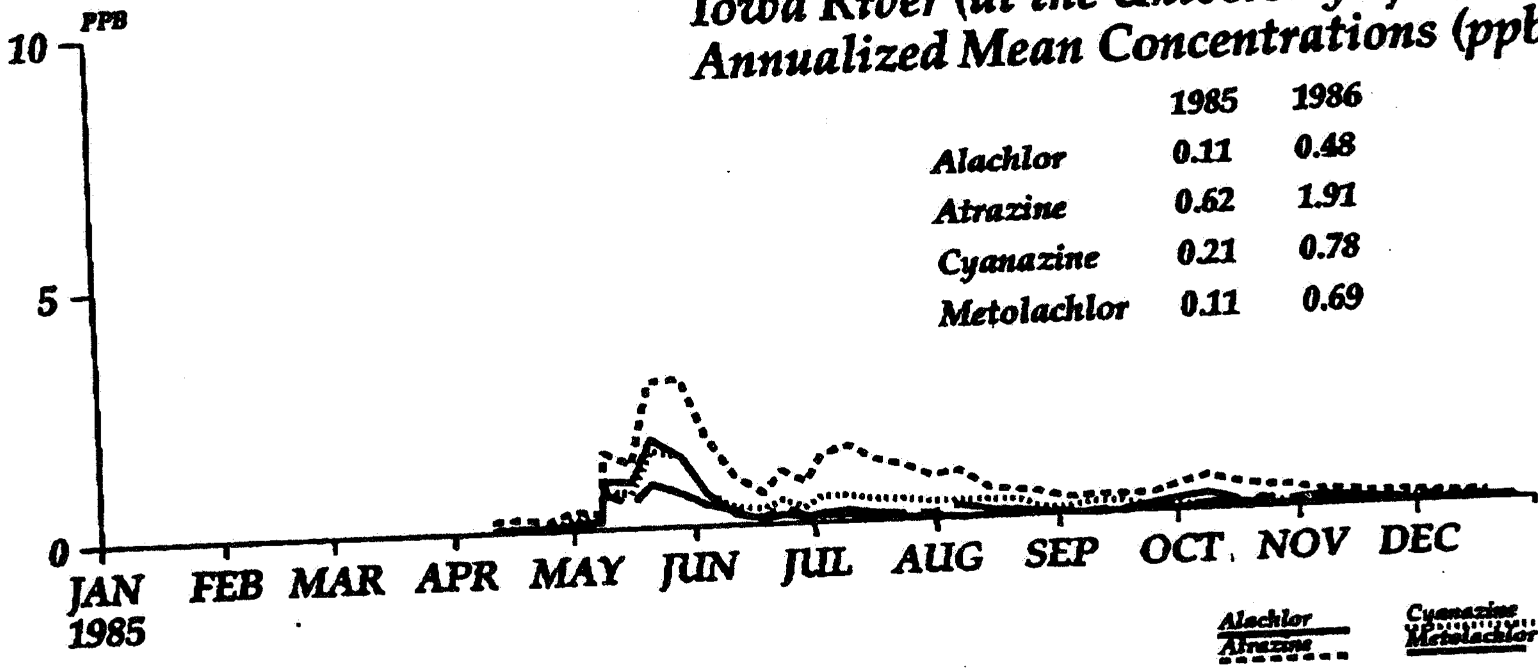
5. Comparison of predicted vs. observed annualized mean concentrations (AMC's) of four commonly used herbicides in the surface waters of the US. The predictions are made using the regression equation summarized in Table IV.

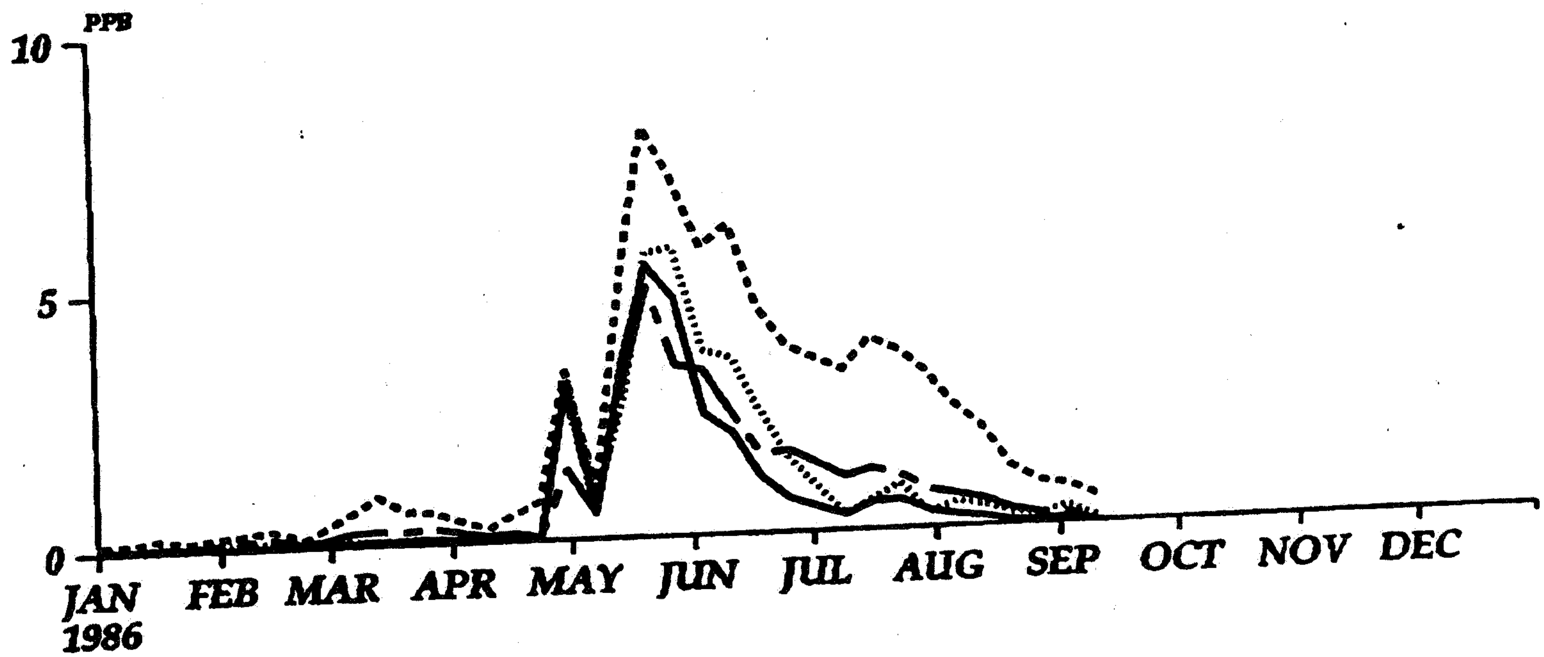

Found in both Iowa and Ohio Surface Water
Looked for but not found in either Iowa or Ohio Surface Water
All compounds numbered according to key in Table 1
Koc (mL/g)
Half-life (days)

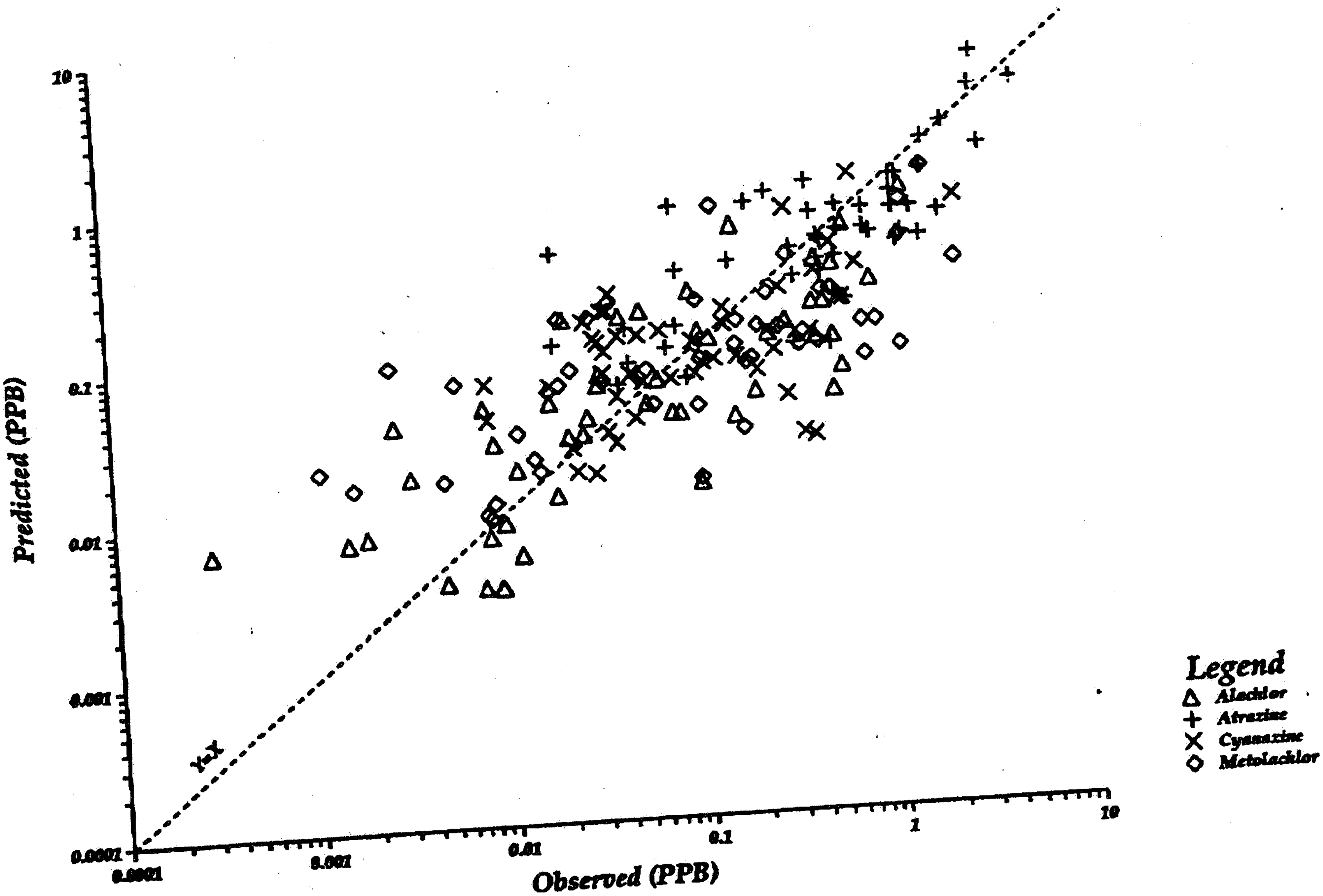

US Surface Water Systems
Sampled by Monsanto
Uses a Great Lake
Uses a Major River ‡
Uses a Smaller River
‡ Mississippi, Missouri, or Ohio

Iowa River (at the University of Iowa)
Annualized Mean Concentrations (ppb)

	1985	1986
Alachlor	0.11	0.48
Atrazine	0.62	1.91
Cyanazine	0.21	0.78
Metolachlor	0.11	0.69



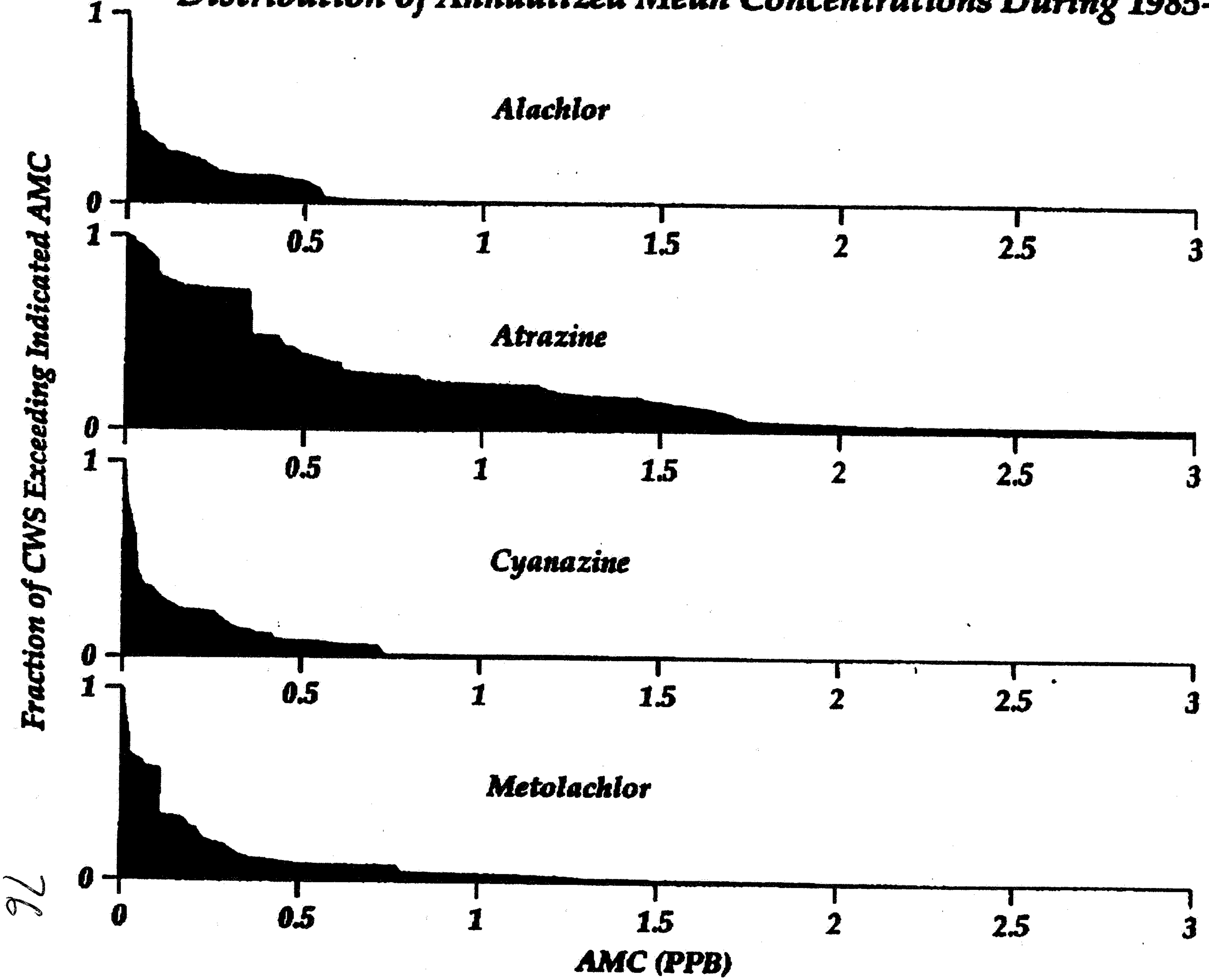




Predicted (PPB)
10
1
0.1
0.01
0.001
0.0001
Y=X
0.0001
0.001
0.01
0.1
1
10
Observed (PPB)
Legend
Alachlor
Atrazine
Cyanazine
Metolachlor

7.5

Distribution of Annualized Mean Concentrations During 1985-6



ATTACHMENT E

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

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

MEMORANDUM: January 25, 1993

SUBJECT: Summary of data on alachlor concentrations in surface waters.

TO: Jack Housenger, Chief
Special Review Branch
Special Review and Re-registration Division

FROM: Henry Nelson, Ph.D., Head H Nelson
Surface Water Section
Environmental Fate and Groundwater Branch/EFED

THRU: Hank Jacoby, Chief Hank Jacoby
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division

This summary of data on alachlor in surface waters is in response to your July 21, 1992 memo to H. Jacoby of EFED in which you asked if the conclusions reached in the Alachlor PD 4 regarding surface water were accurate, and posed several other questions.

This data summary is based upon the EFGWB review of 8 studies including the 2 (Lauer etal 1986 and Smith etal 1987) on community water systems submitted by the registrant and discussed in the Alachlor PD 4. The data summary for those studies in the Alachlor PD 4 is accurate except possibly for the "annualized means". It is unclear how these were computed. The sampling intervals for those 2 studies were 4/85-1/86 and 4/86-9/86, respectively. Consequently, any means computed from actual data would not be annual. Without actual data covering the entire year, "annualized means" are guesses. However, given the typical rapid decline in alachlor concentrations from the peak concentrations in May and June, annual concentrations are likely to be substantially less than the 4/85-1/86 and 4/86-9/86 means. Since none of the 4/85-1/86 means in the Lauer etal 1986 study exceeded the MCL of 2 ug/L, none of the 1985 annual means at the sampled systems were likely to have exceeded the MCL. One 4/86-9/96 mean (2.39 ug/L for Jacksonville) exceeded the MCL, but the annual mean was likely less than the MCL.

The only population data provided in the studies were from the 2 community water system studies. The other surface water questions posed in the memo are addressed in the data summary below.

DRINKING WATER REGULATIONS:

Under the revised Federal drinking water regulations, public water supply systems are required to sample their systems a minimum of once each quarter year and analyze them for 18 regulated pesticides for which MCLs have been established. If the annual average concentration of one or more regulated pesticides (based upon the average of 4 consecutive quarterly samples) exceeds its MCL, the supply is considered to be out of compliance. Systems out of compliance are required to notify their customers and to ensure through additional monitoring and if necessary additional treatment that the system is brought back to compliance.

Since the annual mean that is compared to the MCL will generally be computed from the average of 4 consecutive quarterly samples, any one of the samples having a concentration of greater than 4 times the MCL of one or more regulated pesticides would automatically place the system out of compliance. Consequently, the American Water Works Association is not only concerned about annual mean concentrations exceeding the MCL, but also about individual concentrations of pesticides exceeding 4 times their MCL.

EFGWB REVIEW METHODOLOGIES:

EFGWB reviewed 8 surface water monitoring studies conducted over the last 10 years which contain alachlor data. Several month to annual (the longest average that could be computed less than or equal to one year was computed) mean alachlor concentrations were compared to the alachlor MCL of 2 ug/L. Maximum and other individual alachlor concentrations (when available) were compared to 4 times the MCL (8 ug/L) for reasons previously discussed.

Alachlor concentration distributions are provided with respect to its detection limit (varies), 1 ug/L, its MCL (2 ug/L), and 4 times its MCL (8 ug/L). Mean concentrations exceeding the MCL, maximum concentrations exceeding 4 times the MCL, and numbers of samples exceeding 4 times the MCL are shaded in the Tables.

Although much of the data reviewed was for raw surface water, alachlor concentrations in raw surface waters and most finished drinking waters from surface sources are expected to be comparable due to the ineffeciency of the primary treatment systems of most water supply systems in effectively removing compounds with low soil/water partition coefficients such as alachlor. This was demonstrated by one of the reviewed studies (Lauer etal 1986) in which alachlor concentrations in raw and finished waters at the same locations were almost identical.

OVERALL DATA SUMMARY:

Alachlor concentrations tend to peak in May to early June during the first runoff events following application and then decline rapidly to almost pre-application levels of well below 1 ug/L by July or August. Peak concentrations of alachlor often exceeded 4 times the MCL in some of the studies reviewed. The frequency of such exceedences was greatest in one of the USGS studies (Goolsby and Thurman 1991) in which samples were collected during the first major runoff events following application and in the Baker (1988) study where samples were apparently collected at least 3 times a week and not time composited. Exceedences of 4 times the MCL were much less frequent in the other studies where samples were collected at set intervals instead of during runoff events and where time composite samples were often collected.

Data were not usually available to compute annual means. Spring to Summer arithmetic and time weighted mean alachlor concentrations only rarely exceeded the MCL in the studies reviewed. In most cases where the computed several month means do exceed the MCL, it appears from their magnitude and generally low observed alachlor concentrations in Fall, Winter, and early Spring that the corresponding annual means would generally be unlikely to exceed the MCL. However, in the Squillace and Engberg 1984/1985 study of the Cedar River, dissolved arithmetic mean alachlor concentrations for 1984 exceeded the MCL of 2 ug/L in 4 of the 6 locations sampled. Only one other computed annual arithmetic mean exceeded the MCL in the other studies reviewed.

Alachlor concentrations in surface waters appear to depend upon numerous factors including the quantity of alachlor use on the drainage area upstream, the infiltration characteristics of the drainage area soils, the drainage area upstream, and the timing, numbers and intensities of post-application runoff events. In addition, alachlor concentrations in finished drinking water may reflect water management practices such as the amount of pumping during runoff events, and the hydraulic residence times of holding reservoirs.

As previously stated, individual alachlor concentrations often exceeded 4 times the MCL in some of the studies reviewed whereas annual arithmetic means based on much greater than 4 samples generally appeared unlikely to exceed the MCL except in a few cases. That along with time series plots of alachlor concentrations showing sharp peaks during post-application runoff events, but rapid decline to very low concentrations thereafter, suggests that computations of annual means based upon the arithmetic average of 4 quarterly samples may frequently substantially overestimate actual annual time weighted means. That may be particularly true if one of the 4 quarterly samples is collected during post-application runoff events when peak alachlor concentrations occur.

RECOMMENDATIONS:

Although HED/OPP does not base its assessment of pesticides risks due to drinking water consumption on exceedencies of the MCL, they may find that the means, maximums, and concentration distributions provided are useful for generating their exposure assessments. EEB may also find them useful for generating exposure assessments. Consequently, please provide those groups with a copy of this review.

Time series plots for atrazine and cyanazine in streams and rivers resemble those for alachlor in showing sharp post-application peaks and then relatively rapid decline to low levels. However, recent 6(a)(2) data submissions have indicated that atrazine and cyanazine concentrations in some lakes and reservoirs remain elevated throughout the year. Since alachlor is resistent to abiotic hydrolysis just like atrazine and cyanazine, it is theoretically possible that elevated concentrations of alachlor may also occur throughout the year in some reservoirs and lakes with low microbiological activities and high hydraulic residence times. Data on the concentrations of alachlor in lakes and reservoirs have not as yet shown elevated alachlor concentrations throughout the year. However, the available alachlor data for lakes and reservoirs are scarce and do not include alachlor data for lakes and reservoirs in which year long elevated concentrations of atrazine and cyanazine have been reported (eg., Rathburn Reservoir, West Lake). The monitoring requirements of the revised drinking water regulations should provide EFGWB with additional alachlor data on lakes and reservoirs. Please forward any such data received by OPP to EFGWB for review.

STUDIES REVIEWED:

(1) Lauer R, Smith RG, Baszis SR, Horner LM, Rupel FL, Triebe FM, and Klein AJ. 1986. Alachlor in raw and finished drinking water derived from surface sources from 24 community water systems located in regions of extensive Lasso use. MRID 158911. Performed and presented by Monsanto Agricultural Company. Report No. MSL-5412.

(2) Smith RG, Triebe FM, and Baszis SR. 1987. Alachlor, atrazine, cyanazine, metolachlor, and simazine in surface water from 30 community water systems located in regions of Lasso use. MRID 40265901. Performed and presented by Monsanto Agricultural Company. Report No. MSL-6787.

(3) Baker DB. 1988. Sediment, nutrient and pesticide transport in selected lower great lakes tributaries. Performed by Water Quality Laboratory of Heidelberg College for the Great Lakes National Program Office of U.S. EPA. EPA-905/4-88-001. GLNPO Report No. 1.

(4) Squillace P and Engberg R. 1988. Surface-water quality of the Cedar River Basin, Iowa-Minnesota with emphasis on the occurrence and transport of herbicides, May 1984 through November 1985. U.S Geological Survey Water Resources Investigations Report 88-4060.

(5) Moyer L and Cross J. 1990. Pesticide Monitoring: Illinois EPA's Summary of Results 1985-1989. Division of Water Pollution Control, State of Illinois Environmental Protection Agency.

(6a) Goolsby DA and Thurman EM. 1991. Herbicides in rivers and streams of the upper midwestern United States. To be published in : Proc. 46th Ann. Meeting Upper Mississippi River Conservation Committee

(6b) Thurman EM, Goolsby DA, Meyer MT and Kolpln DW. 1991. Herbicides in surface waters of the midwestern United States: The effect of Spring flush. Environ. Sci. & Technol. 25(10): 1794-1796.

(6c) Thurman EM, Goolsby DA, Meyer MT, Mills MS, Pomes ML, and Kolpln DW. 1992. Reconnaissance study of herbicides and their metabolites in surface water of the midwestern United States using immunoassay and gas chromatography/mass spectrometry. Environ. Sci. and Technol. 26(12): 2440-2447

(7) Goolsby DA, Coup RC, and Markovchick DJ. 1991. Distribution of selected herbicides and nitrate in the Mississippi River and its major tributaries, April through June 1991;

(8) Taylor AG. 1992. Pre-compliance testing for pesticides in Illinois surface water supplies. Unpublished report of Illinois Environmental Protection Agency. Submitted under FIFRA 6(a)(2) by DuPont.

SUMMARIES OF INDIVIDUAL STUDIES:

Lauer etal 1986:

Lauer etal 1986 sampled the raw and finished water of 24 community water supply systems whose primary source of water is surface water and which are located in areas of alachlor use (Table 1). Of the 24 systems selected for sampling, only 2 were described as being in high alachlor use areas. The other 22 were described as being in "medium" use areas. Samples were collected daily from April 1985 to January or February 1986. Daily samples collected on 7 consecutive days were time composited for analyses. Concentrations in raw and corresponding finished waters were almost identical at all locations.

None of the April 1985 to January or February arithmetic mean alachlor concentrations in either raw or finished water exceeded the alachlor MCL of 2 ug/L (Table 2). Only the raw and finished water arithmetic mean alachlor concentrations for Columbus, OH exceeded 1 ug/L (1.74 and 1.68 ug/L, respectively).

The only individual alachlor concentrations exceeding 4 times the MCL (8 ug/L) were for 3 samples collected from the raw and 2 samples collected from the finished water of Columbus, OH (Table 2). The highest observed alachlor concentrations were 10.7 ug/L and 12.0 ug/L in the raw and finished waters, respectively, of Columbus, OH.

The highest alachlor concentrations were observed in Columbus, OH followed by Richmond, IN; Breese, IL; and Muncie, IN (Table 2). All were described as being located in intermediate alachlor use areas. The 2 systems described as being in high alachlor use areas (Davenport, IA and Greenville, NC) had among the lowest alachlor concentrations. Such observations may reflect differences in the infiltration characteristics of soils in the different watersheds and/or differences in the numbers and intensities of post-application runoff events. However, no information on soils or hydrology was provided.

Time series plots for alachlor concentrations in raw and finished water are provided in Figures 1 through 4 for the 4 systems with the highest alachlor concentrations. Alachlor concentrations at the 4 locations peaked at above the MCL in mid to late May, then declined throughout June to close to the pre-application levels of April by July.

Smith etal (1987):

Smith etal (1987) sampled the finished water of 30 community water supply systems whose primary source of water is surface water and which are located in areas of alachlor use (Table 3 from Table 5 of the study report and Fig. 5 from Fig. 1 of the study report). The systems sampled were different than those sampled by Lauer etal (1986) in another Monsanto sponsored study. Samples were collected daily from April to August or April to September at all but one site. At one of the Illinois sites (Shipman), samples were collected an additional 8 months. Daily samples collected on 7 consecutive days were time composited for analyses.

Only one of the April to August or April to September 1986 alachlor arithmetic mean concentrations exceeded the alachlor MCL of 2 ug/L (Table 4). However, that arithmetic mean (2.39 ug/L for Jacksonville, IL) was only slightly greater than the MCL, and alachlor concentrations after September and before April are generally much less than those from April to September. Consequently, the annual alachlor arithmetic mean concentration for Jacksonville in 1986 was probably less than the MCL. For example, although the April to August 1986 alachlor arithmetic mean concentration at Shipman, IL was 1.7 ug/L, the annual arithmetic mean was almost 50% less (0.91 ug/L).

Only one reported individual alachlor concentration (9.5 ug/L at Caledonia, OH) exceeded 4 times the MCL (8 ug/L)(Table 4).

The community water systems selected for sampling represented various combinations of low to high alachlor use areas and low to high susceptibility to runoff (based upon the average soil hydrological grouping). Of the 8 systems with April to August or April to September alachlor arithmetic mean concentrations > 1 ug/L, 7 were in the high alachlor use classification and one was in the intermediate use classification. Only 3 were in the high susceptibility to runoff category. Four were in the low susceptibility to runoff category and one was in the intermediate category. Consequently, the study authors believe that alachlor use is a better predictor of alachlor concentrations in surface source drinking water than susceptibility to runoff based upon hydrological soil classifications.

Source types included small creeks, rivers, large man-made impoundments and small to large lakes. The was no obvious correlation between source type and alachlor concentrations possibly due to the variation in other factors which probably affect alachlor concentrations such as alachlor use and the soil hydrological soil groupings.

Two of the systems in both a high alachlor use category and a high susceptibility to runoff category (Delta, OH and Swanton, OH) had low alachlor concentrations. The study authors attributed the low alachlor concentrations in those systems to water management practices. To keep holding reservoirs from filling up with sediment, neither system pumps water from the sources when the source water is turbid. Consequently, the peak alachlor concentrations which occur in source waters during the first major runoff events following application are not pumped into the system holding reservoirs.

Time series plots for alachlor concentrations in finished water are presented in Figures 6 through 13 for the 8 systems at which the April to August or April to September alachlor arithmetic means were > 1 ug/L. Alachlor concentrations at the 8 locations peaked at above the MCL in mid to late May, then declined throughout June to close to the pre-application levels of April by July.

Baker (1988):

Baker (1988) sampled 8 tributaries of Lake Erie from April 15 to August 15 of 1982 to 1985 (Table 5 from Table 5.1 of the study report; Fig. 15 from Fig. 5.1 of the study report). Individual data and the days, frequencies and compositing of sample collection were not provided. However, based upon the total number of samples and the sampling period (April 15-August 15 of each year), at least 3 samples were probably collected at each location per week.

Four of the 24 April 15-August 15 alachlor time weighted mean concentrations (TWMCs) over 3 of the 8 tributaries exceeded the alachlor MCL of 2 ug/L (Table 6; Fig. 16). However, the highest April 15-August 15 alachlor TWMC was only 3.3 ug/L and alachlor concentrations during the other two thirds of the year tend to be much less than 1 ug/L. Consequently, it is unlikely that annual alachlor TWMCs exceeded the MCL at those locations.

Eighteen of the 30 maximum observed alachlor concentrations over 7 of the 8 tributaries sampled exceeded 4 times the MCL (8 ug/L)(Table 6; Figs. 17 and 18).

The study author attributes the low pesticide concentrations including those of alachlor in the Cuyahoga River to the small percentage of agricultural use in the Cuyahoga watershed (see Table 7 from Table 5.2 of the study report). Although much of the River Raisin watershed drains agricultural areas, pesticide concentrations including those of alachlor tended to be lower than in the other 6 surface waters sampled which drain high agriculture use areas. The study author suggests that may be due to many of the soils in the River Raisin watershed being more permeable to water infiltration than those in the other watersheds. That would favor leaching over runoff in the Raisin River watershed.

Squillace and Engberg (1988):

Cross sectional composite samples were collected at 6 locations within the Cedar River Basin alomg the Iowa-Minnesota border (Fig. 19 from Fig. 2 of the study report. Except for bimonthly samples in June 1984, samples were collected monthly May 1984 through September 1985 at the Floyd and Cedar Falls sampling locations, and monthly from May 1984 through November 1985 at the other 4 sampling locations.

Dissolved and total alachlor concentrations were almost identical. Dissolved alachlor concentrations peaked in late May to early June frequently at concentrations above the MCL (2 ug/L) and often at concentrations above 4 times the MCL (8 ug/L). Dissolved alachlor concentrations exceeded 4 times the MCL in samples collected on June 9, 1984 in the Cedar River at Floyd (21.0 ug/L), on June 10, 1984 in the Cedar River near Carville (22 ug/L), on June 10 and 20, 1984 in the Cedar River at Cedar Falls (22.0 and 8.2 ug/L), and on June 10, 1984 in the Cedar River at Gilbertville (17.0 ug/L)(Table 8).

Dissolved arithmetic mean alachlor concentrations for 1984 exceeded the MCL of 2 ug/L in 4 of the 6 locations sampled(Table 8). None of the 1985 arithmetic mean alachlor concentrations exceeded 0.46 ug/L. The highest dissolved arithmetic mean alachlor concentration was 3.1 ug/L for 1984 in the Cedar River near Carville.

Time series plots for dissolved alachlor are presented in Figures 20 through 23 for the 4 sampling locations where the 1984 arithmetic mean alachlor concentration exceeded the MCL.

Moyer and Cross (1990):

Samples for pesticide analyses were collected from a 30 station subnetwork of the 208 station Illinois Ambient Water Quality Monitoring Network (Table 9 and Figure 24 from Table 2 and Fig. 2 of the study report). Twenty-six of the 30 stations reportedly receive drainage from agricultural watersheds. The 4 stations draining non-agricultural watersheds (Des Plaine R., upper Illinois R., the Big Muddy R., and Lusk Creek) served as controls.

Cross-sectional composite samples were collected at each location twice in the Spring, twice in the summer, and once in the winter from October 1985 to October 1988.

Annual alachlor arithmetic mean concentrations were calculated for each of 3 years for each location (Table 10). One of the annual arithmetic mean concentrations (3.41 ug/L for Bay Creek in 1988) exceeded the alachlor MCL of 2 ug/L. Two other annual arithmetic means (1.47 ug/L for the middle fork of the Saline River in 1987 and 1.08 ug/L for Silver Creek in 1987) exceeded 1 ug/L.

Two of the observed maximum alachlor concentrations (18.0 ug/L for Bay Creek in 1988 and 8.5 ug/L for the middle fork of the Saline River in 1987) exceeded 4 times the MCL (8 ug/L)(Table 10).

Time series plots for alachlor concentrations are presented in Figs. 25 through 28 for the 4 locations with arithmetic means $\geq$ 1 ug/L.

Goolsby and Thurman (1991); Thurman etal (1991); Thurman etal 1992:

The USGS sampled 129 corn and soybean production locations over 10 midwestern states in 1989 (Fig. 29 from figure in the study report). At each location, one cross-sectional composite sample was collected during the first major runoff event following pesticide application. In addition, at many of the locations, one sample was collected in the early Spring prior to pesticide application and in the Fall at harvest several months after application. Alachlor concentrations in the pre-application and Fall samples were generally much less than 1 ug/L (Table 11). However, concentrations in the post-application samples exceeded 4 times the alachlor MCL (8 ug/L) at 10 locations in Iowa, 4 locations in Illinois, 4 locations in Indiana, and 2 locations in Ohio (Table 11; Figs. 30 through 33). Approximately 1/3 of the sampling locations were re-sampled pre- and post-application during 1990.

The results of the 1990 sampling program were reported to be comparable to those of the 1989 program.

Goolsby etal 1991:

The USGS sampled 8 locations within the Mississippi drainage basin from April 1991 through March 1992 (Fig 34 from Fig. 1 of the study report). Cross-sectional composite samples were collected biweekly during May through July and weekly during other months.

The April 1991 through January 1992 data are summarized in Table 12. None of the 4/91-1/92 alachlor arithmetic mean concentrations for the 8 locations sampled exceeded the alachlor MCL of 2 ug/L. The highest 4/91-1/92 alachlor arithmetic mean concentration (0.42 ug/L for the Platte River at Louisville NE) was less than 25% of the MCL. The annual arithmetic means could not be computed by EFGWB because the February through March 1992 were not yet available for review. However, since pre-application alachlor concentrations are generally the lowest of the year, the annual arithmetic means are probably lower than the 4/91-1/92 arithmetic means.

None of the individual concentrations exceeded 4 times the MCL (8 ug/L). The highest observed alachlor concentration (3.6 ug/L in the Platte River at Louisville, NE) was less than 50% of 4 times the MCL.

Time series plots are presented for alachlor in Figures 35 through 37 for the 3 Mississippi Basin sampling locations at which at least one alachlor concentration exceeded the MCL. Alachlor concentrations at the 3 locations peaked at above the MCL in mid to late May, then declined throughout June to close to the pre-application levels of April by July.

Taylor 1992:

Taylor (1992) reported that in the Springs of 1991 and 1992, the Illinois EPA sampled the finished water of the 129 IL water supply systems whose primary sources are surface water. One sample was collected each Spring at each system. Collection times varied but were all within April to July of each year.

In April to July 1991, alachlor was detected (detection limit <=0.02 ug/L) in 67 of the 129 systems sampled. However, alachlor concentrations exceeded 1 ug/L in only 3 samples and none exceeded the alachlor MCL of 2 ug/L. The highest observed concentrations were 2 ug/L collected on 5/28/91 from the Greenfield system, 1.5 ug/L collected on 5/29/91 from the Gillepsie system, and 1.2 ug/L collected on 6/5/91 from the Mount Carmel system.

In April to July of 1992, alachlor was detected in 22 of the 128 systems sampled. None of the concentrations exceeded the MCL of 2 ug/L and none exceeded 1 ug/L.

Table 1) Community Water Systems sampled, their primary sources of water, and population served (Lauer etal 1986).

System	Source	Population Served
Bethany, MO	Old L./New L.	3090
Blanchester, OH	Whiteacre Run/Stonelick Cr.	3750
Breese, IL	Shoal Creek	4095
Charleston, IL	Embarrass River	18162
Clarinda, IA	Nodaway River	5458
Columbus, OH	Scioto River	250,000
Davenport, IA	Mississippi R.	133,264
Decatur, IL	Decatur Lake	91,018
Greenville, NC	Tar River	37,000
Kankakee, IL	Kankakee River	56,232
Lexington, MO	Missouri River	5356
Marion, IL	Crab Orchard Lake	14,016
Michigan City, IN	Lake Michigan	36,250
Monroe, MI	Lake Erie	23,531
Mt. Vernon, IN	Ohio River	7610
Muncie, IN	White River	80,000
Piqua, OH	Miami River	21,500
Quincy, IL	Mississippi R.	48,000
Richmond, IN	Whitewater River	41,260
Roanoke Rapids, N	Roanoke River	48,000
Toledo, OH	Lake Erie	388,000
Univ. of Iowa	Iowa River	8560
Wyaconda, MO	Wyaconda River	356
Ypsilanti, MI	Huron River	24,031

Table 2) Alachlor maximum concentrations, arithmetic means, and concentration distributions for surface water source raw (top line) and finished (bottom line) water of 24 community water systems sampled 4/85-1/86. The concentration distributions of alachlor are with respect to its detection limit (0.2 ug/L), 1 ug/L, its MCL (2 ug/L), and 4 times its MCL (8 ug/L). Maximum concentrations exceeding 8 ug/L (4 times the MCL) and means exceeding the MCL of 2 ug/L are shaded. Data are from Lauer etal (1986).

System	Source	Alachlor Maximum (ug/L)	Alachlor Ar. Mean (ug/L)	Alachlor Concentration Distribution C<=0.2	0.2<C<=1	1<C<=2	2<C<=8	C>8
Bethany, MO	Old L./New L.	0.2	0.2	43	0	0	0	0
		0.2	0.2	43	0	0	0	0
Blanchester, OH	Whiteacre Run/Stone	1.26	0.36	31	8	3	0	0
		1.1	0.34	31	9	2	0	0
Breese, IL	Shoal Creek	4.57	0.51	33	8	2	2	0
		4.45	0.49	29	11	4	1	0
Charleston, IL	Embarrass River	0.2	0.2	43	0	0	0	0
		0.2	0.2	43	0	0	0	0
Clarinda, IA	Nodaway River	0.2	0.2	42	0	0	0	0
		0.2	0.2	42	0	0	0	0
Columbus, OH	Scioto River	10.72	1.74	15	17	2	8	3
		12.03	1.68	21	11	3	8	2
Davenport, IA	Mississippi R.	0.72	0.22	39	2	0	0	0
		0.35	0.2	40	1	0	0	0
Decatur, IL	Decatur Lake	0.28	0.2	44	2	0	0	0
		0.3	0.21	40	6	0	0	0
Greenville, NC	Tar River	0.26	0.2	43	2	0	0	0
		0.28	0.2	43	2	0	0	0
Kankakee, IL	Kankakee River	0.85	0.26	32	12	0	0	0
		0.79	0.25	34	10	0	0	0
Lexington, MO	Missouri River	0.84	0.25	35	6	0	0	0
		0.59	0.22	36	5	0	0	0
Marion, IL	Crab Orchard Lake	0.2	0.2	44	0	0	0	0
		0.2	0.2	44	0	0	0	0
Michigan City, IN	Lake Michigan	0.2	0.2	45	0	0	0	0
		0.2	0.2	45	0	0	0	0
Monroe, MI	Lake Erie	0.2	0.2	43	0	0	0	0
		0.2	0.2	43	0	0	0	0
Mt. Vernon, IN	Ohio River	1.46	0.26	37	5	1	0	0
		1.21	0.24	37	5	1	0	0
Muncie, IN	White River	2.54	0.44	30	10	2	3	0
		2.86	0.43	27	14	1	3	0
Piqua, OH	Miami River	1	0.25	39	4	0	0	0
		0.63	0.22	39	4	0	0	0
Quincy, IL	Mississippi R.	0.54	0.22	37	5	0	0	0
		0.7	0.24	37	5	0	0	0
Richmond, IN	Whitewater River	3.49	0.82	21	9	6	6	0
		3.55	0.83	22	8	6	6	0
Roanoke Rapids, N	Roanoke River	0.2	0.2	44	0	0	0	0
		0.2	0.2	44	0	0	0	0
Toledo, OH	Lake Erie	0.2	0.2	41	0	0	0	0
		0.2	0.2	41	0	0	0	0
Univ. of Iowa	Iowa River	1.71	0.3	38	2	3	0	0
		1.83	0.31	37	4	2	0	0
Wyaconda, MO	Wyaconda River	0.29	0.21	36	5	0	0	0
		0.2	0.2	41	0	0	0	0
Ypsilanti, MI	Huron River	0.2	0.2	37	0	0	0	0
		0.2	0.2	37	0	0	0	0

RIN 2556-94 ACETOCHLOR REVIEW (121601)

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Table 4) Alachlor maximum concentrations, arithmetic means, and concentration distributions for the surface source finished water of 30 community water systems sampled 4/86-9/86. The concentration distributions of Alachlor are with respect to its detection limit (0.20 ug/L), 1 ug/L, its MCL (2 ug/L) and 4 times its MCL (8 ug/L). Maximum concentrations exceeding 8 ug/L (and 4 times the MCL) and arithmetic mean concentrations exceeding the MCL of 2 ug/L are shaded. Data from Smith etal (1987).

System	Source	Alachlor Maximum (ug/L)	Alachlor Ar. Mean (ug/L)	Alachlor Concentration Distribution C<=0.2	0.2<C<=1	1<C<=2	2<C<=8	C>8	
Appleton, WI	Lake Winnebago	0.2	0.2	19	0	0	0	0	
Bowling Green, OH	Maumee River	5.21	1.25	8	6	4	5	0	
Caledonia, OH	Olentangy River	9.48	1.41	13	3	1	5	1	
Carlinville, IL	Lake Carlinville	0.2	0.2	19	0	0	0	0	
Columbus, OH	Scioto River	3.45	1	6	10	2	6	0	
Creston, IA	12 Mile Reservoir	0.2	0.2	22	0	0	0	0	
Crewe, VA	Crystal Lake	0.2	0.2	20	0	0	0	0	
Dearborn, MI	Unspecified Lake	1.12	0.35	12	7	1	0	0	
Delta, OH	Bad Creek	0.2	0.2	21	0	0	0	0	
Eskridge, KS	Lake Wabaunese	0.2	0.2	21	0	0	0	0	
Fort Wayne, IN	St. Joseph River	5.03	1.13	12	5	5	4	0	
Hettick, IL	Lake Treesen	0.2	0.2	21	0	0	0	0	
Iowa City, IA	Iowa River	5.07	1.06	7	9	2	4	0	
Jacksonville, IL	Mauviasterre R.	6.12	2.39	5	8	4	13	0	
Jaratt, VA	Nottaway River	0.2	0.2	21	0	0	0	0	
Jefferson Co., KS	Perry Lake	0.29	0.21	16	4	0	0	0	
Macomb, IL	Spring Lake	1.42	0.36	15	5	2	0	0	
Maysville, OH	Frasier's Quarry	0.2	0.2	20	0	0	0	0	
Olathe, KS	New Olathe Lake	0.51	0.25	15	10	0	0	0	
Ottawa, KS	Maraisdes Cygnes R.	0.2	0.2	19	0	0	0	0	
Plattsburg, MO	Unspecified Lake	0.2	0.2	19	0	0	0	0	
Pomona Lake, KS	Pomona Lake	0.45	0.26	10	9	0	0	0	
Sabetha, KS	Sabetha Lake	0.91	0.4	7	17	0	0	0	
Shelbina, MO	Shelbina Lake	0.3	0.21	18	2	0	0	0	
Shipman, IL	Shipman R./Res.	7.43	0.91	6	39	1	6	0	
Swanton, OH	Swan Creek	0.33	0.21	16	3	0	0	0	
Univ. of IA	Iowa River	5.29	1.16	9	7	2	5	0	
Waterville, OH	Maumee River	5.25	1.08	9	6	3	4	0	
Westerville, OH	Alum Creek	1.25	0.26	19	1	1	0	0	
White House, TN	Old Hickory Lake	0.2	0.2	21	0	0	0	0	
Total Alachlor		9.48	0.54	446 (65.8%)	151 (22.3%)	28 (4.1%)	52 (7.7%)	1 (0.1%)	678

Table 52. Summary of land use and gross erosion rates for Lake Erie Basin tributary watersheds.

(Baker 1988)

Watershed	Cropland %	Pasture %	Forest %	Water %	Other %	Gross Erosion Rate kg/ha/yr
Maumee R.	75.6	3.2	8.4	3.5	9.4	6,840
Sandusky R.	79.9	2.3	8.9	2.0	6.8	8,250
Cuyahoga R.	4.2	43.1	29.1	3.0	20.6	896.*
[illegible] R.	67.1	6.8	9.0	3.0	14.1	9,750
[illegible] Cr.	82.6	0.6	10.0	0.5	6.3	6,860
[illegible] Honey Cr.	89.1	---	7.5	---	3.4	7,060
[illegible]	80.9	2.3	11.8	0.9	4.2	9,540
[illegible] Cr.	83.0	---	10.6	1.4	5.0	7,610.**

[illegible] gross erosion rate was calculated using the normal cover factor for forested areas. Due to unusual [illegible]ations of soils and slopes in portions of the Cuyahoga River basin, erosion from this watershed [illegible] much higher than the calculated value.

[illegible]alculation was completed in 1987 by the U.S. Soil Conservation Service and includes the [illegible] of conservation tillage demonstration programs to increase residue levels on the soil.

[illegible] Honey Creek, a second sampler, set to collect samples at one or two hour intervals, is [illegible] used. The second sampler is either triggered automatically when the river stage reaches [illegible] level or is manually triggered during a runoff event. In either case, the time of [illegible] collection is recorded on a printer. During low flow periods analyses are performed [illegible] one sample per day. During storm events, as evidenced either by turbidity in the [illegible] or by high stream discharges, all available samples are analyzed (four or more per [illegible]pending on the station).

[illegible] stations in Michigan and New York, grab samples are collected by local observers. [illegible] River Raisin five samples per week are collected on a year-around basis. For the [illegible] tributaries the local observers are instructed to collect at predetermined intervals [illegible] 2 per week) and to collect extra samples during high flow periods. In general, the [illegible] programs for the tributaries to Lake Ontario have been much less satisfactory than [illegible]tributaries to Lake Erie, because local observers had to decide whether a particular [illegible] was a "large" event for a particular year, and because storms don't always come [illegible] times.

[illegible] samples for Lake Erie Basin sampling stations are collected with automatic [illegible] at the Maumee River, Lost Creek, Sandusky River, Honey Creek, Upper Honey Creek and Rock Creek stations. For the Maumee and Sandusky rivers, ISCO Model 2100 [illegible] containing 24 400 ml glass bottles, are used. In order to obtain sufficient volume

92

Table 6) April 15-August 15 time weighted mean concentrations (TWMCs) and maximum observed concentrations of alachlor in surface water samples collected from 8 tributaries of Lake Erie from 1982 to 1985. April 15-August 15 TWMCs greater than the alachlor MCL of 2 ug/L are shaded along with maximum observed concentrations greater than 8 ug/L (4 times the MCL). Data from Baker (1988).

TWMCs	Maumee River	Sandusky River	Honey Creek	Rock Creek	UHoney Creek	Lost Creek	Raisin River	Cuyahoga River
1983	1.046	0.508	1.381	0.525	0.287	2.348	0.54	0.09
1984	1.688	1.206	2.062	0.24	0.274	1.657	0.754	0.092
1985	0.738	2.933	3.324	0.882	0.399	0.104	1.603	0.021

Maximums	Maumee River	Sandusky River	Honey Creek	Rock Creek	UHoney Creek	Lost Creek	Raisin River	Cuyahoga River
1982	9.266	18.2	74.99			18.46	8.163	0.603
1983	7.485	4.924	8.871	11.88	8.688	34.44	8.522	1.164
1984	17.64	8.754	22.01	7.137	0.817	31.84	4.837	0.336
1985	5.64	26.31	27.06	20.19	2.25	1.61	8.76	0.38

Table 5 Listing of tributary monitoring stations, watershed areas, mean annual discharges, and, for the 1982-1985 water years, the water year discharges and the number of nutrient and pesticide samples analyzed (BAKER 1988)

Station USGS No.	Area Km^2 (Mean Annual Discharge, $10^6 m^3$)	Water Year	USGS Annual Discharge $10^6 m^3$	Samples Analyzed Nutrients	Samples Analyzed Pesticides
Maumee R. 04193500	16,395 km^2 (4,422)	1982	7,107	479	53
		1983	4,748	546	62
		1984	5,878	482	88
		1985	4,365	454	56
Sandusky R 04198000	3,240 km^2 (891.3)	1982	1,390	469	51
		1983	649.6	448	58
		1984	1,940	441	79
		1985	769.8	502	82
Cuyahoga R. 04208000	1,831 km^2 (738)	1982	919.8	447	24
		1983	919.9	475	25
		1984	1,030	437	20
		1985	921.7	502	29
Raisin R. 04176500	2,699 km^2 (650.2)	1982	925.3	223	25
		1983	874.4	312	32
		1984	753.0	313	43
		1985	816.7	310	31
Honey Cr. 04197100	386 km^2 (124.1)	1982	157.7	538	65
		1983	88.72	514	68
		1984	168.2	483	100
		1985	91.43	480	121
Upper Honey Creek 04197020	44.0 km^2 (15.36)	1982	16.58	151	--
		1983	11.06	416	58
		1984	21.07	409	32
		1985	12.07	430	85
Rock Cr. 04197170	83.0 km^2	1983	--	434	46
		1984	43.13	522	87
		1985	19.83	540	143
Lost Creek Trib. 04185440	11.3 km^2	1982	6.799*	518	51
		1983	5.175*	784	51
		1984	4.956*	399	57
		1985	4.840*	457	63
Genesee R. 04232000	6,390 km^2 (2,512)	1982	3,362.3	56	--
		1983	2,431.4	60	--
		1984	3,826.4	43	--
		1985	2,201.0	75	--
Oswego R 04249000	13,209 km^2 (5,991)	1982	6,715.1	52	--
		1983	5,085.3	60	--
		1984	6,748.7	43	--
		1985	4,682.1	75	--
Black R. (NY) 04260500	4,854 km^2 (3,598)	1982	3,976	61	--
		1983	3,570	65	--
		1984	4,295	62	--
		1985	3,802	30	--

* Discharge records subject to revision.

94

Table 8) Alachlor maximums, arithmetic means, and concentration distributions for samples collected 5/84-9/85 or 11/85 from 6 locations in the Cedar River Basin on the Iowa-Minnesota border. The concentration distributions of alachlor were computed with respect to its detection limit (0.1 ug/L), 1 ug/L, its MCL (2 ug/L), and 4 times its MCL (8 ug/L). Maximums greater than 4 times the MCL and means greater than the MCL are shaded. Data are from Squillace and Engberg (1988).

Sampling Location	1984 Alachlor Maximum (ug/L)	1984 Alachlor Ar. Mean (ug/L)	1985 Alachlor Maximum (ug/L)	1985 Alachlor Ar. Mean (ug/L)	Alachlor Concentra Distribution C<=0.1	0.1<C<=1	1<C<=2	2<C<=8	C>8
Cedar R. Floyd	23	3.01	1.5	0.46	10	3	1	1	1
Cedar R. Carville	21	3.1	0.61	0.28	11	4	0	0	2
Shell Rock R.	6.8	0.73	0.18	0.11	14	3	0	1	0
Ced. R. Cedar Falls	21	2.57	0.48	0.26	10	4	0	0	2
Ced.R. Gilbertsvil	17	2.57	0.33	0.14	10	3	0	1	1
Cedar R. Bertram	7.7	1.48	0.24	0.17	13	2	0	3	0

Table 9. Pesticide Subnetwork Stations

Moyer and Cross (1990)

IEPA STATION CODE	STREAM NAME	VERBAL DESCRIPTION
AK 02*	Lusk Creek	Co. Rd. Br., 2.8 mi. SE of Eddyville
ATG 03	M. Fork Saline River	Co. Rd. Br., 2.7 mi. SE of Harrisburg
BE 07	Embarras River	Co. Rd. Br. at N edge of St. Marie
BPJ 07	Salt Fork Vermilion River	Co. Rd. Br., 2.5 mi. N. of St. Joseph
C 19	Little Wabash River	Co. Rd. Br., NE edge of Louisville
D 23*	Illinois River	Marseilles downstream from Nabisco Bld.
DA 06	Macoupin Creek	Rt. 267 Br., 3.5 mi. NW of Kane
DG 01	LaMoine River	U.S. Rt. 24 Br. at Ripley
DG 04	LaMoine River	Rt. 61 Br. at Colmar
DJ 06	Spoon River	Rt. 17 Br., 2 mi. W of Wyoming
DJ 08	Spoon River	Rt. 95, 0.4 mi. NE of Seville
DK 13	Mackinaw River	4 mi. SE of Deer Creek at CO. Rd. Br.
DQ 03	Big Bureau Creek	Rt. 6 Br. near Princeton
DS 07	Vermilion River	Co. Rd. Br., 3 mi. NE of Leonore
E 25	Sangamon River	Rt. 97 Br. near Oakford
E 28	Sangamon River	Co. Rd. Br. (Allerton Park) 4.5 mi. SW of Monticello
EI 02	Salt Creek	Rt. 29 Br., 4 mi. N of Greenview
F 01	Kankakee River	I-55 Br., 3 mi. NW of Wilmington
G 15*	Des Plaines River	Irving Park Rd. Br. at Schiller Park
KCA 01	Bay Creek	Twp. Road Br. at W edge of Nebo
KI 02	Bear Creek	Co. Rd. Br., 2.2 mi. NE of Marcelline
LD 02	Henderson River	Rt. 94 Br., 1 mi. S of Bald Bluff
LF 01	Edwards River	Rt. 17 Br., 2 mi. NE of New Boston
MJ 01	Plum River	U.S. 52 Br. at E edge of Savanna
MN 03	Apple River	U.S. 20 Br., 2 mi. W of Elizabeth
N 11*	Big Muddy River	Rt. 149 Br., 0.7 mi. W of Plumfield
O 08	Kaskaskia River	U.S. Rt. 51 Br. at SE edge of Vandalia
OD 07	Silver Creek	Rt. 460 Br., 2.2 mi. SE of Freeburg
PB 04	Green River	Rt. 82 Br., N of Geneseo
PH 16	Elkhorn Creek	2 mi. NW of Penrose Co. Rd. Br.

* = "Control"

2. Pesticide Selection

The candidate list of pesticides initially considered for the pesticide subnetwork included a total of 58 herbicides and insecticides (see Appendix A). Criteria utilized in selecting pesticides to be monitoring included:

- quantities used statewide
- potential for offsite movement

96

Table 10) Alachlor maximums, arithmetic means, and concentration distributions for surface water samples collected 10/85-10/88 from 30 locations in Illinois. The concentration distributions of alachlor were computed with respect to its detection limit (0.02 ug/L), 1 ug/L, its MCL (2 ug/L), and 4 times its MCL (4 ug/L). Maximums greater than 4 times the MCL and means greater than the MCL are shaded. Data are from Moyer and Cross (1990; Illinois EPA).

Location	1986 Alachlor Maximum (ug/L)	1986 Alachlor Ar. Mean (ug/L)	1987 Alachlor Maximum (ug/L)	1987 Alachlor Ar. Mean (ug/L)	1988 Alachlor Maximum (ug/L)	1988 Alachlor Ar. Mean (ug/L)	Alachlor Concentration Distribution C<=0.02	0.02<C<=	1<C<=2	2<C<=8	C>8
Lusk Creek	0.02	0.02	0.02	0.02	0.02	0.02	19	0	0	0	0
Middle F. Saline R.	1.30	0.26	8.50	1.47	0.08	0.03	10	7	1	0	1
Embarass River	0.97	0.20	0.54	0.20	0.13	0.05	4	14	0	0	0
Salt F. Vermillion R	1.20	0.21	2.10	0.35	0.46	0.10	9	9	1	1	0
Little Wabash River	1.60	0.32	1.40	0.50	0.08	0.05	14	3	2	0	0
Illinois R. (Harbour	1.30	0.36	0.24	0.10	2.10	0.37	8	7	1	1	0
Macoupin Creek	2.30	0.36	0.91	0.17	0.03	0.03	10	10	0	1	0
Lamoine R. (Ripley)	3.20	0.61	1.40	0.23	0.09	0.05	8	11	1	1	0
Lamoine R. (Colmar)	0.75	0.19	0.36	0.09	0.11	0.06	9	11	0	0	0
Spoon R. (Wyoming)	0.37	0.07	0.04	0.03	0.08	0.03	17	4	0	0	0
Spoon R. (Seville)	0.24	0.08	0.22	0.06	0.07	0.03	11	8	0	0	0
Mackinaw River	0.30	0.08	3.50	0.62	0.08	0.03	12	6	0	1	0
Big Bureau Creek	0.85	0.18	0.45	0.12	0.39	0.09	11	9	0	0	0
Vermillion R.	5.30	0.90	1.40	0.34	0.72	0.14	10	6	1	1	0
Sangamon R. (Oakfor)	0.08	0.04	0.45	0.14	0.04	0.02	9	5	0	0	0
Sangamon R. (Montic)	0.90	0.17	0.12	0.04	0.10	0.04	12	9	0	0	0
Salt Creek	0.57	0.14	0.14	0.04	2.50	0.44	12	7	0	1	0
Kankakee River	1.30	0.24	2.20	0.41	0.40	0.11	8	8	1	1	0
Des Plaines River	1.00	0.16	0.06	0.03	0.02	0.02	16	2	0	0	0
Bay Creek	0.44	0.12	2.00	0.34	18.00	3.41	7	10	1	1	1
Bear Creek	2.70	0.50	0.47	0.10	1.80	0.37	8	10	1	1	0
Henderson Creek	1.20	0.20	0.04	0.02	0.32	0.06	13	7	1	0	0
Edwards River	5.60	0.98	0.37	0.09	0.05	0.03	10	9	0	1	0
Plum River	1.60	0.25	5.60	0.95	0.04	0.02	15	2	1	1	0
Apple River	0.46	0.08	0.53	0.11	0.02	0.02	16	3	0	0	0
Big Muddy River	0.32	0.07	0.12	0.04	0.04	0.02	15	4	0	0	0
Kaskaskia River	0.57	0.13	0.07	0.03	0.09	0.03	12	7	0	0	0
Silver Creek	3.50	0.64	3.60	1.08	1.40	0.26	11	4	1	3	0
Green River	0.22	0.09	0.60	0.12	1.60	0.30	7	11	1	0	0
Elkhorn Creek	0.21	0.06	0.16	0.06	0.41	0.09	16	2	0	0	0
	5.60	0.26	5.60	0.26	18.00	0.21	339 (58.9%)	205 (35.7%)	14 (2.4%)	15 (2.6%)	2 (0.3%)

97

Table 11) The maximum, arithmetic mean, and concentration distribution of alachlor with respect to its detection limit (0.05 ug/L), 1 ug/L, its MCL (2 ug/L), and 4 times its MCL (8 ug/L). Values are provided for 3 sampling times (pre-application, post-application, and Fall 1989) collected from up to 142 surface water locations over 10 midwestern states. Maximums greater than 8 ug/L (4 times the MCL) are shaded as our #s of concentrations exceeding 8 ug/L. Data are from Goolsby and Thurman (1991).

Alachlor (Pre-application)	Alachlor Maximum (ug/L)	Alachlor Ar. Mean (ug/L)	Alachlor Concentration Distribution C<=0.05	0.05<C<=1	1<C<=2	2<C<=8	C>8
Iowa	0.19	0.07	7	2	0	0	0
Illinois	0.13	0.06	9	2	0	0	0
Indiana	0.08	0.06	5	2	0	0	0
Kansas	0.05	0.05	2	0	0	0	0
Minnesota	0.11	0.06	4	1	0	0	0
Missouri	0.44	0.16	3	2	0	0	0
Nebraska	0.05	0.05	5	0	0	0	0
Ohio	0.19	0.09	3	1	0	0	0
South Dakota	0.05	0.05	3	0	0	0	0
Wisconsin	0.05	0.05	4	0	0	0	0
Total (Pre-application)		0.07	45	10	0	0	0
			(81.8%)	(18.2%)	(0.0%)	(0.0%)	(0.0%)

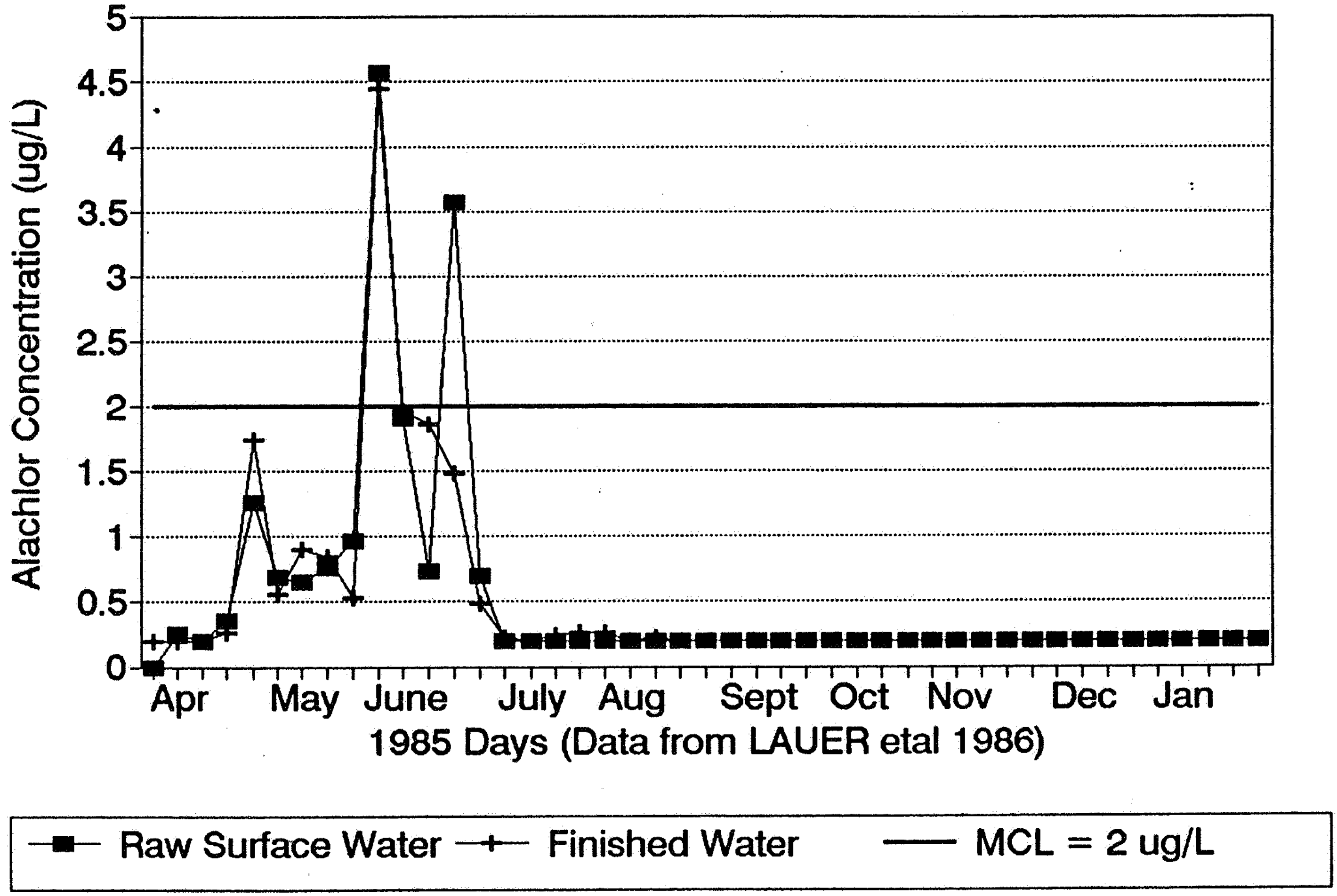
Alachlor (Post-application)	Alachlor Maximum (ug/L)	Alachlor Ar. Mean (ug/L)	Alachlor Concentration Distribution C<=0.05	0.05<C<=1	1<C<=2	2<C<=8	C>8
Iowa	51.30	15.54	0	1	0	4	10
Illinois	47.10	5.70	0	17	2	3	4
Indiana	12.80	3.67	0	7	3	6	4
Kansas	1.60	0.51	2	1	1	0	0
Minnesota	1.10	0.29	5	6	2	0	0
Missouri	0.97	0.76	1	5	1	0	0
Nebraska	4.70	1.67	1	5	3	6	0
Ohio	16.70	3.54	0	7	0	4	2
South Dakota	0.12	0.06	6	2	0	0	0
Wisconsin	4.50	1.03	3	3	1	1	0
Total (Post-application)		3.28	18	54	13	24	20
			(14.0%)	(41.9%)	(10.1%)	(18.6%)	(15.5%)

Alachlor (Fall)	Alachlor Maximum (ug/L)	Alachlor Ar. Mean (ug/L)	Alachlor Concentration Distribution C<=0.05	0.05<C<=1	1<C<=2	2<C<=8	C>8
Iowa	0.40	0.08	23	3	0	0	0
Illinois	0.21	0.06	25	1	0	0	0
Indiana	0.23	0.07	15	5	0	0	0
Kansas	0.05	0.05	6	0	0	0	0
Minnesota	0.05	0.05	14	0	0	0	0
Missouri	0.18	0.08	6	2	0	0	0
Nebraska	0.11	0.06	14	2	0	0	0
Ohio	0.30	0.12	10	3	0	0	0
South Dakota	0.05	0.05	4	0	0	0	0
Wisconsin	0.06	0.05	8	1	0	0	0
Total (Fall)		0.07	125	17	0	0	0
			(88.0%)	(12.0%)	(0.0%)	(0.0%)	(0.0%)

Table 12) The maximum concentrations, arithmetic mean concentrations, and conconcentration distributions of alachlor in surface water samples collected 4/91-1/92 from the Mississippi Basin. The distributions are with respect to its detection limit (0.05 ug/L), 1 ug/L, its MCL (2 ug/L), and 4 times its MCL (8 ug/L). Data are from Goolsby and Coup (1991).

Sampling Location	Alachlor Maximum (ug/L)	4/91-1/92 Ar. Mean (ug/L)	Alachlor Concentration Distribution C<=0.05	0.05<C<=1	1<C<=2	2<C<=8	C>8
White River near Hazelton, IN	3.2	0.29	33	12	3	2	0
Ohio River near Grand Chain, IL	0.4	0.08	26	9	0	0	0
Mississippi R. near Clinton, IA	0.85	0.16	24	20	0	0	0
Illinois R. near Valley City, IL	3	0.39	22	17	2	1	0
Platte River near Louisville, NE	3.6	0.42	21	16	2	3	0
Missouri River near Hermann, MO	0.92	0.18	24	21	0	0	0
Mississippi R. near Thebes, IL	0.85	0.26	12	33	0	0	0
Mississippi R. at Baton Rouge, LA	0.46	0.12	28	22	0	0	0
Alachlor over all sites	3.6	0.24	190	150	7	6	0
			(53.8%)	(42.5%)	(2.0%)	(1.7%)	(0.0%)

Fig. 1) Alachlor in Raw/Finished Surface Water Breese, IN



100

Fig. 2) Alachlor in Raw/Finished Surface Water Columbus, OH

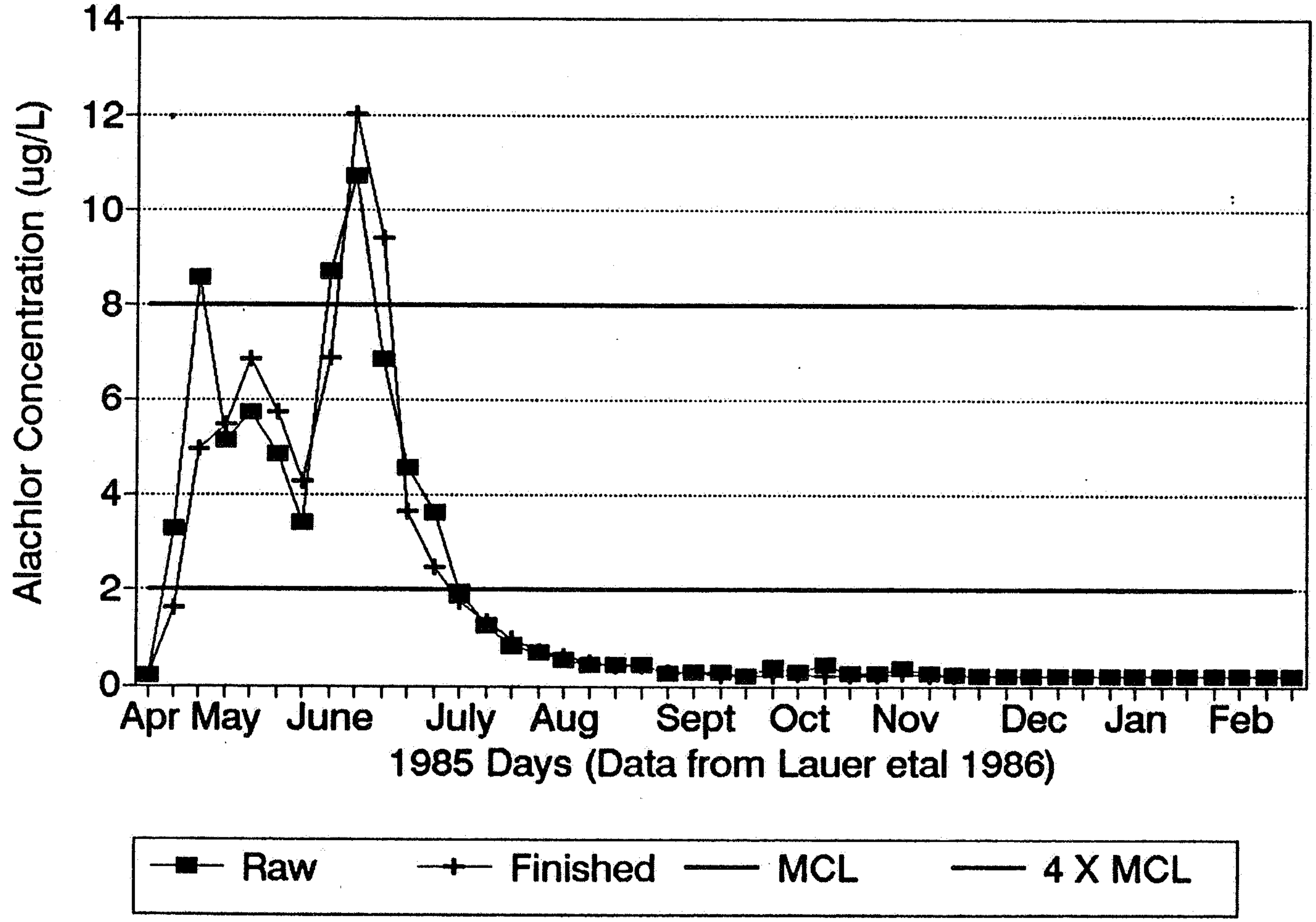


Fig. 3) Alachlor in Raw/Finished Surface Water Muncie, IN

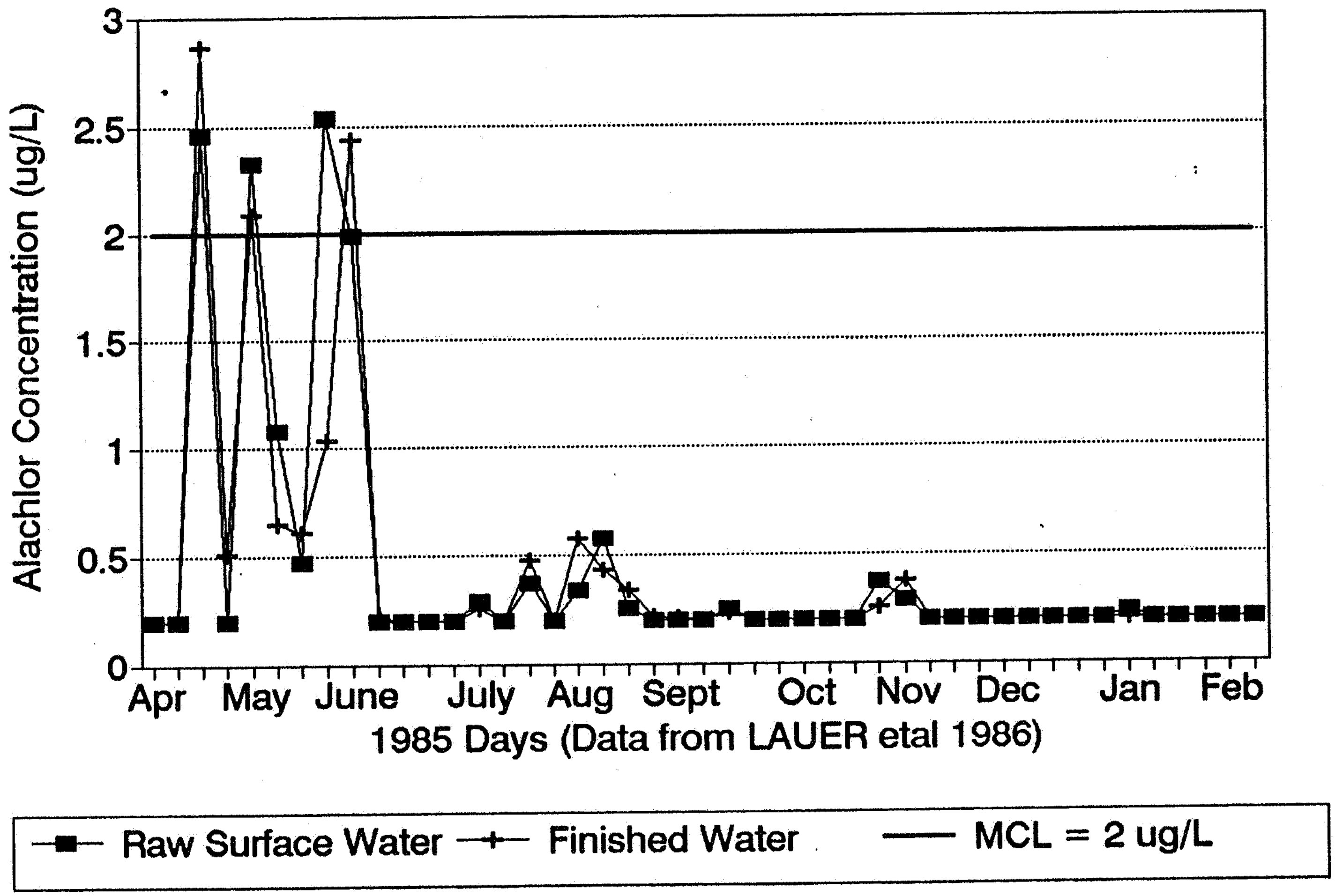
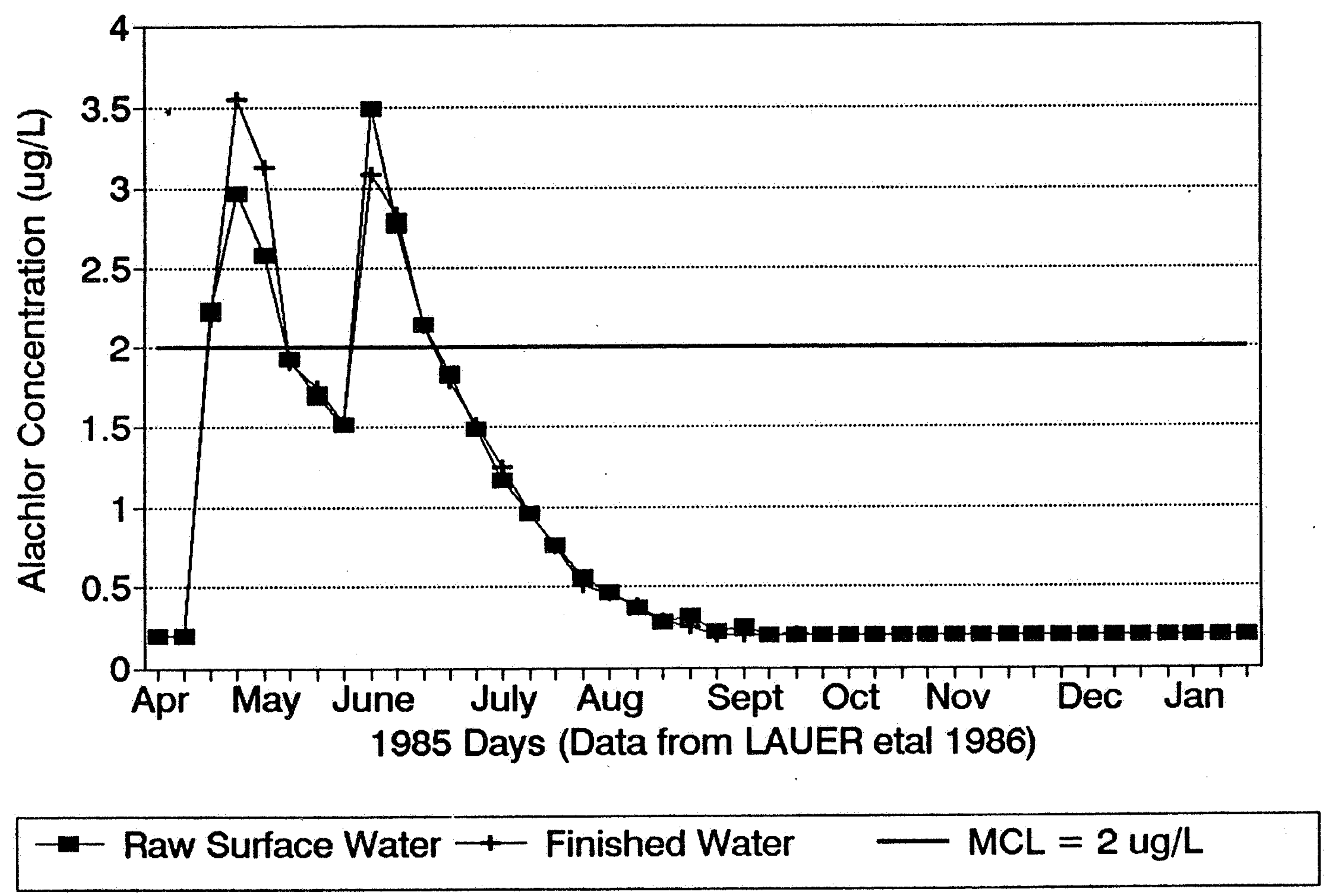


Fig. 4) Alachlor in Raw/Finished Surface Water Richmond, IN



RIN 2556-94 Acetochlor Review (121601)

Page 104 is not included in this copy.

Pages _____ through _____ 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.

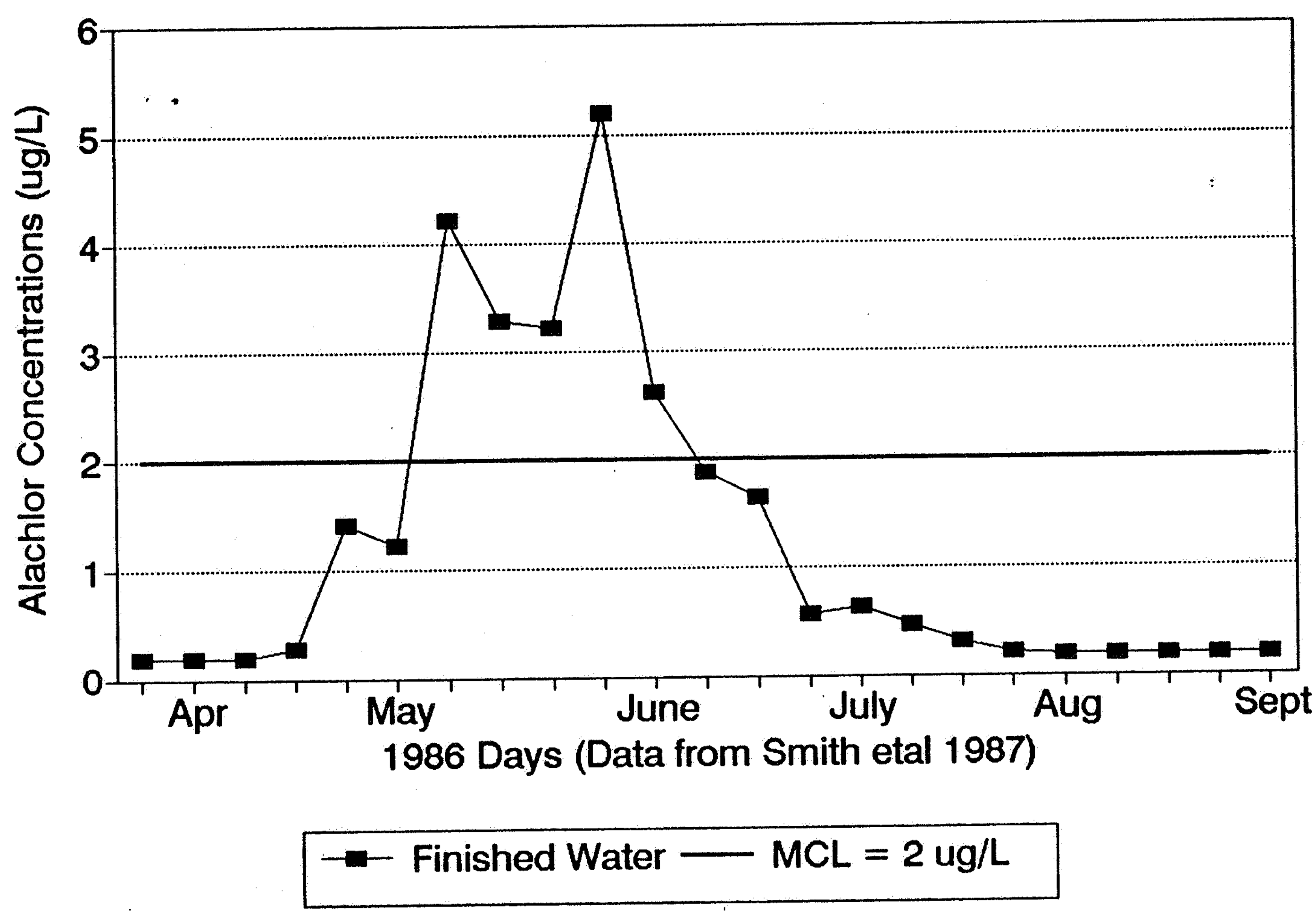
✓ FIFRA registration data.

____ The document is a duplicate of page(s) __________.

____ The document is not responsive to the request.

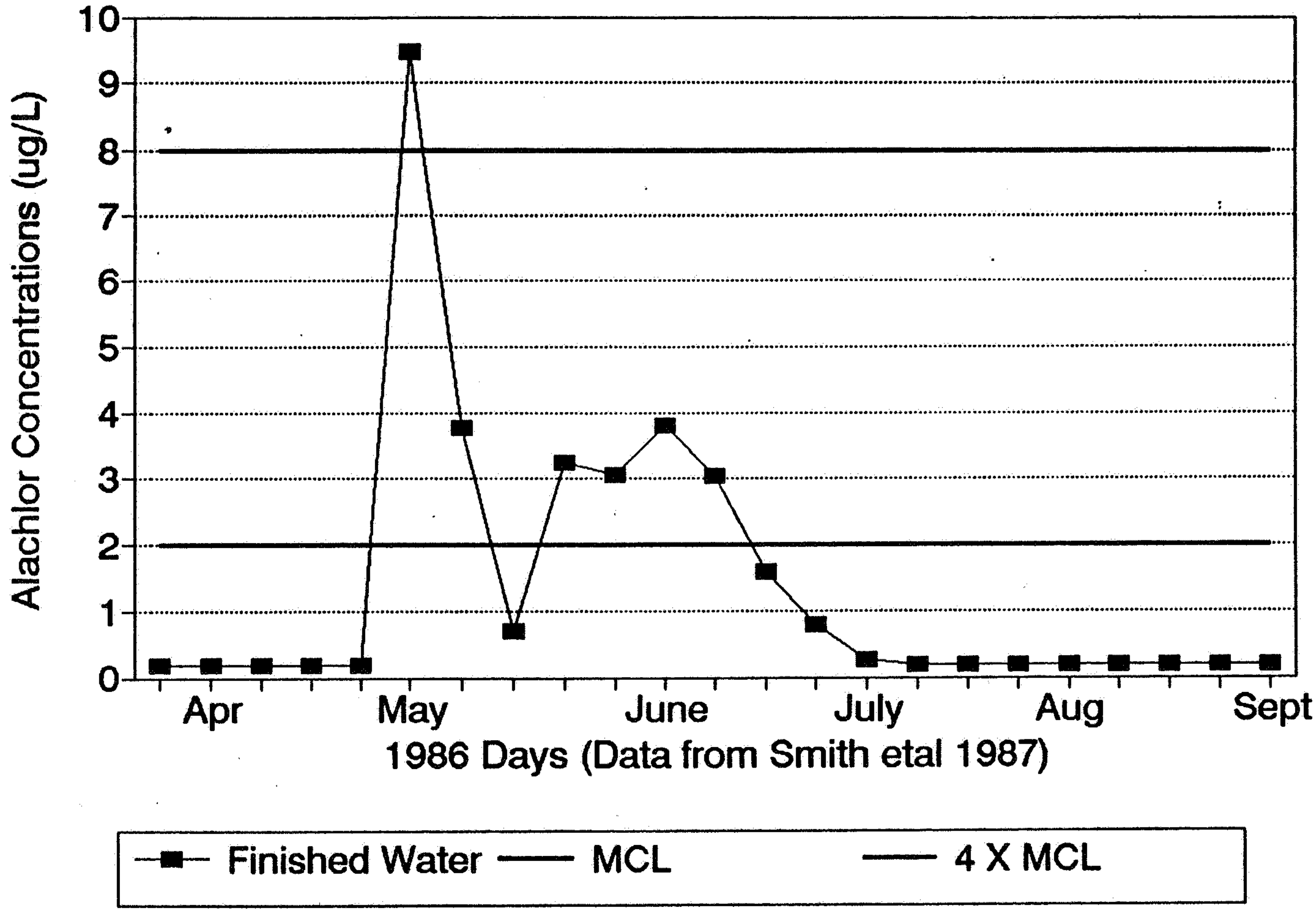
The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

Fig. 6) Alachlor in Finished
Surface Water Bowling Green, OH



105

Fig. 7) Alachlor in Finished Surface Water Caledonia, OH



106

Fig. 8) Alachlor in Finished Surface Water Columbus, OH

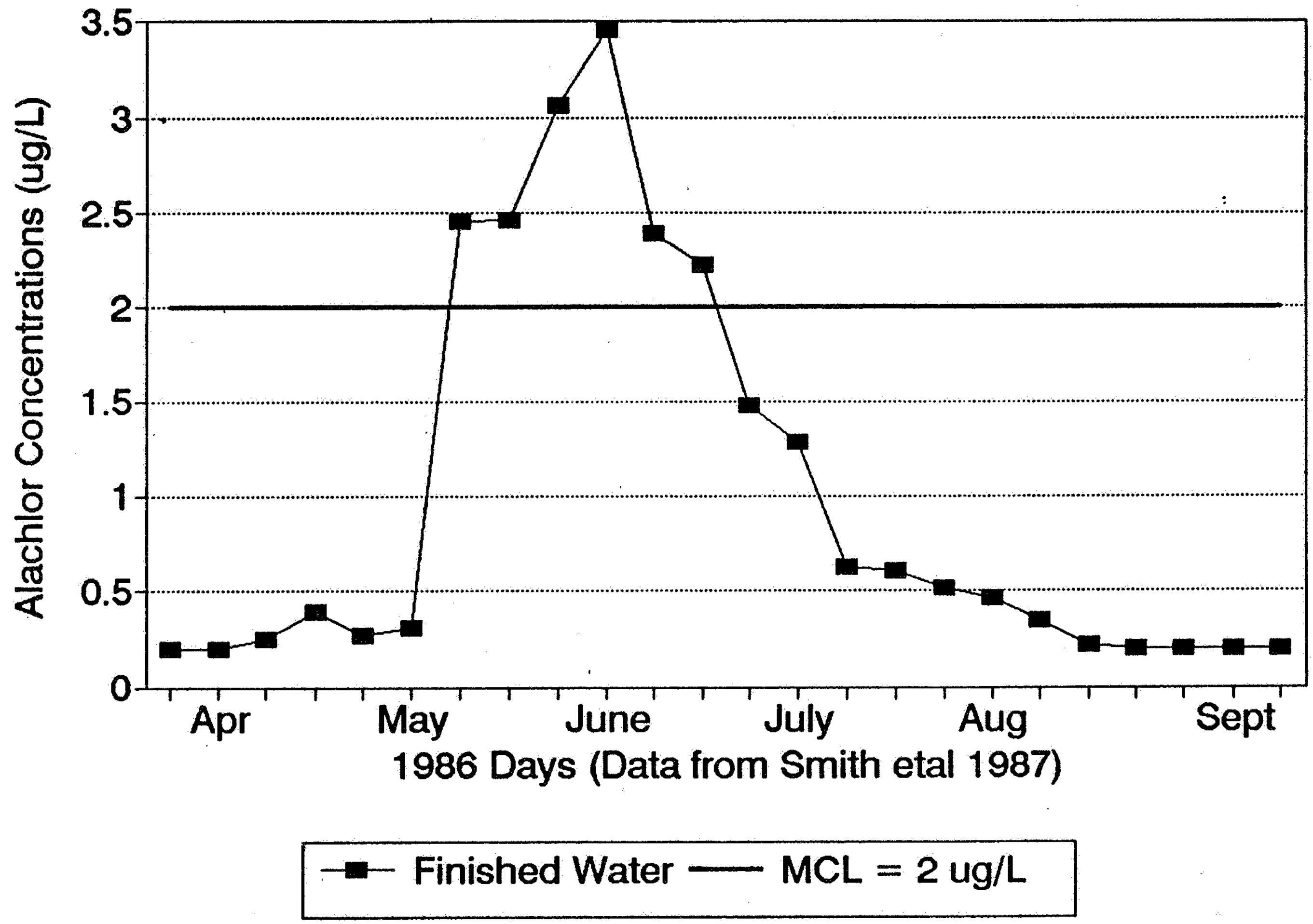


Fig. 9) Alachlor in Finished
Surface Water Fort Wayne, IN

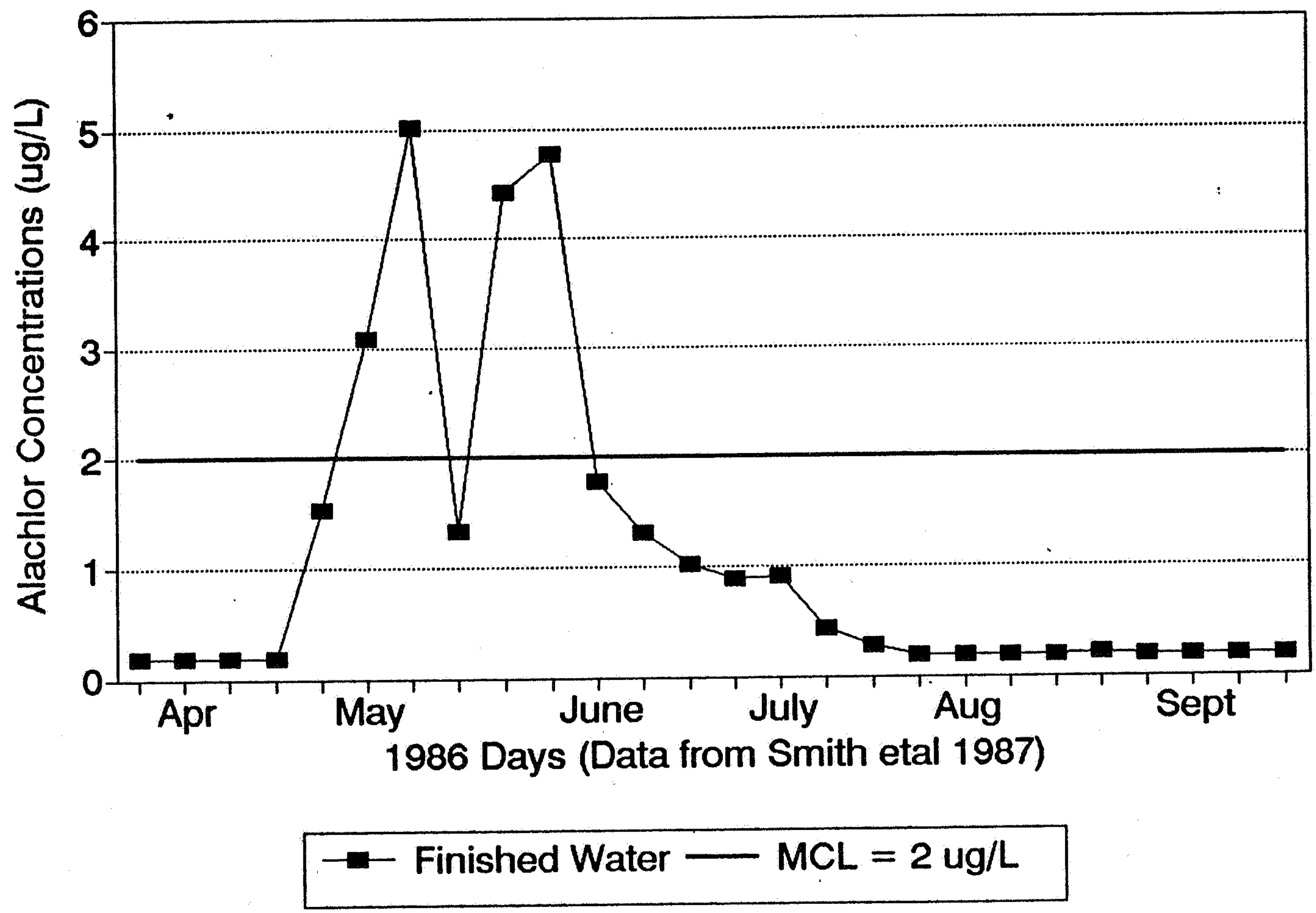


Fig. 10) Alachlor in Finished Surface Water Iowa City, IA

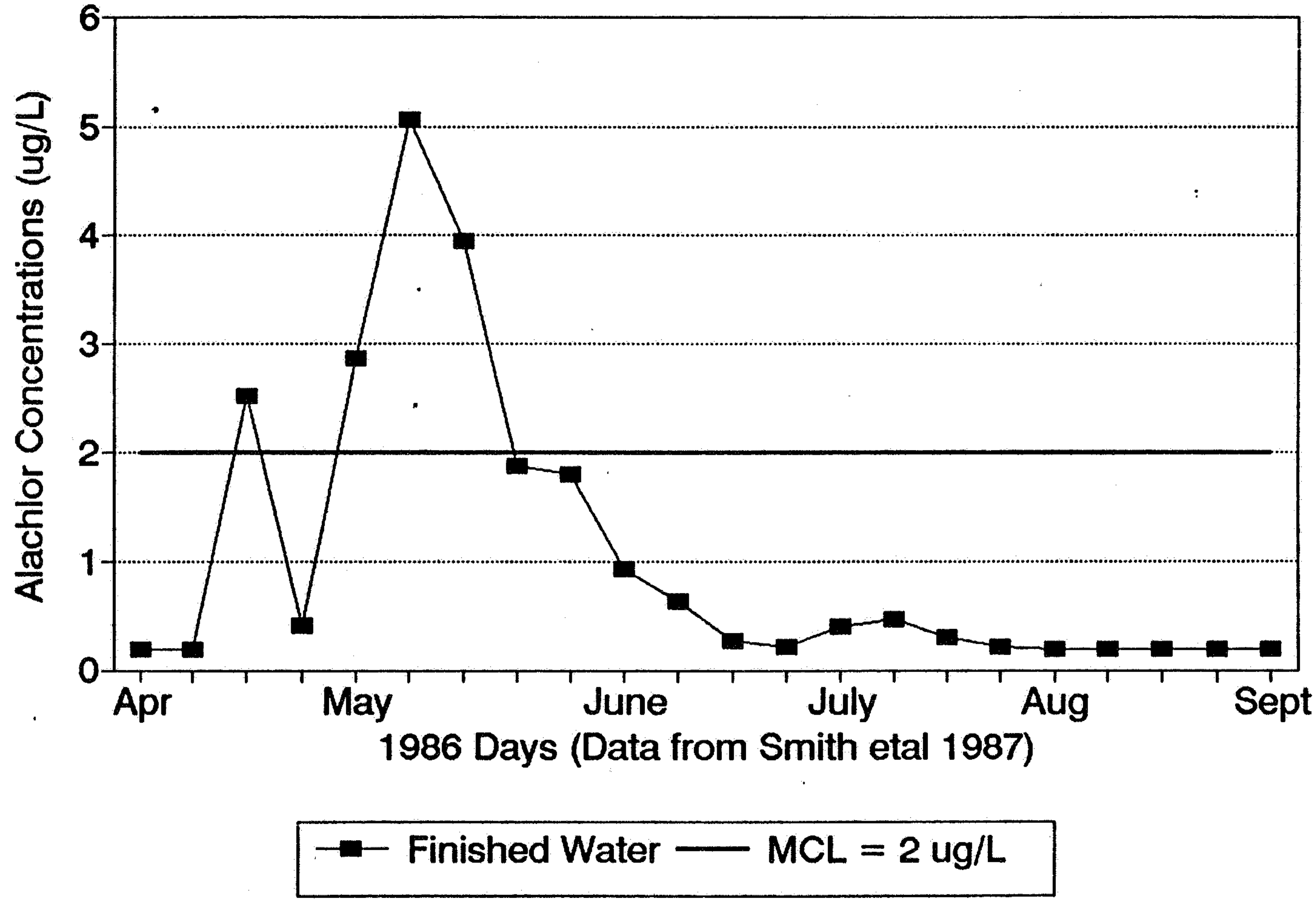


Fig. 11) Alachlor in Finished Surface Water Jacksonville, IL

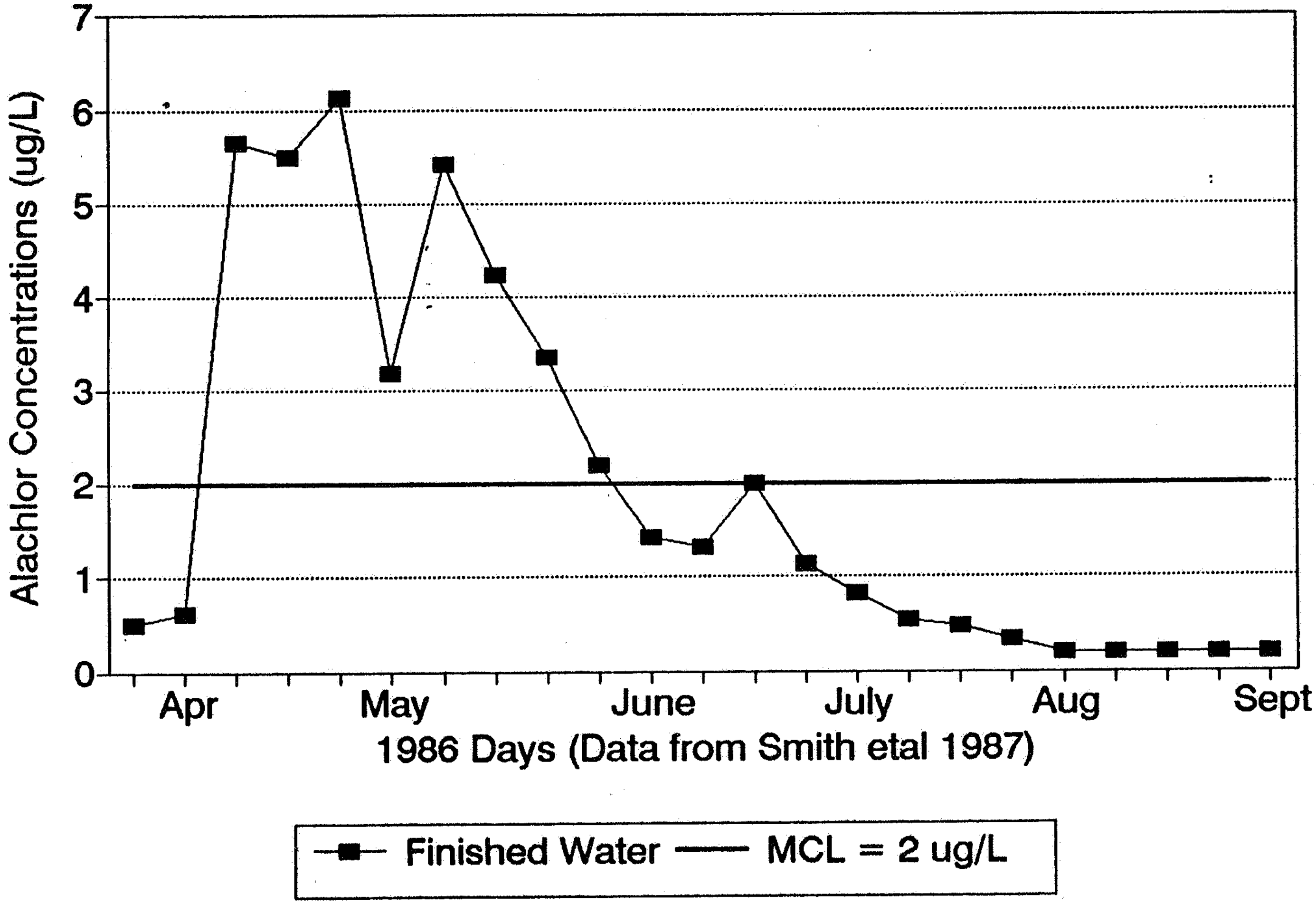


Fig. 12) Alachlor in Finished Surface Water Shipman, IL

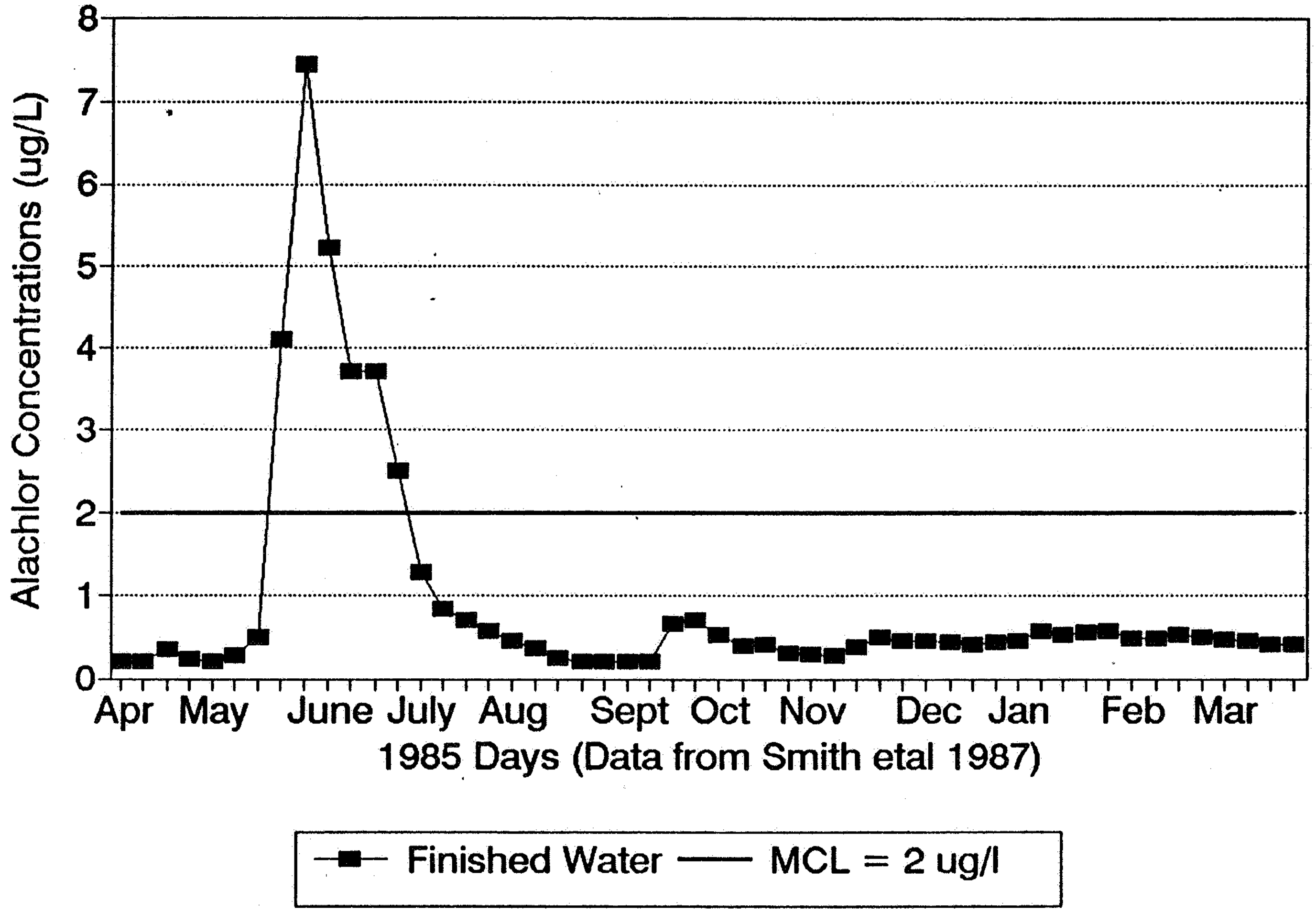


Fig. 13) Alachlor in Finished Surface Water Univ. of Iowa

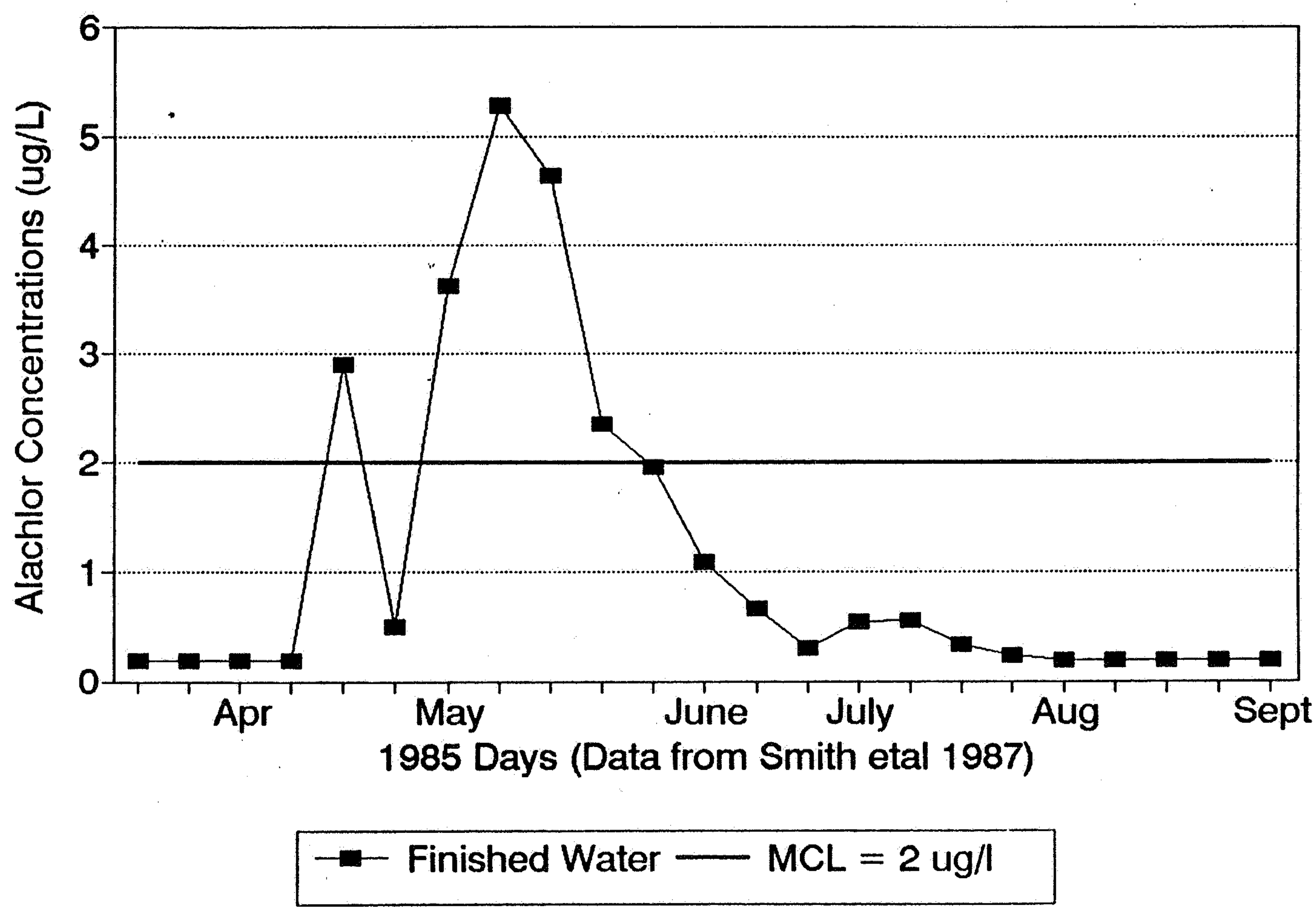
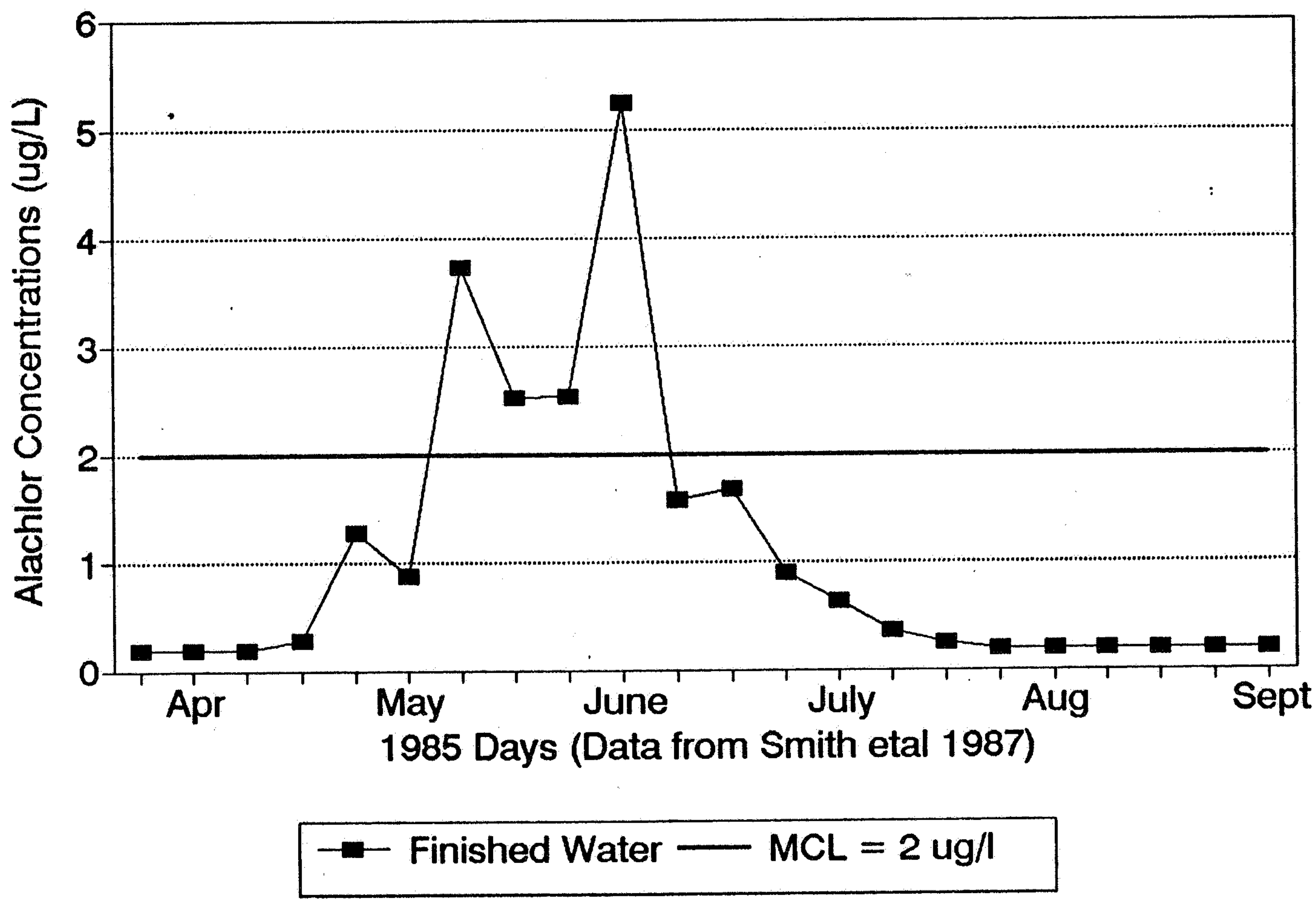
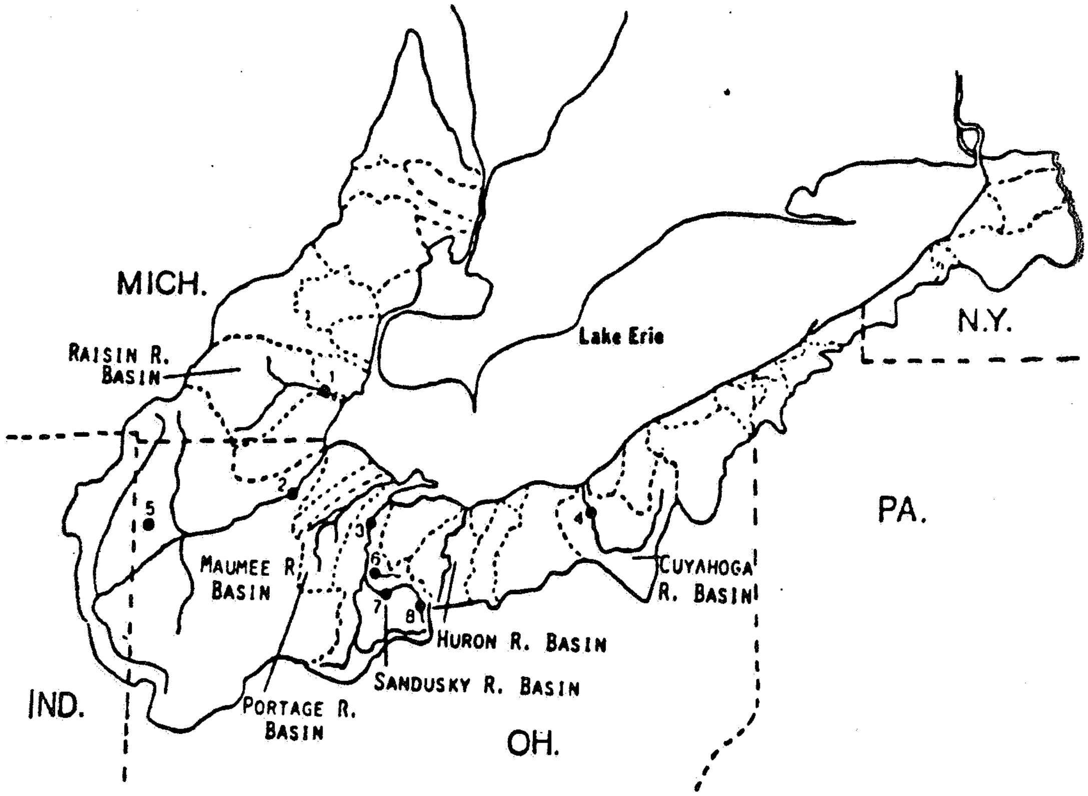


Fig. 14) Alachlor in Finished Surface Water Waterville, OH



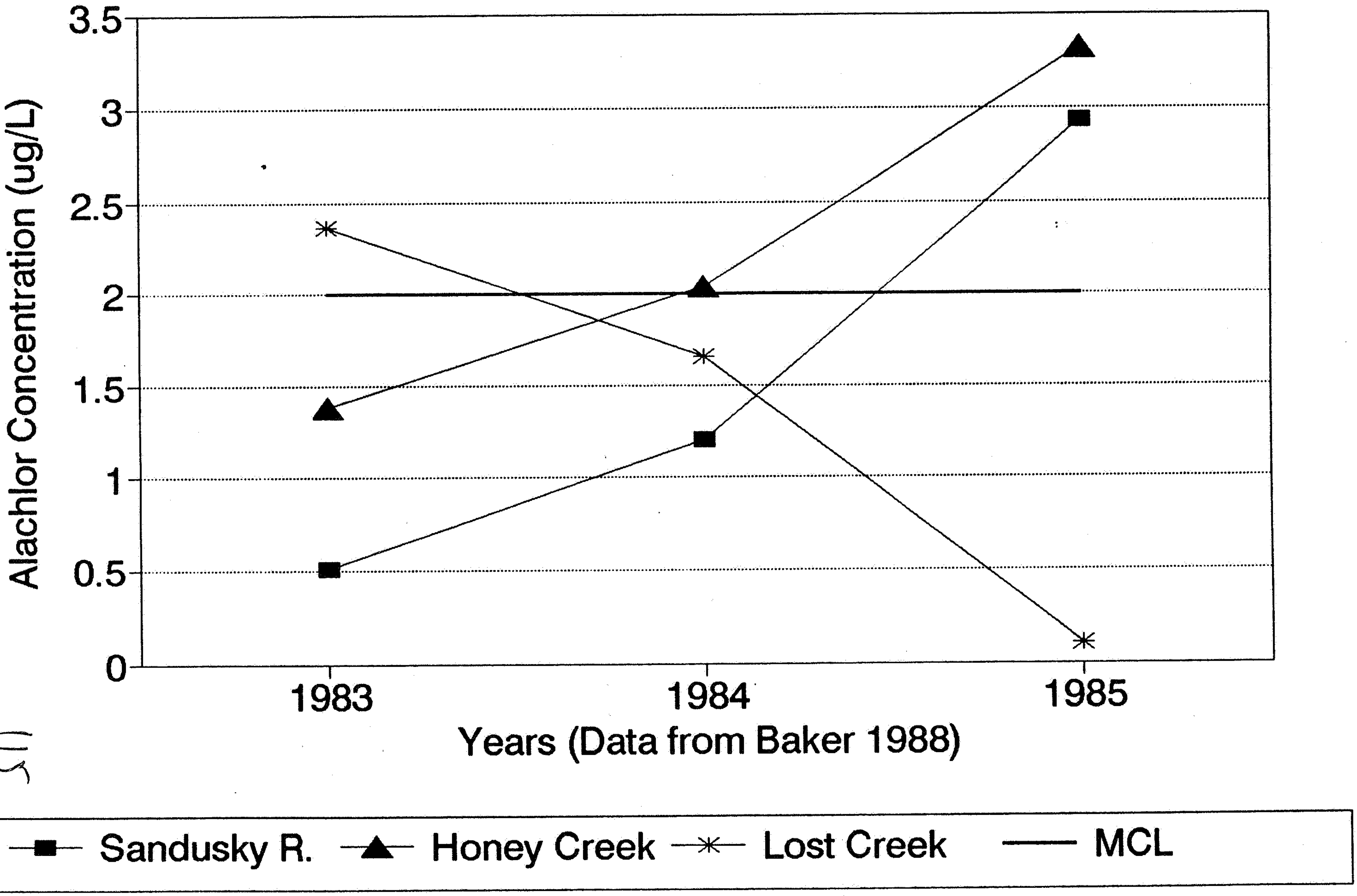


Sampling Locations:

1. River Raisin near Monroe, MI
2. Maumee R. at Bowling Green, OH water intake
3. Sandusky R. near Fremont, OH
4. Cuyahoga R. at Independence, OH
5. Lost Cr. tributary near Defiance, OH
6. Rock Cr. at Tiffin, OH
7. Honey Cr. at Melmore, OH
8. Upper Honey Cr. at New Washington, OH

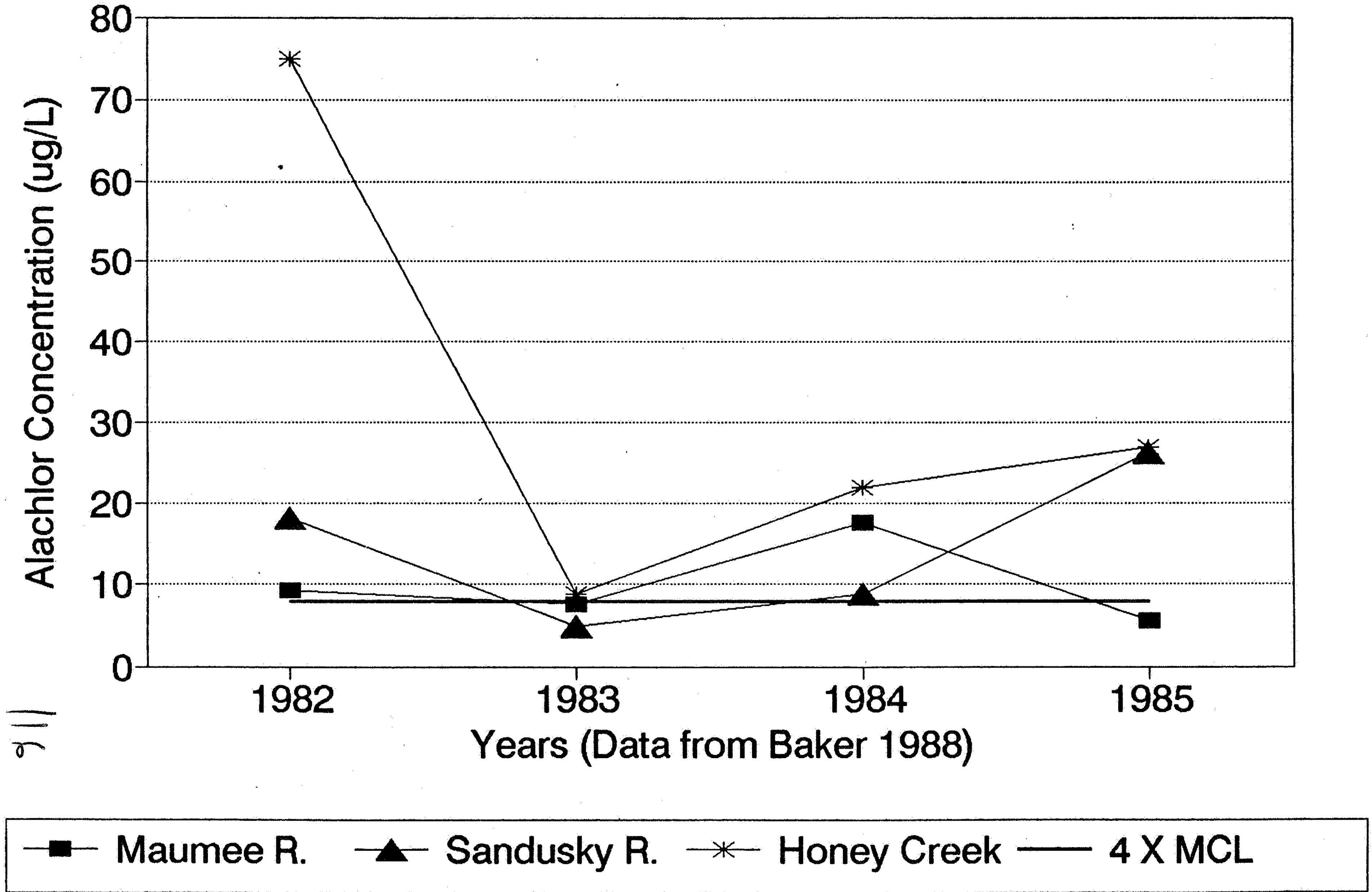
Figure 15 Locations of the tributary monitoring stations in the Lake Erie Basin.
(BAKER 1988)

Fig. 16) Alachlor Apr.15-Aug.15
Time Weighted Mean Concentrs.



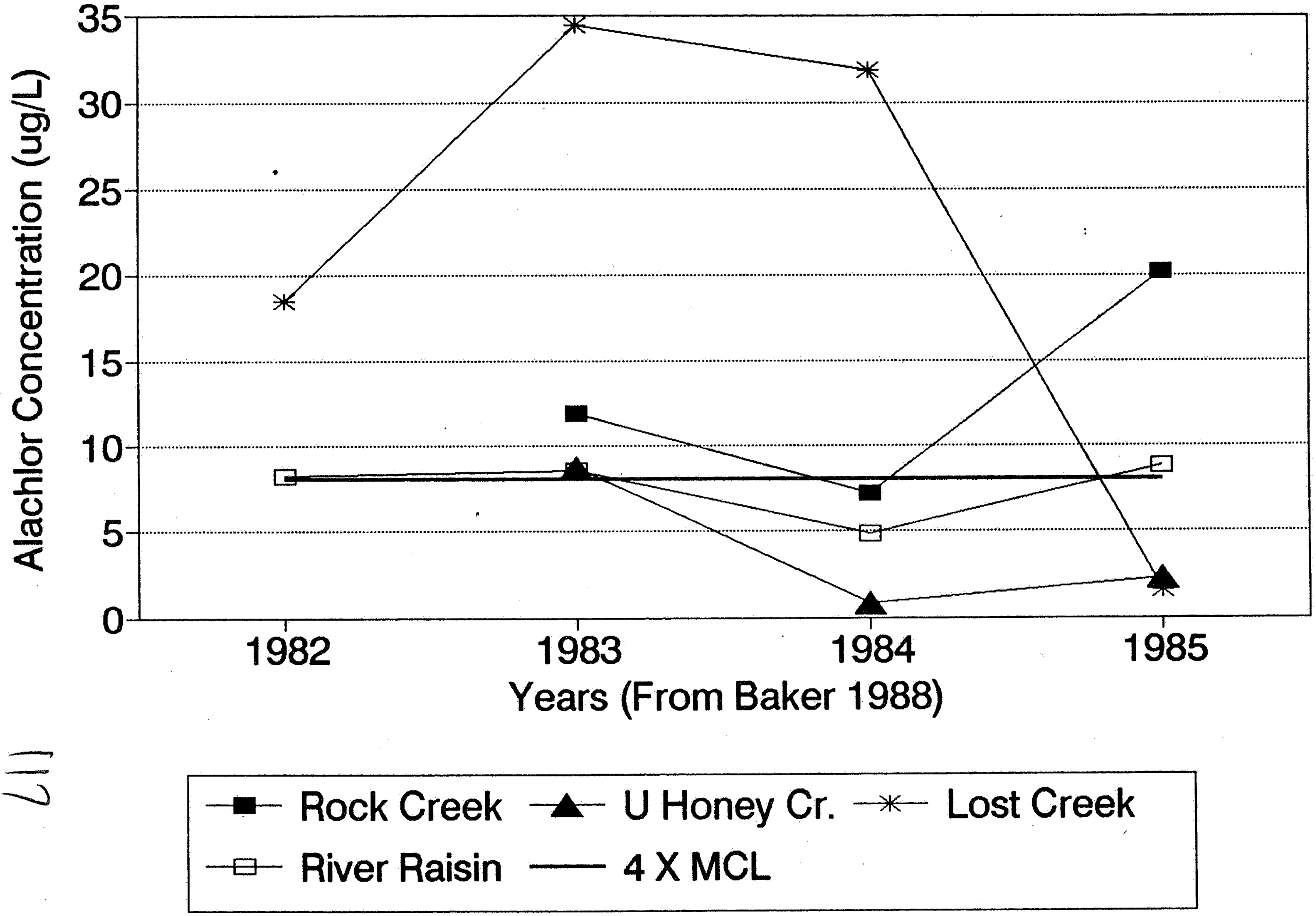
115

Fig. 17) Alachlor Maximum Observed Concentrations



117

Fig. 18) Alachlor Maximum Observed Concentrations



117

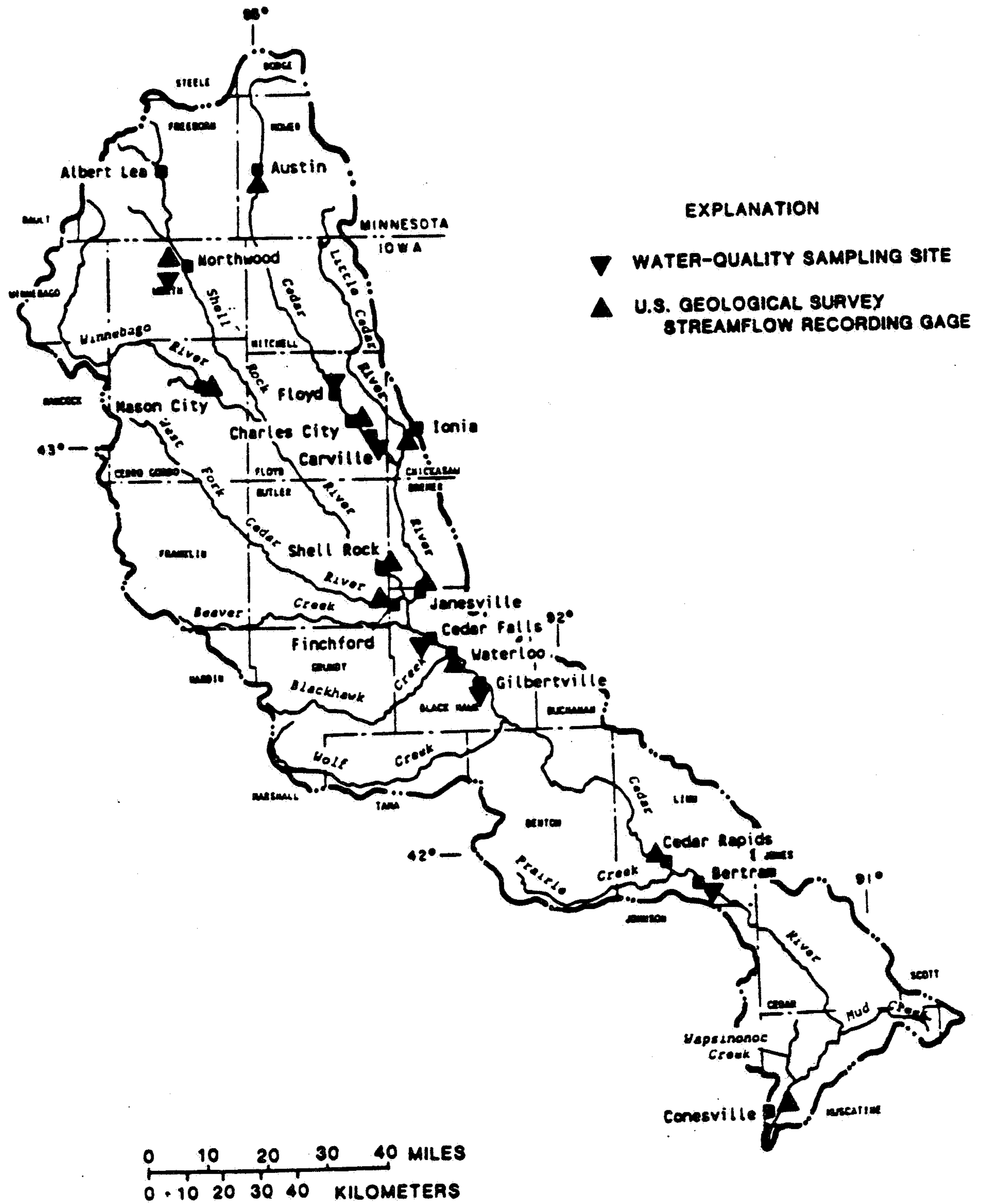


Figure 14.—Location of water-quality sampling sites and U.S. Geological Survey streamflow recording gages.

118

Fig. 20) Alachlor in Cedar R.
at Floyd, IA

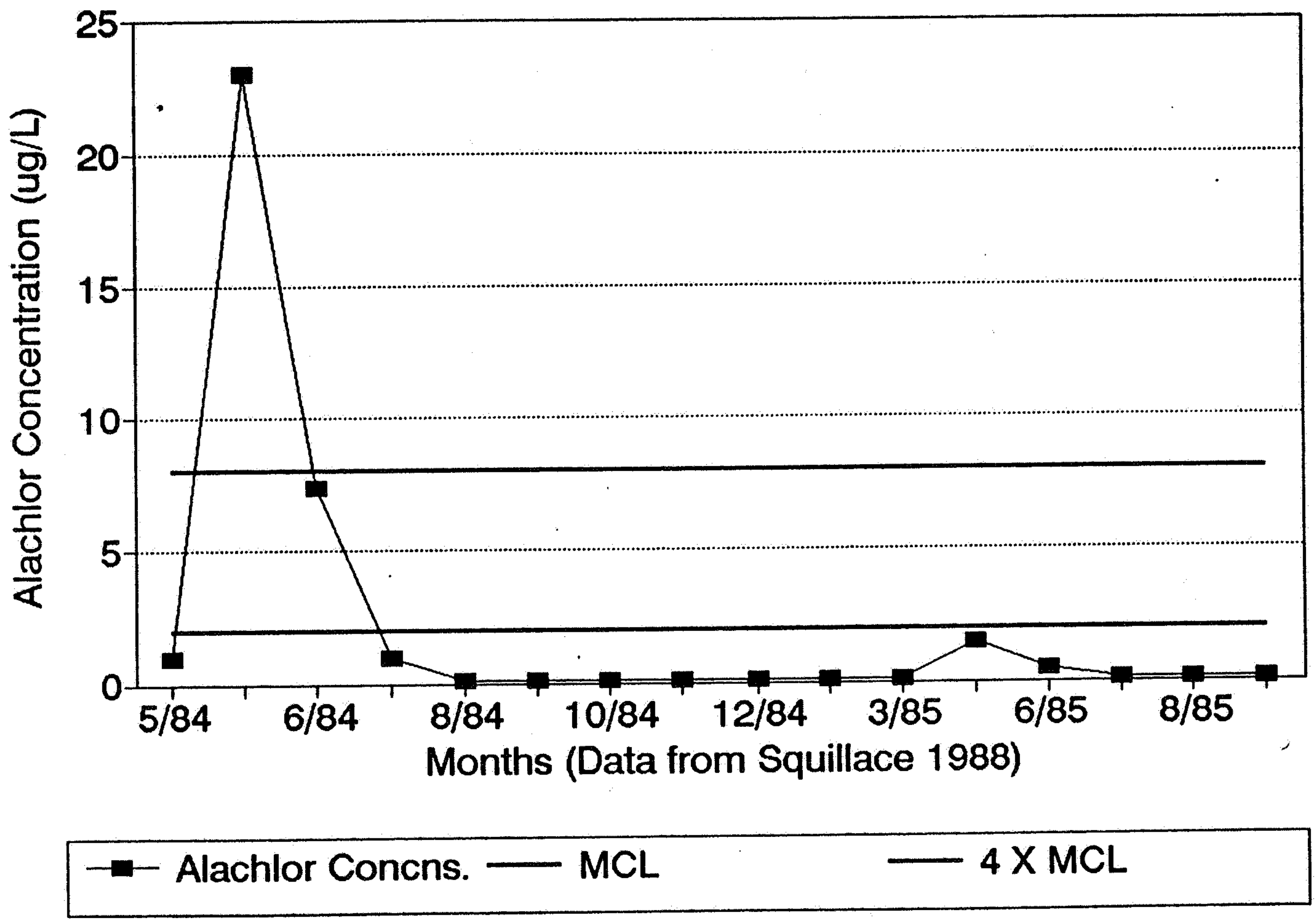


Fig. 21) Alachlor in Cedar R. near Carville, IA

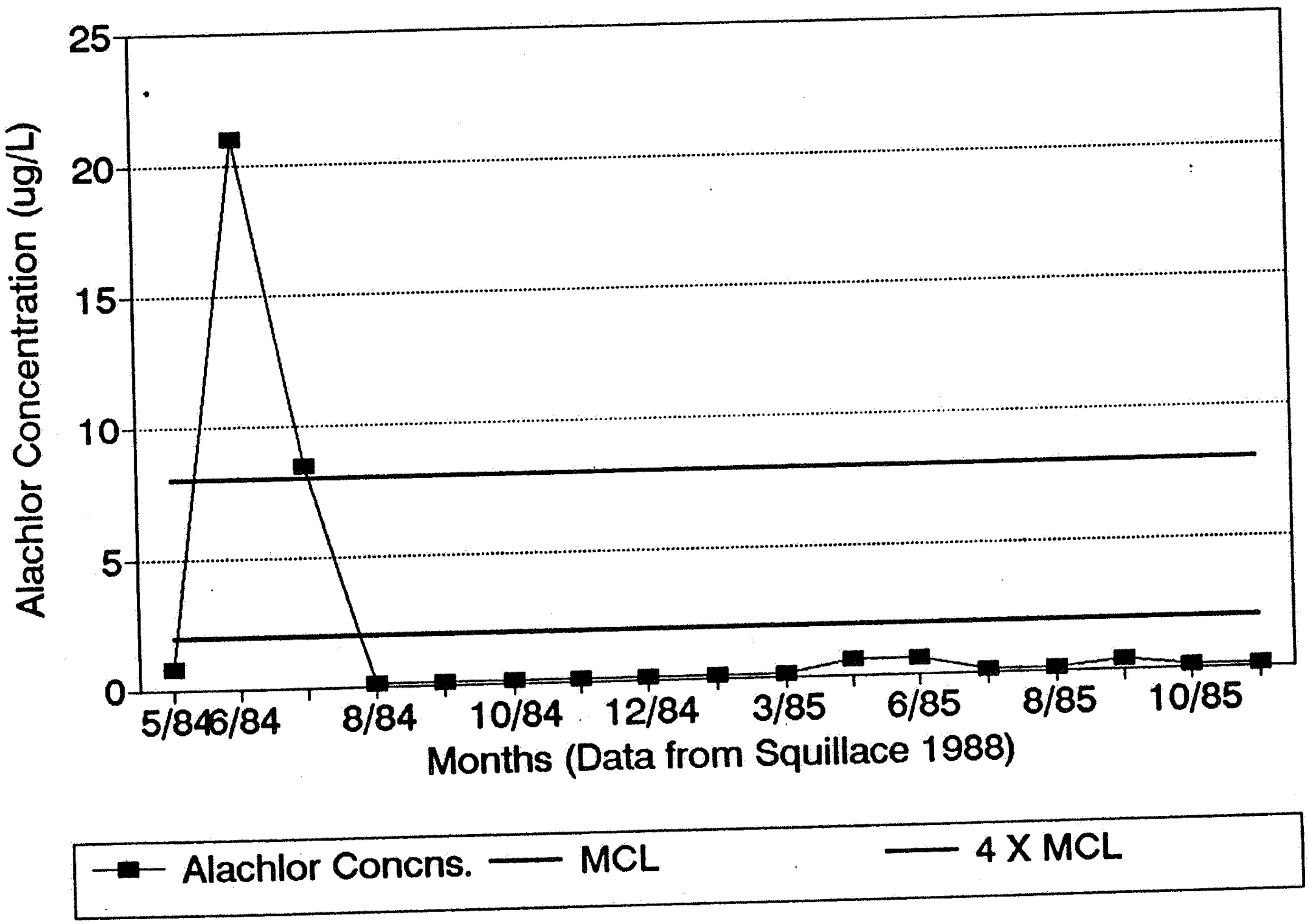


Fig. 22) Alachlor in Cedar R.
at Cedar Falls, IA

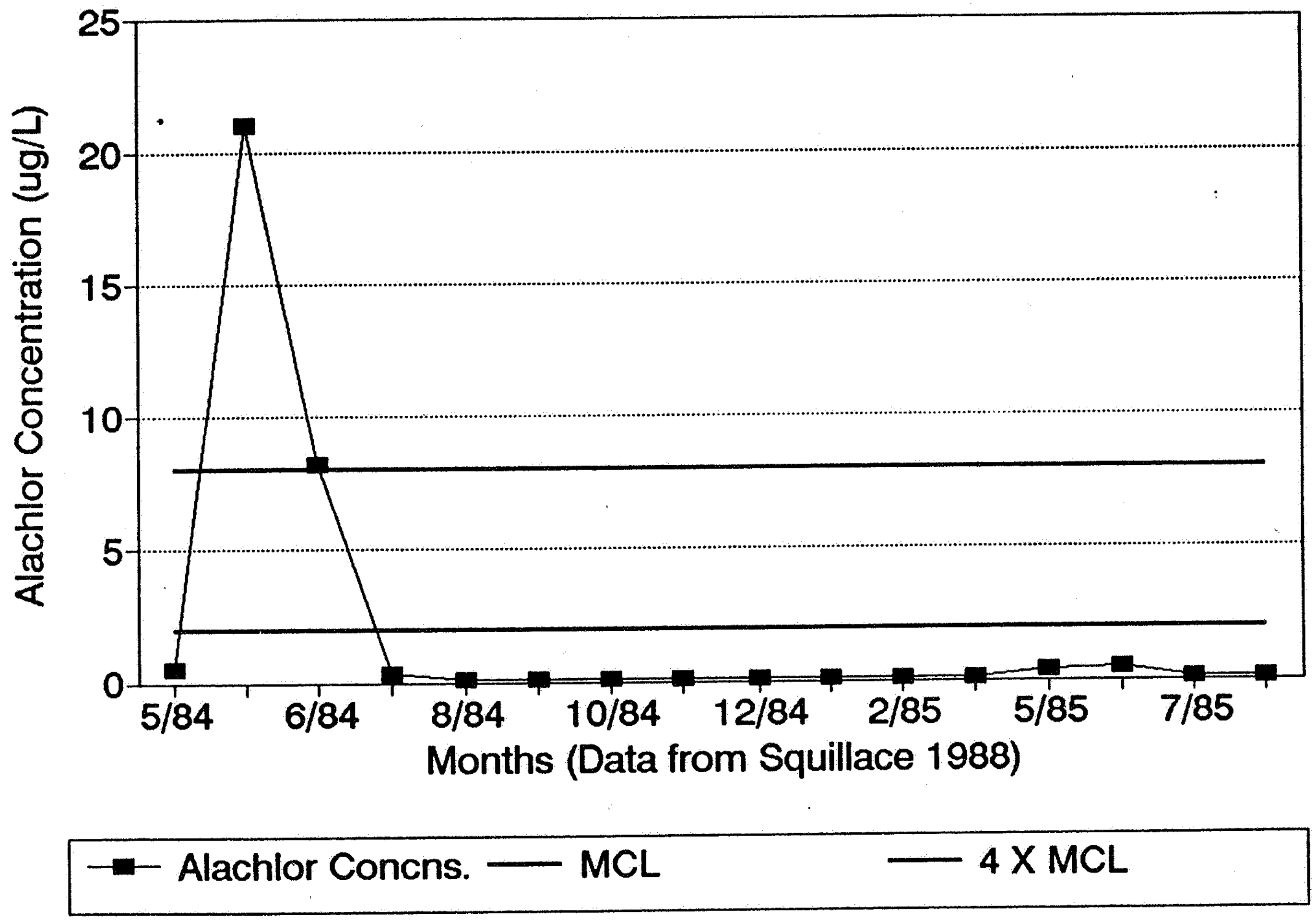


Fig. 23) Alachlor in Cedar R. at Gilbertville, IA

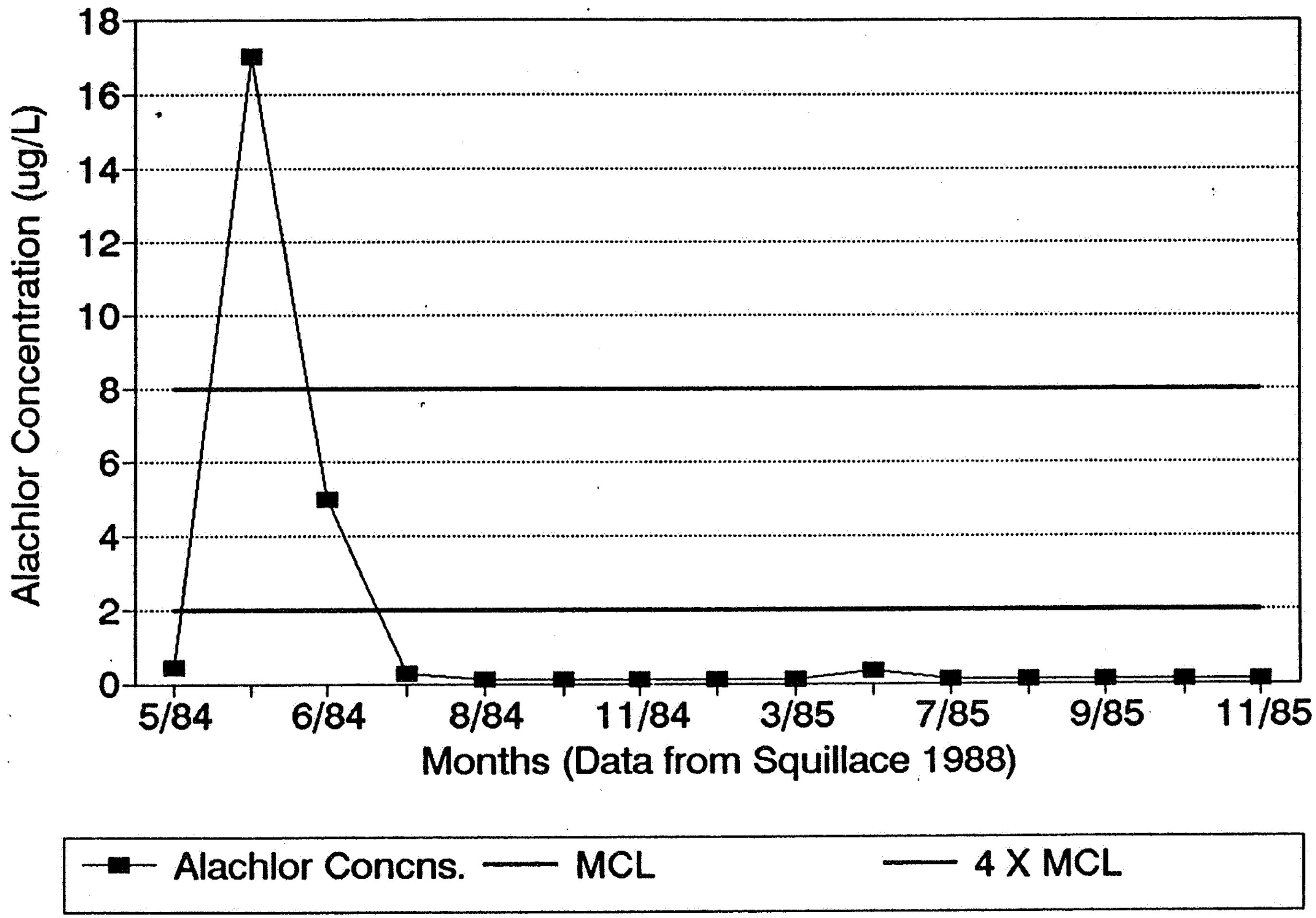


Figure 2.4 Ambient Water Quality Monitoring Network Map with Pesticide Subnetwork

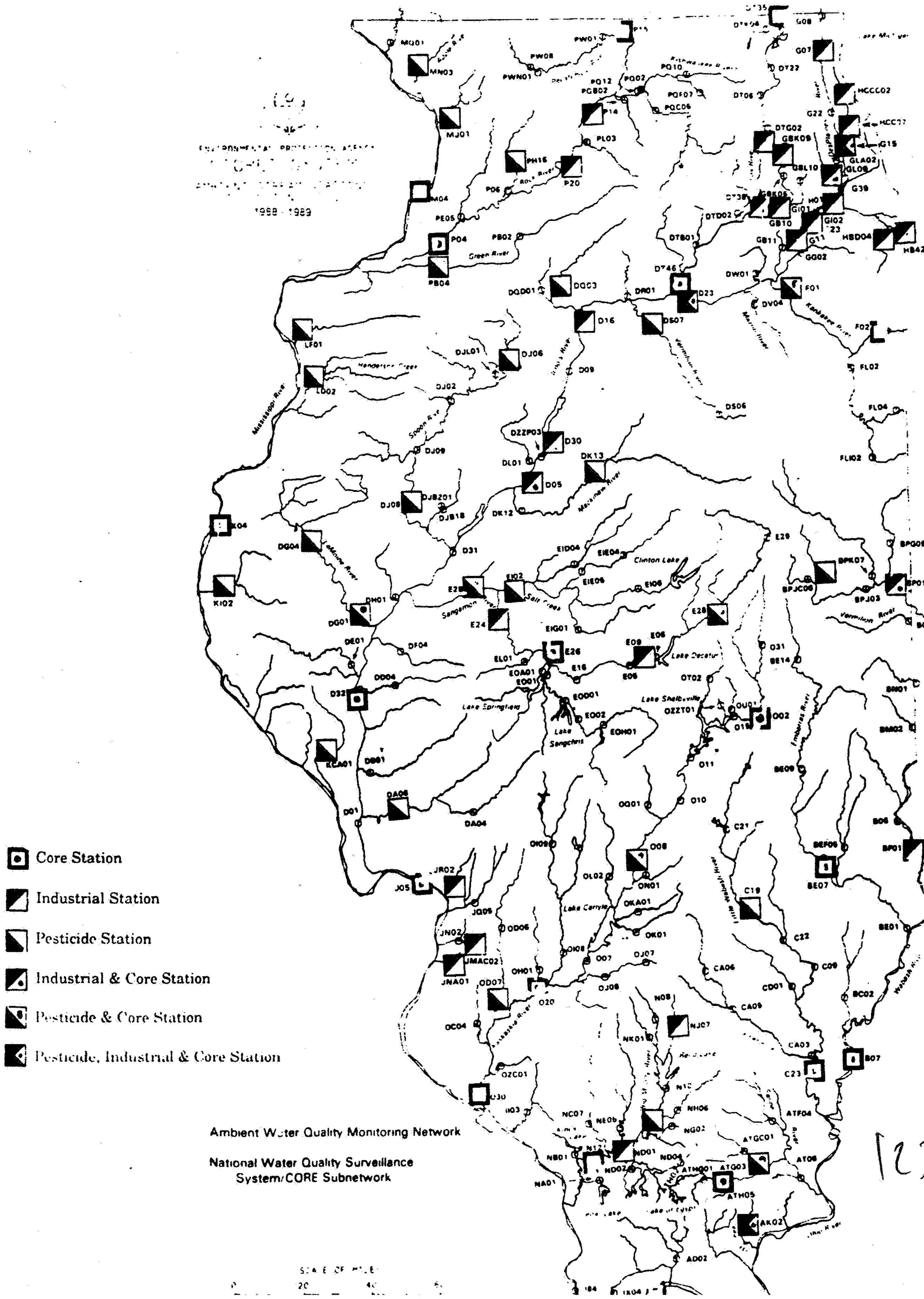


Fig. 25) Alachlor Time Series
Middle F. Saline R. IL

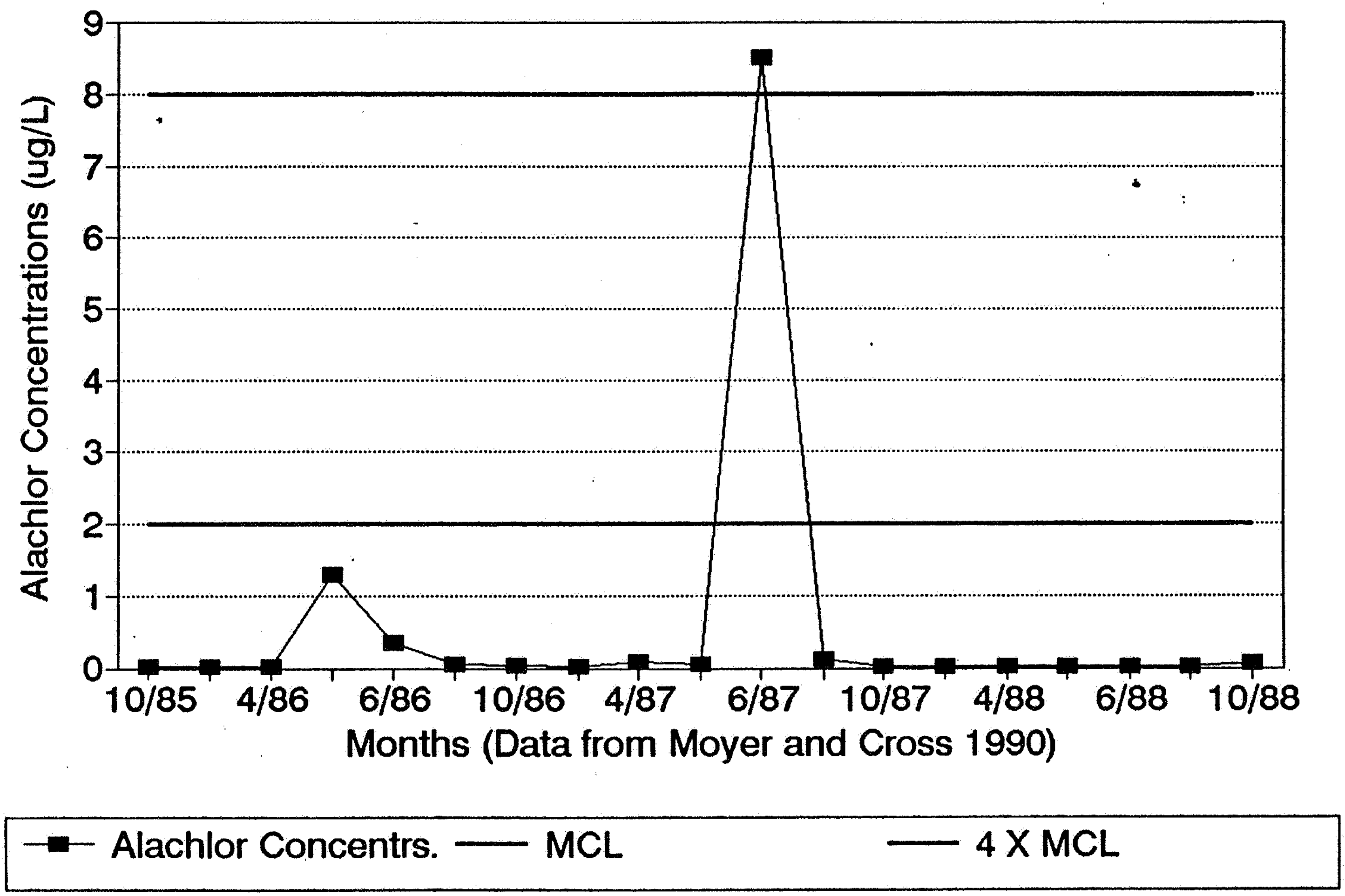


Fig. 26) Alachlor Time Series
Bay Creek IL

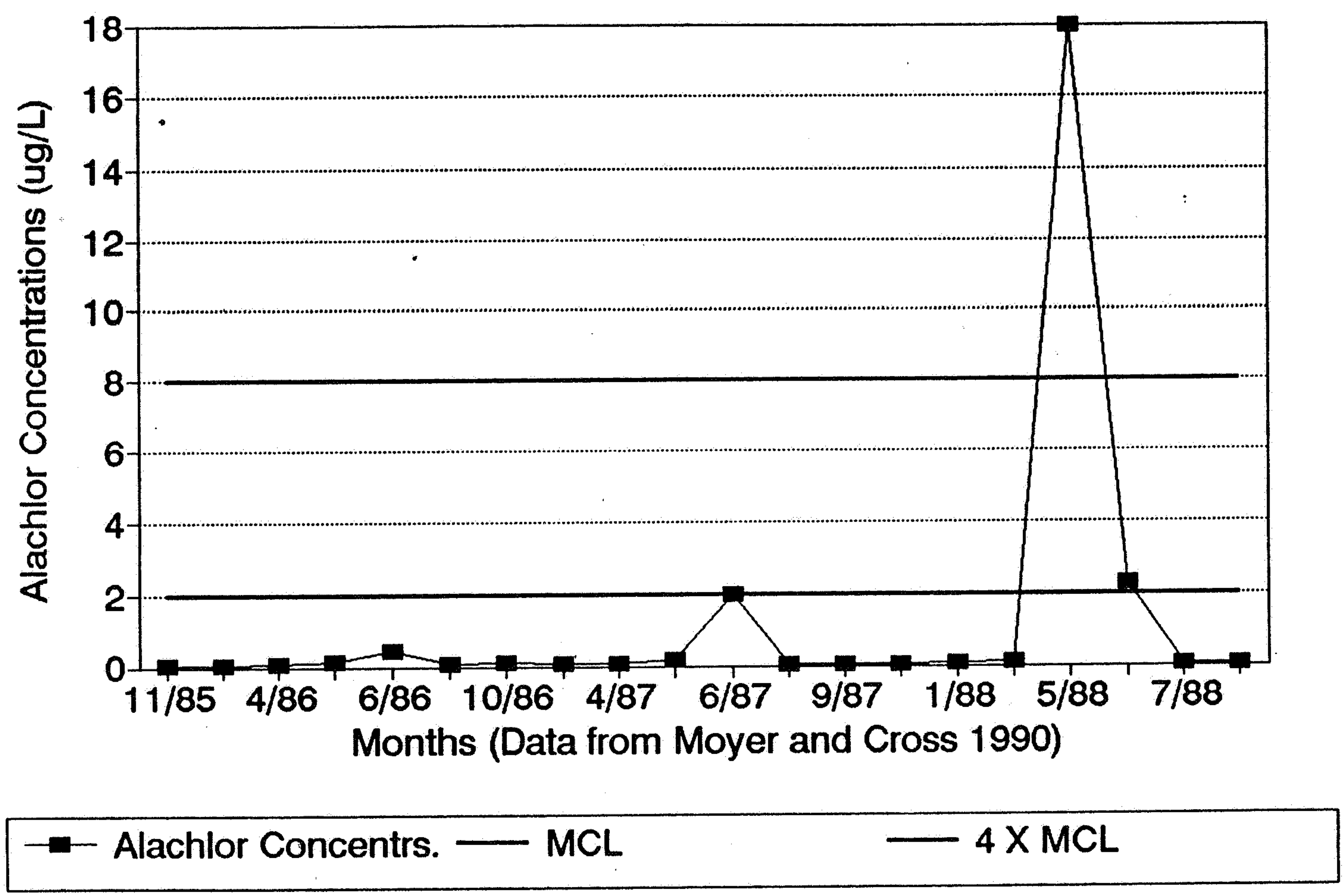
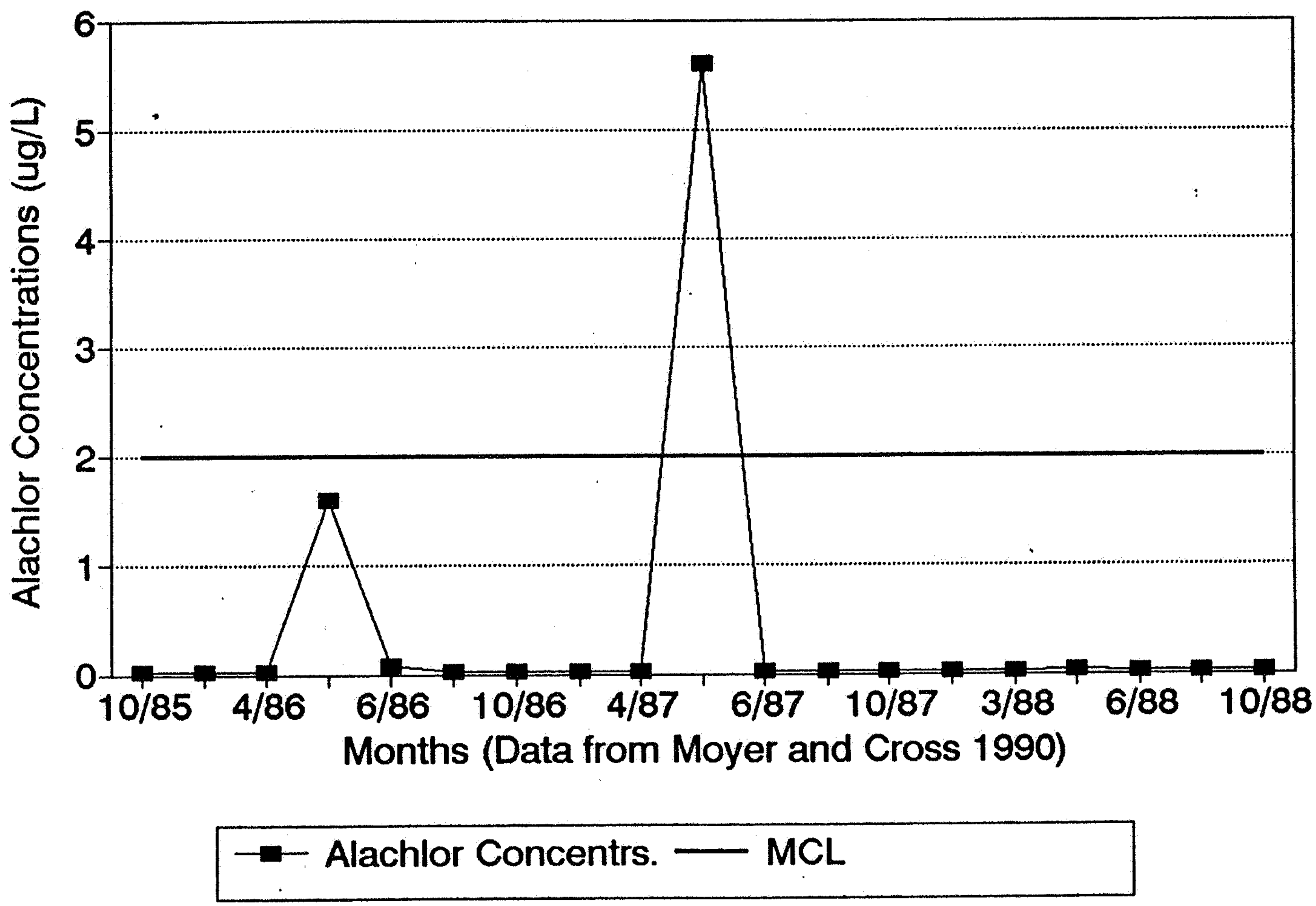
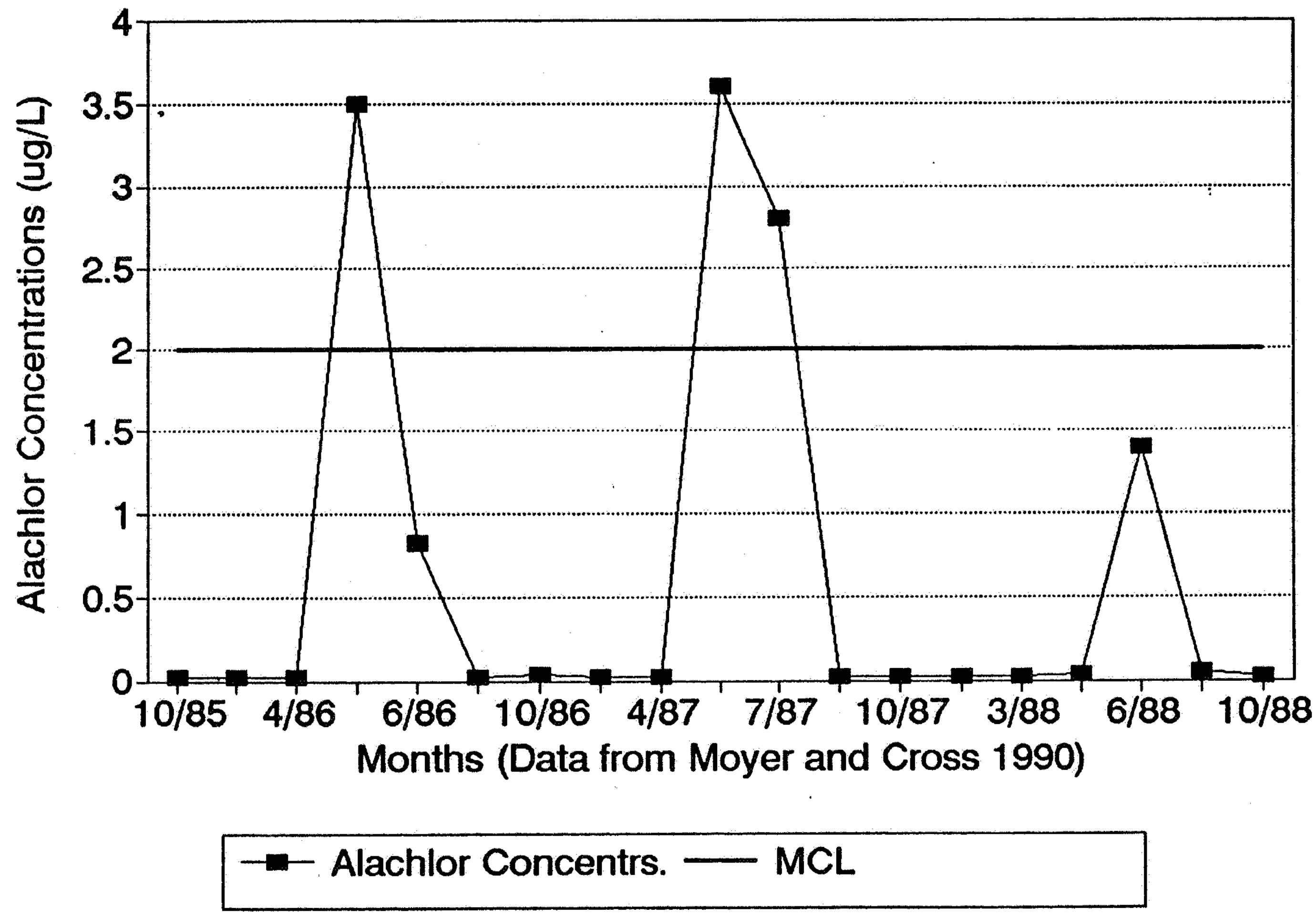


Fig. 27) Alachlor Time Series
Plum River IL



126

Fig. 28) Alachlor Time Series
Silver Creek IL



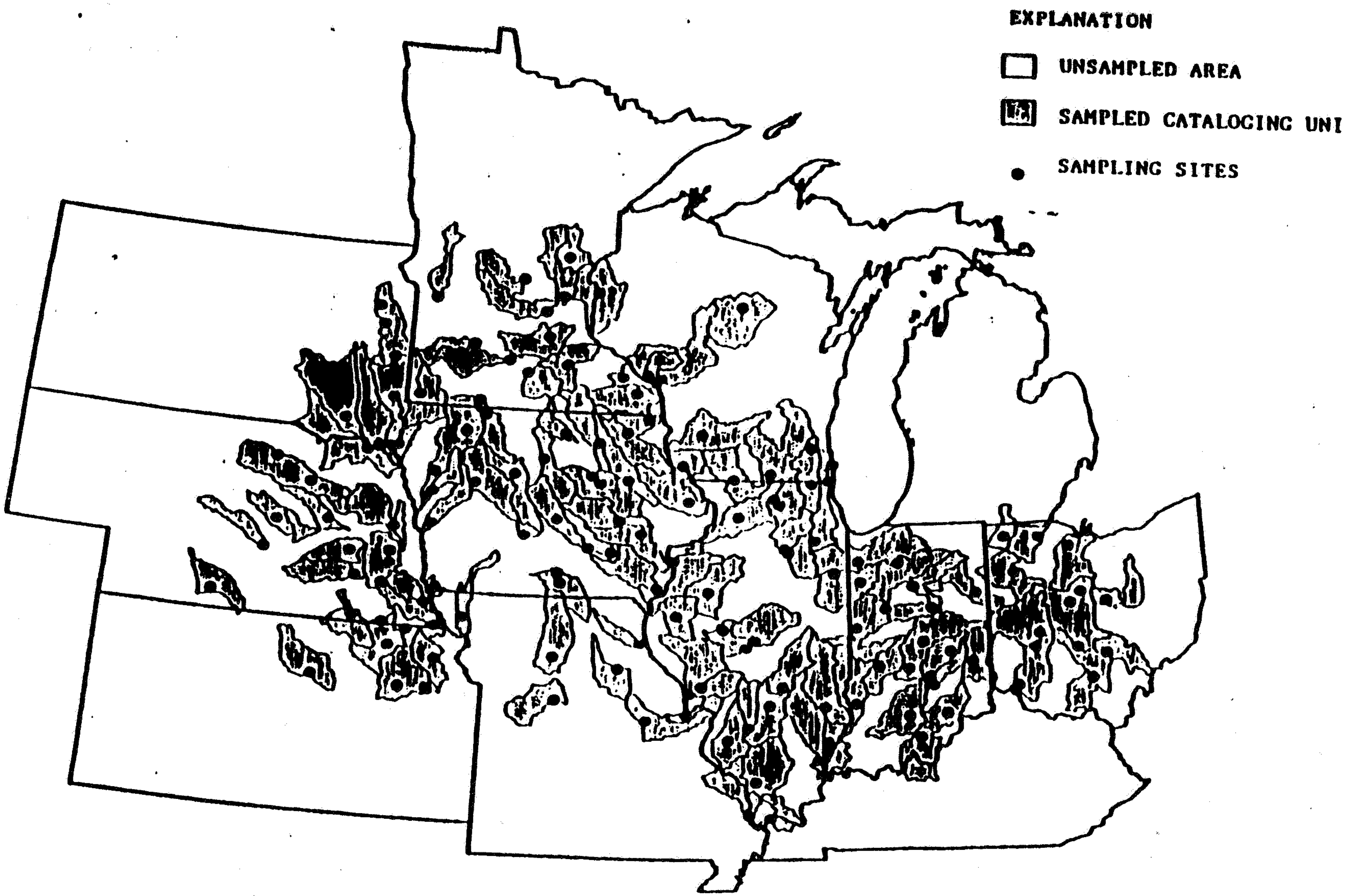
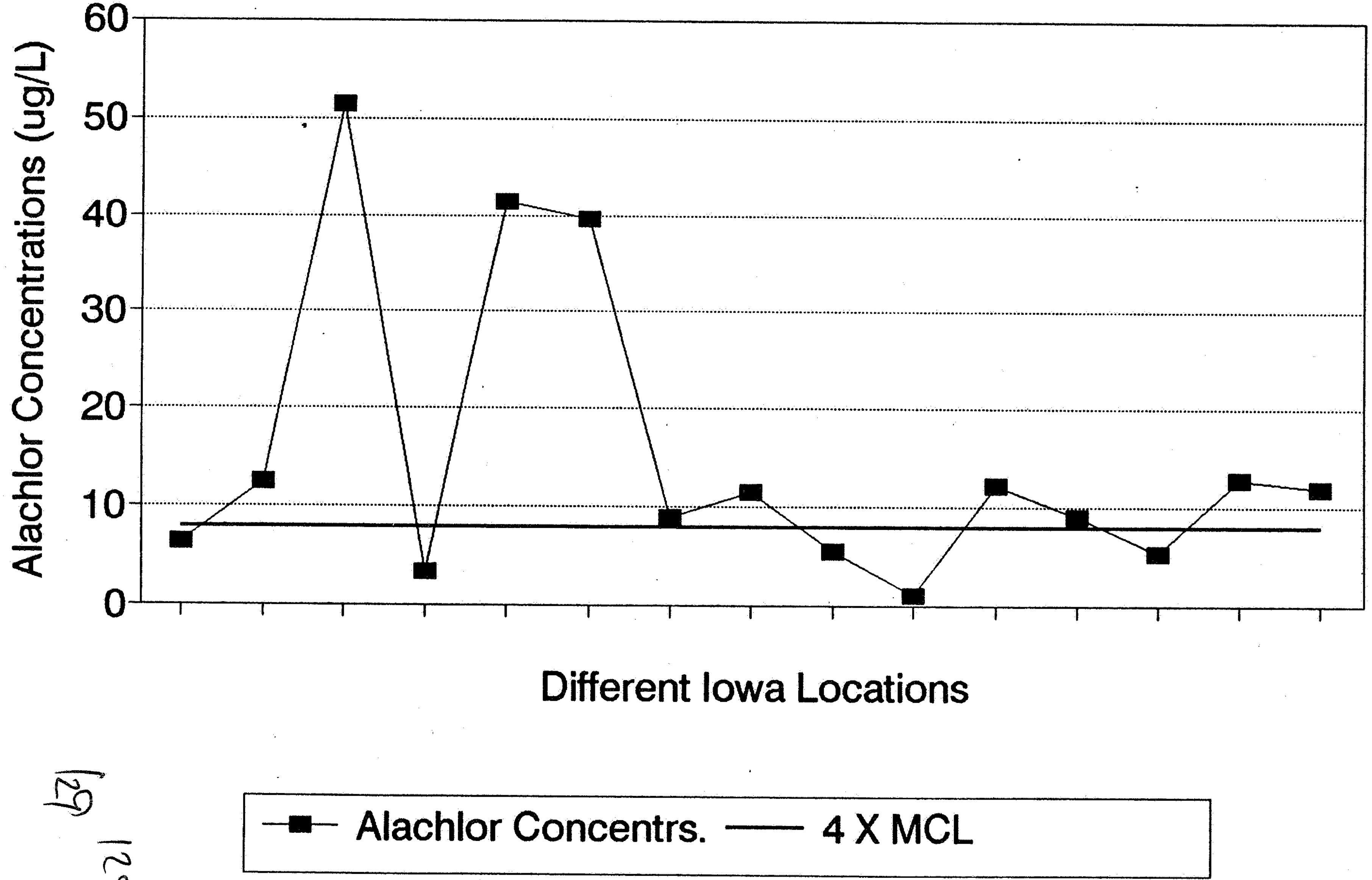


FIGURE 19 - Location of sites and hydrologic cataloging units sampled for midwestern United States herbicide reconnaissance during 1989.

128

Fig. 30) Post-Appl. Alachlor Concentrations Iowa 1989



129

129

Fig. 31) Post-Appl. Alachlor Concentrs. Illinois 1989

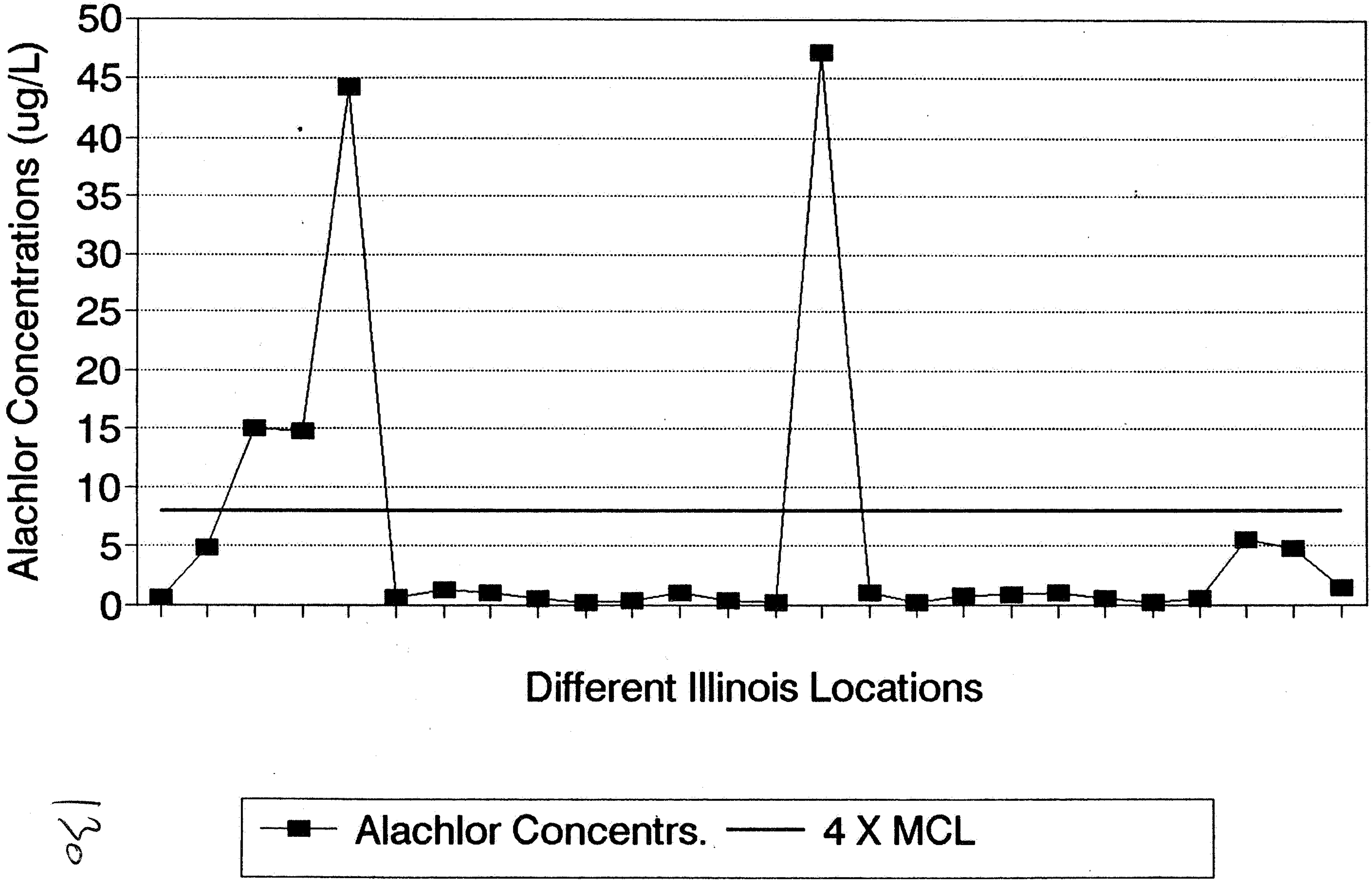


Fig. 32) Post-Appl. Alachlor Concentrs. Indiana 1989

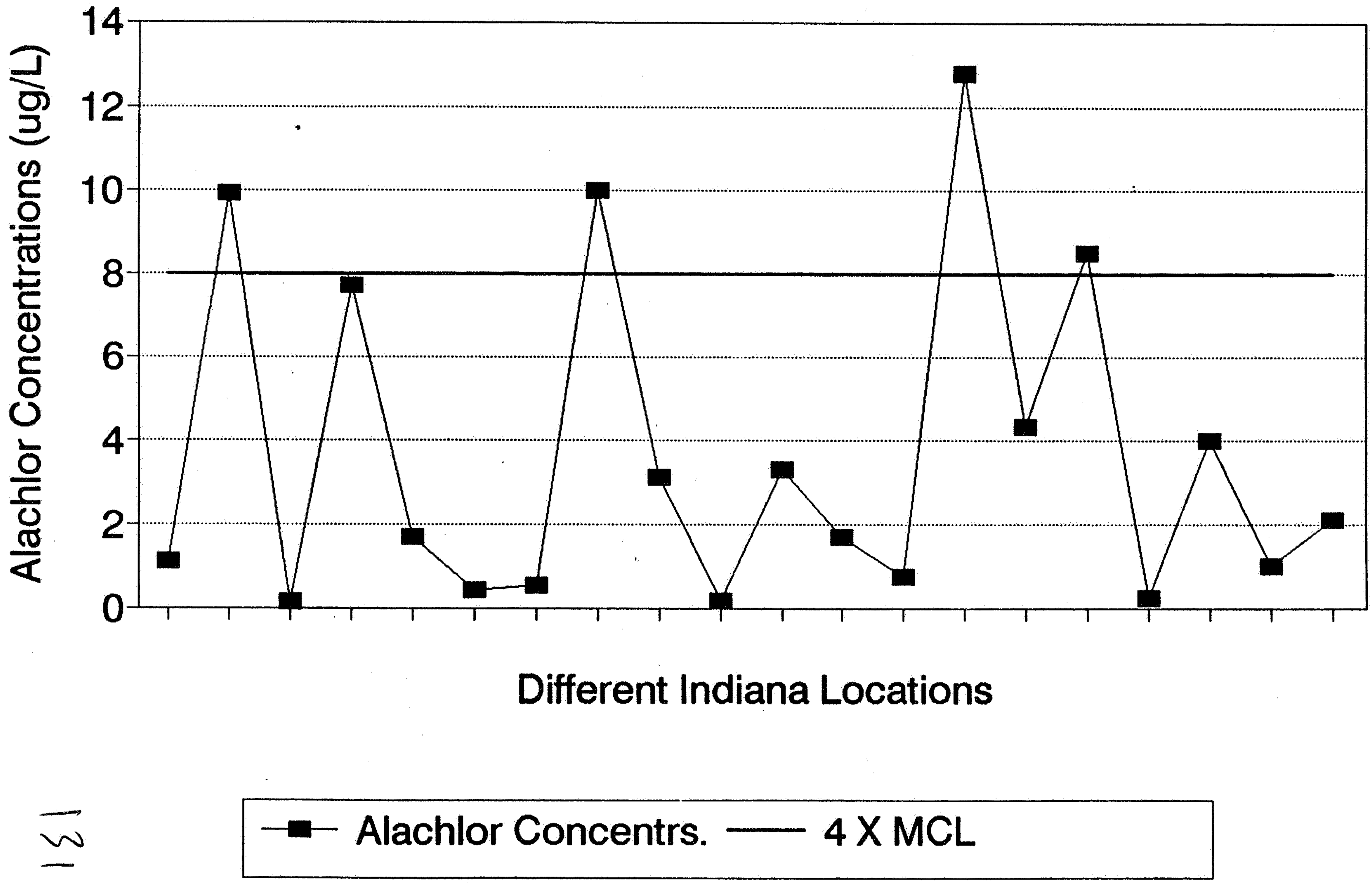
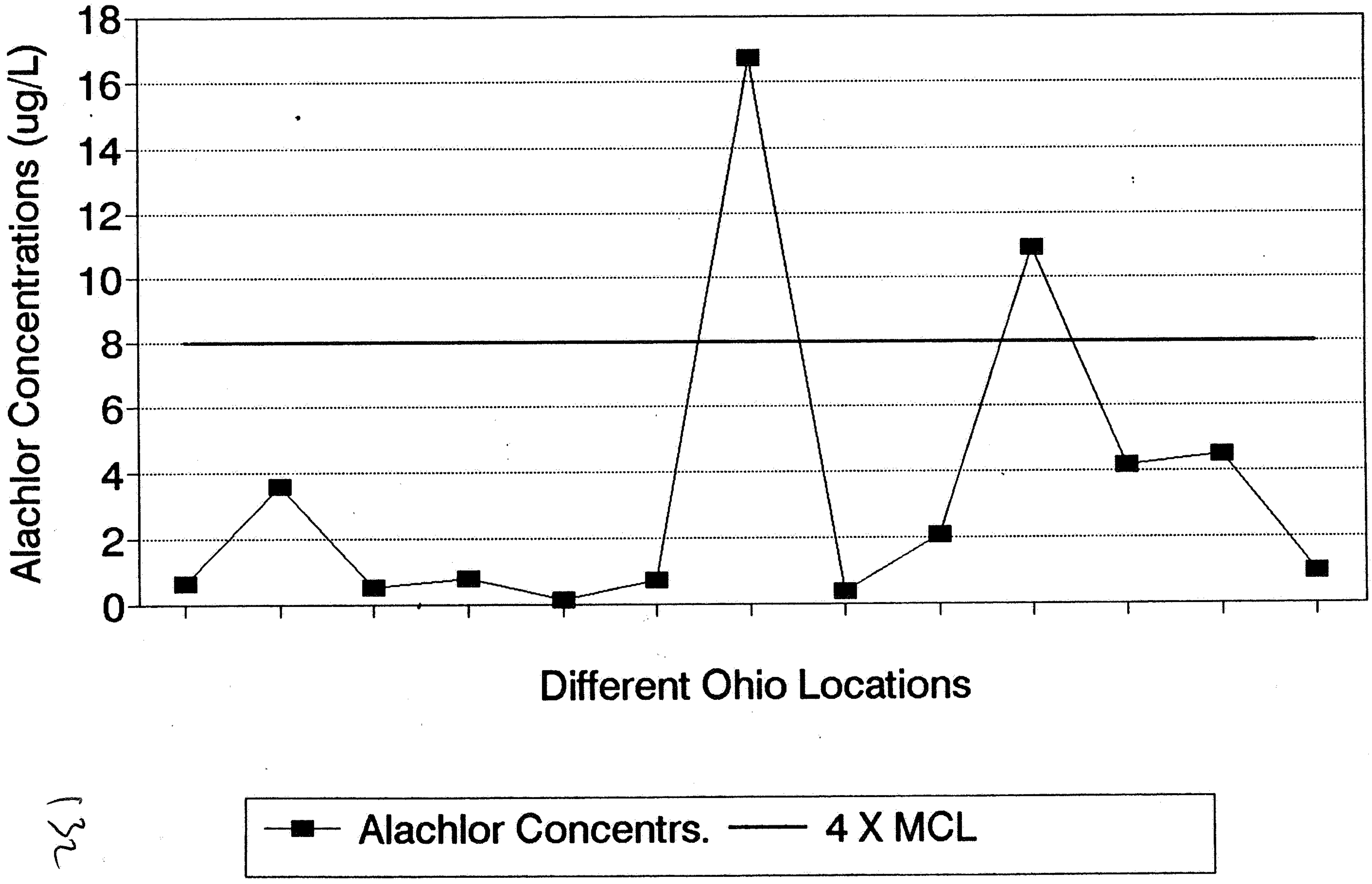


Fig. 33) Post-Appl. Alachlor Concentrations Ohio 1989



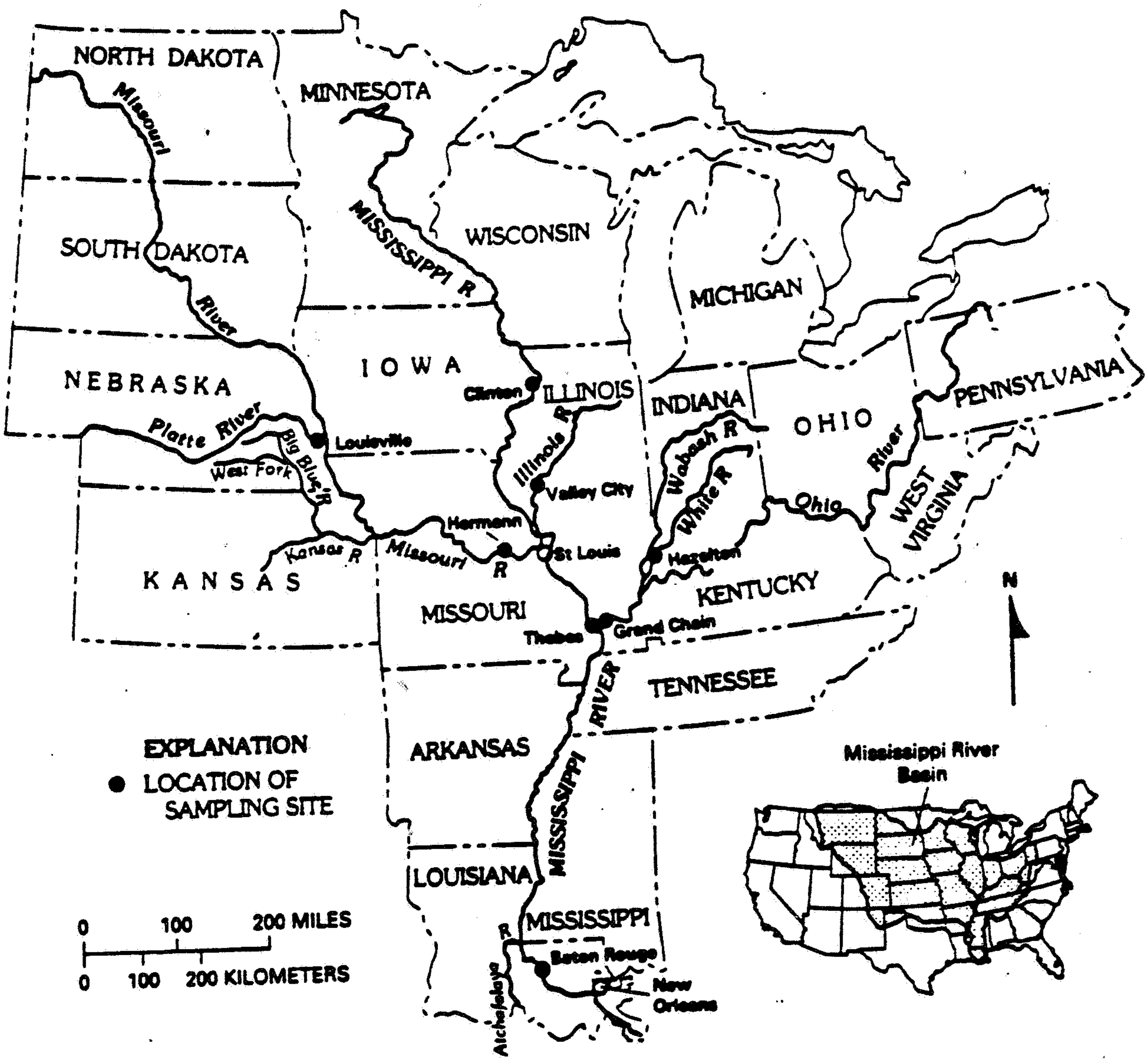


Figure 34 Location of sampling sites.

133

Fig. 35) Alachlor Time Series
White River near Hazelton, IN

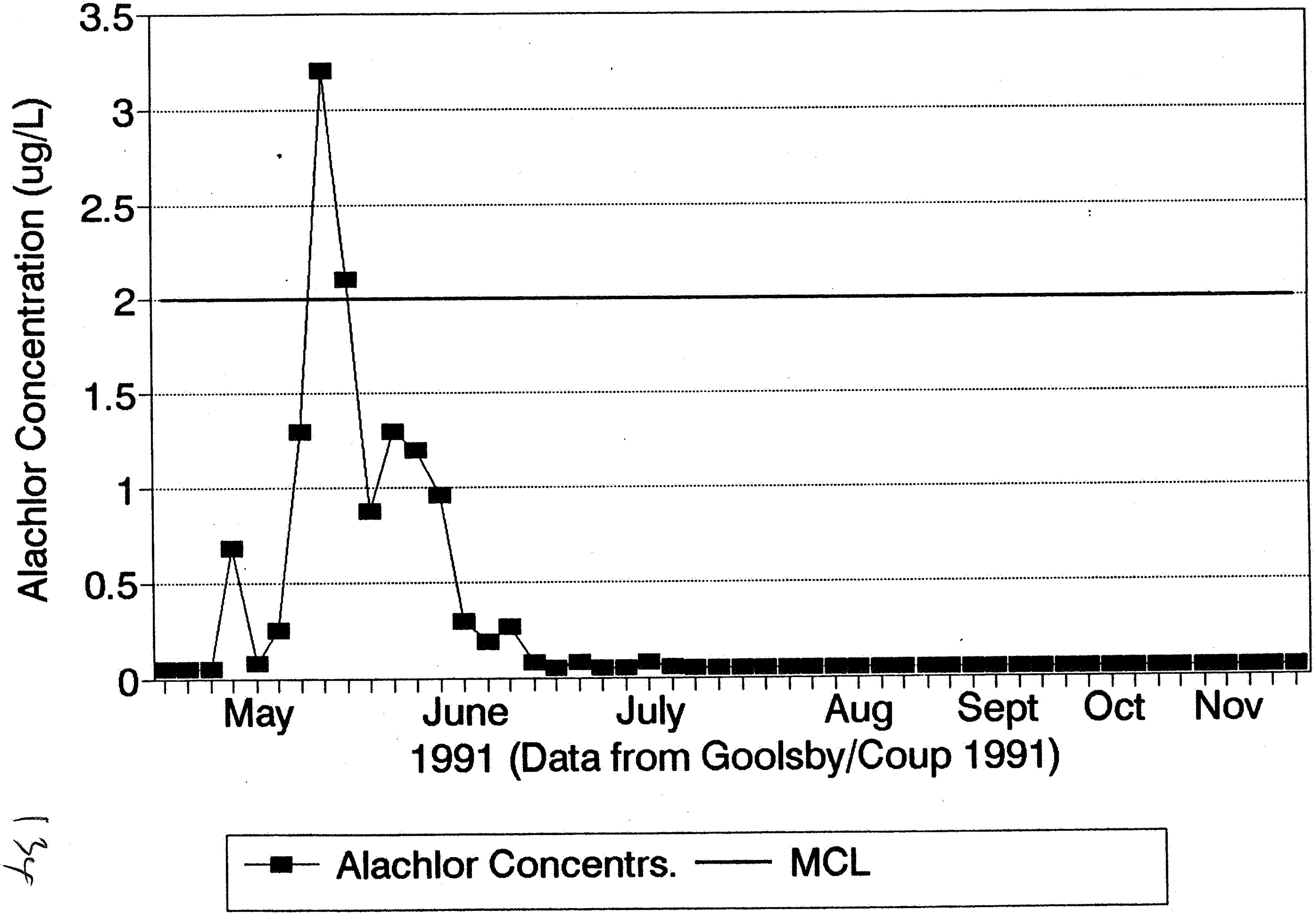
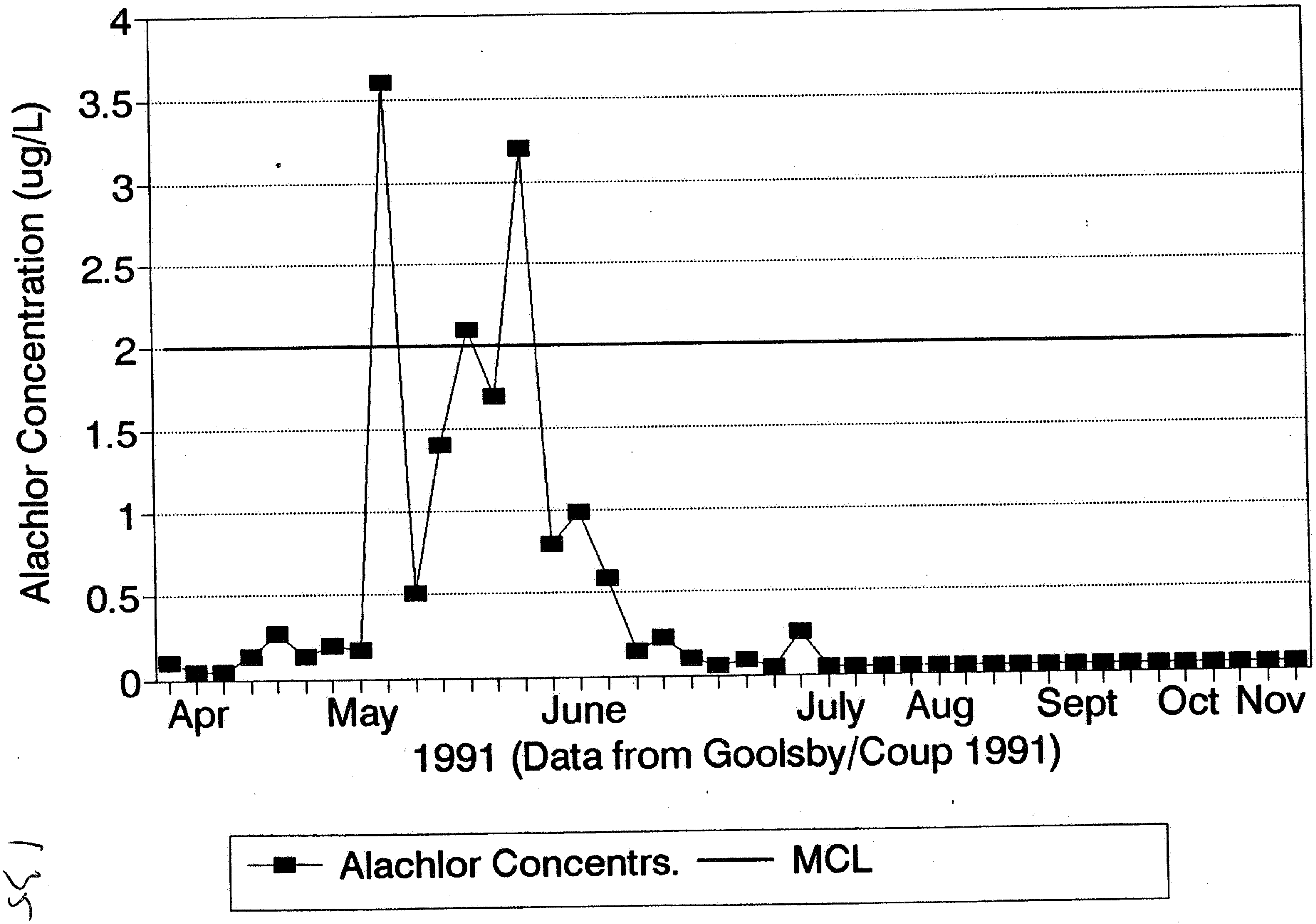
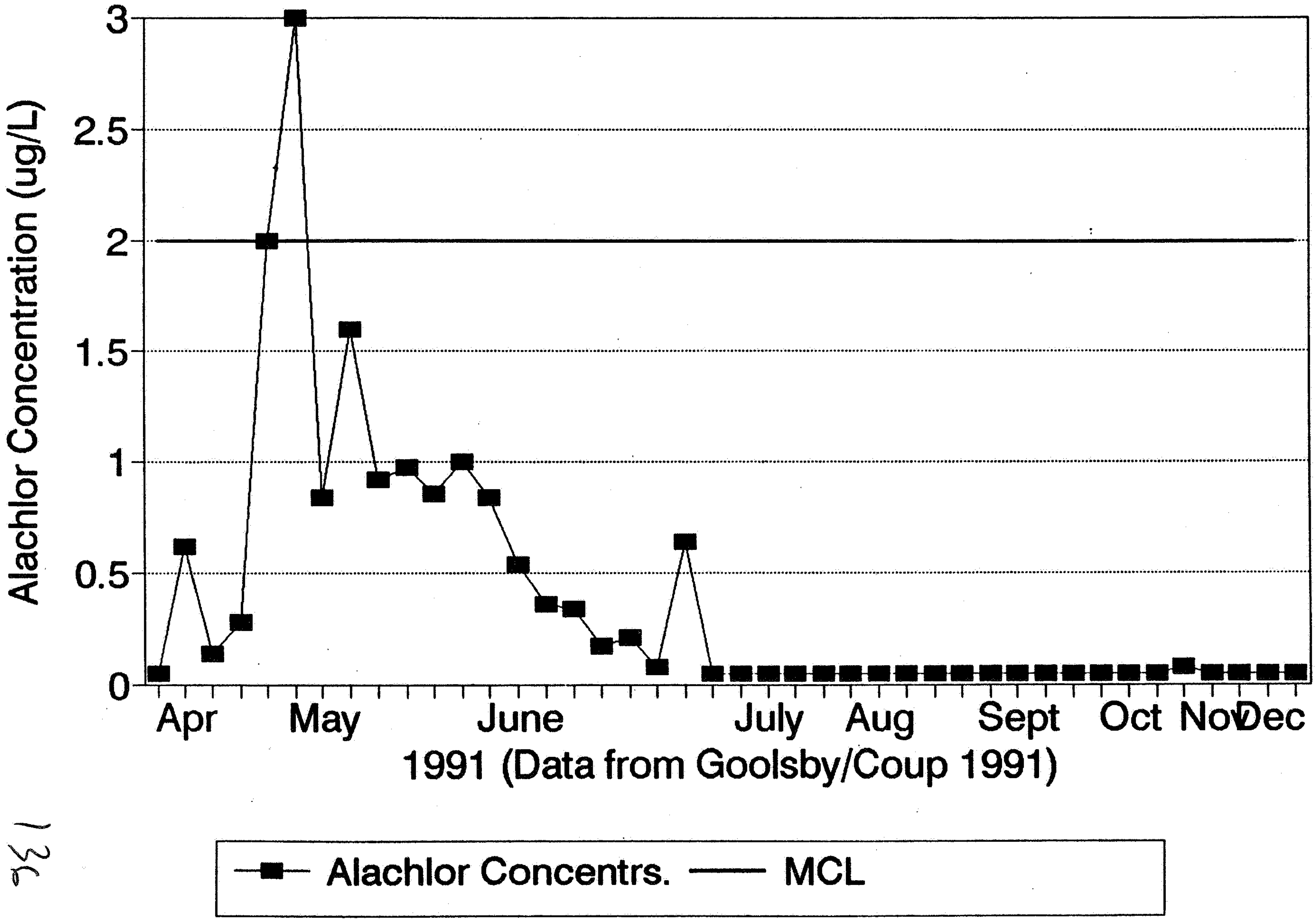


Fig. 37) Alachlor Time Series
Platte R. nr. Louisville NE



135

Fig. 36) Alachlor Time Series
Illinois R. nr. Valley City IL



Henry Nelso

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

JUL 21 1992

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

MEMORANDUM

SUBJECT: Alachlor

FROM: Jack Housenger, Chief
Special Review Branch
Special Review and Reregistration Division (H7508W)

TO: Hank Jacoby, Chief
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division (H7507C)

In December 1987, the Agency issued its final determination regarding carcinogenic risks resulting from dietary and non-dietary exposure to alachlor. This final determination deferred a decision on the groundwater risk of alachlor until the results of the 1990 "National Alachlor Well Water Survey" (NAWWS) were submitted and reviewed.

Now that EFGWB has reviewed the NAWWS study, we need answers to the following questions in order to determine if the Special Review on alachlor groundwater issues should proceed. Additionally, we need to determine if the conclusions reached in the alachlor PD 4 regarding surface water were accurate (see highlighted sections of the attached PD 4).

- Briefly describe the NAWWS study.

- What do the data from the NAWWS study and data from other monitoring which are available to us suggest about the problem of alachlor in groundwater and surface water?

- In the PD 4, dietary exposure/risk was calculated for alachlor and its two metabolites, DEA and HEEA. Would we expect these metabolites to be present in groundwater and surface water? If so, are there methods

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developed for testing for the metabolites? If so, are there monitoring results showing the levels?

- o How geographically widespread is the problem?
- o How many states in the U.S. have alachlor contaminated groundwater and surface water?
- o Which states are these?
- o Are there common contamination areas?
- o Is the contamination from a point source or a non-point source? If both, which is the larger concern?
- o Is it possible to determine how much of the population is exposed?
- o What are the levels of exposure?
- o How many detections above or below the MCL was alachlor found in groundwater and surface water?
- o Has the Agency received any new surface water contamination data since the final determination which would confirm or alter surface water contamination conclusions?
- o Which is the best way to deal with the problem of both groundwater and surface water contamination - state or national regulations?
- o What are some of the measures most likely to be effective in preventing groundwater and surface water contamination on a national basis?
- o Is there any other information which would help to determine whether or not OPP needs to proceed with a Special Review?

Please contact Beth Edwards (308-8023) of my staff to discuss due dates or if you have any questions regarding this request. Thank you.

[a] Data of Loper et al., 1985. 20 ppb finding attributed to point source; mean without 20 ppb case is 0.80 ppb.
[b] Libra, 1984.
[c] Hallberg, et al., 1985.
[d] Findings discussed in text.

In several States, alachlor was not detected in any of the wells sampled: Vermont, 165 wells; Kansas, 58 wells; Nebraska, 75 wells; and Arkansas, 28 wells. However, in each of these surveys, the limit of detection was higher than usual, being 0.4 ppb in the Kansas study and 1.0 ppb in the other three. Limits of detection for alachlor in water are usually between 0.15 and 0.25 ppb, and lower levels have been achieved in some studies.

As noted in Table 3, several high detections in these studies are attributable to point source contamination. For example, in the Ontario study (which also used a 1.0 ppb detection limit), the authors attributed 8 out of 21 positive wells to leaching following normal agricultural use, and the rest to runoff incidents or spills. These 8 wells showed a range of 1.0 to 12 ppb, with a mean of 4.2 ppb. Similarly, the Pennsylvania data show that the highest detection of 20 ppb occurred near a chemical distribution center, which suggests a point source for that positive reading.

High levels of alachlor reported in 1 of the 2 positive wells in Florida (out of about 250 wells sampled) appear to be anomalous. The Florida Department of Agriculture and Consumer Services is unsure of the cause of contamination for the well in question, but consistently high levels ranging from 42 to 99 ppb in monthly samples suggest a point source. For the second well, alachlor was initially detected at 83 ppb, but subsequent testing found levels between 2 ppb and 4 ppb. The Florida Department of Environmental Regulation attributes the presence of alachlor in this well to leaching following normal agricultural applications.

The two wells positive for alachlor in Florida are in different counties. Since the Florida study tested a high number of drinking water wells in five counties near farms known to have used alachlor, and found only these two positive results, the Agency cannot reach any definitive conclusions regarding alachlor contamination of ground water in Florida.

The rate of positive alachlor detections in private wells varies considerably from study to study, ranging from 0.8 percent to 13.3 percent. It appears that the rate of positives for private wells is greater than the rate in public wells, although this is not considered to be a statistically valid data base.

Only one on-going study is available involving wells dug for the purpose of studying alachlor leaching to a shallow aquifer (between 8 and 19 feet from the soil surface) beneath treated fields. This is a joint study by the Wisconsin Department of Natural Resources and the Department of Agriculture, Trade and Consumer Protection (Postle and Jones, 1986; Postle, 1987). Nine fields in 5 counties were monitored with 3 wells per field. It was concluded that one field, with readings up to 113 ppb, had been the site of a spill. Of the remaining 8 fields/24 wells, 3 fields/5 wells were positive, with a range of 0.1 to 7.7 ppb, and a mean of 2.1 ppb. In July and August of 1987, 5 additional fields were sampled once, with no positive detections of alachlor.

In summary, the additional data on ground water received and evaluated by EPA are essentially consistent with the data reported in the previous alachlor position documents. The available information shows that alachlor residues do occur in ground water, and that leaching following normal agricultural use is one of the likely causes for such contamination, as are spills, careless handling or disposal, and surface runoff events in conjunction with improper or inadequate well construction. It appears that detected alachlor residues in ground water attributable to leaching after normal use are rarely higher than 10 ppb and typically fall in the range of 0.2 to 2.0 ppb. The available data base does not provide an adequate basis for a risk assessment, because it is not considered adequately representative of alachlor's use in terms of geographic areas and associated hydrogeologic conditions. Also, the data base consists of various studies employing different criteria, methodologies and levels of quality control. The registrant's large scale monitoring study, conducted under a single, consistent protocol approved by EPA, should provide a more appropriate data base for determining the actual extent to which alachlor use may pose a threat to ground water.

b. *Surface water.* Additional data on alachlor residues in surface water were submitted in response to the PD-1. The TSD presented surface water sampling data involving over 80 sites from a number of States and Canada. Only some of these data concerned sources of drinking water. The registrant submitted monitoring data gathered in 1985 on 24 community water supplies (CWSs).

The registrant's 1985 data showed alachlor residues in 14 of the 24 CWSs (42 percent). The communities were located in areas of high alachlor use in seven States. Results were reported for weekly composites of daily samples over the entire calendar year. The highest weekly composite concentration was 10.9 ppb. Annualized mean concentrations ranged from the limit of detection (0.2 ppb) to a high of 1.5 ppb.

The registrant's data and other studies show that alachlor levels tend to peak just after the application season, in May and June, and decline rapidly thereafter. In some bodies of water, alachlor levels drop below the limits of detection in later months, while in some studies, alachlor has been detected throughout the year.

The registrant submitted a similar study of 30 CWSs in areas of high alachlor use for 1986. Alachlor was detected in 13 of these locations, with the highest weekly composite concentration at 9.5 ppb, and annualized mean concentrations from the limit of detection (0.2 ppb) to 0.98 ppb.

The Agency noted in the TSD that the monitoring data on alachlor runoff to surface waters under various conditions tended to confirm the results of mathematical modeling predictions. Thus, the Agency is reasonably confident in estimating that for areas of high alachlor use, residues which may occur in some sources of drinking water will, on an annualized basis, generally be below 2 ppb, and more likely fall in the range of 0.5 to 1.0 ppb.

Finally, it should be noted that alachlor residues have been reported in rain water samples collected at several sites between 1984 and 1986 by Dr. David Baker of Heidelberg College. All positive alachlor detections reported for rain water have been in the low parts per billion range. The highest peak level reported is 6.59 ppb, and the mean levels (simple arithmetic means) for the various sites range from 0.02 ppb to 1.67 ppb. The mechanism by which these residues occur in rain water is unknown, but presumably has to do with volatilization of alachlor after it is applied. Since the aerial application of alachlor was largely discontinued after the 1984 season due to labeling amendments, and essentially identical levels in rain water are reported for 1985

139

ATTACHMENT F

PERSISTENCE OF HERBICIDES IN SELECTED RESERVOIRS IN THE MIDWESTERN UNITED STATES: SOME PRELIMINARY RESULTS

By Donald A. Goolsby, William A. Battaglin, James D. Fallon, Diana S. Aga, Dana W. Kolpin, and E. Michael Thurman

ABSTRACT

Preliminary results from a study of herbicides in 76 midwestern reservoirs show that some herbicides and metabolites of atrazine and alachlor are detected more frequently throughout the year in reservoirs than in streams. Except for a short period after application to cropland, herbicide concentrations also are generally higher in reservoirs than in streams. Herbicides or their metabolites were detected in 82 to 92 percent of the reservoirs sampled during four periods from late April through early November 1992. Atrazine was detected most frequently and in highest concentrations, followed by an alachlor metabolite (alachlor ethanesulfonic acid), and two atrazine metabolites (desethylatrazine and deisopropylatrazine). The longer persistence of some herbicides and metabolites in reservoirs than streams is attributed to longer half lives for these compounds in the water column than in the soil where concentrations of organic matter and microorganisms are much higher and contribute to rapid biodegradation of herbicides. A second contributing factor is long-term storage of water in reservoirs that originates as spring and summer storm runoff from cropland and which contains high concentrations of herbicides.

INTRODUCTION

Reservoirs are an important part of hydrologic systems in the Midwestern United States. According to data compiled by Ruddy and others (1990), about 440 large reservoirs (normal storage capacity greater than 5,000 acre-feet) in 11 upper Midwestern States discharge streamflow to the Mississippi River by way of tributaries. The primary function of these reservoirs is to impound surface water for many uses, including flood control, hydropower, recreation, and aquatic life habitat. These large reservoirs and numerous smaller reservoirs also can serve as sources of drinking water for public supplies. In addition to storing surface water, reservoirs also can store undesirable substances such as sediment and toxic chemicals including pesticides. Most of the sediment entering reservoirs is permanently trapped and deposited on the bottom of the reservoir. However, chemicals such as soluble herbicides generally remain in the water column and are stored only temporarily until they are flushed from the reservoir or removed from solution by biotic and abiotic processes.

Storage of herbicides is a potential problem in reservoirs that receive drainage from agricultural areas in the upper Midwest. Recent studies by the U.S. Geological Survey (USGS) (Thurman and others, 1991, 1992; Goolsby and others, 1991) have shown that most streams in the upper Midwest contain herbicides at some time during the year. Large quantities of herbicides are flushed from agricultural fields each spring and summer during rainfall following application of herbicides. Median concentrations of the herbicides atrazine, alachlor, cyanazine, and metolachlor in streams increased by at least an order of magnitude from March and April 1989 to May and June 1989. For example, the median concentrations of herbicides in Midwestern streams, in 1989, ranged from less than 0.3 µg/L before planting to as much as

140

3 μg/L after planting, and the maximum concentrations in a few streams reached 100 μg/L (Thurman and others 1991). During late spring and early summer, concentrations of atrazine can exceed the U.S. Environmental Protection Agency's maximum contaminant level (MCL) for drinking water of 3 μg/L for several weeks to several months in both small streams and large rivers, such as the Mississippi River.

Because reservoirs collect and store water, they can be affected by storm runoff that contains large concentrations of herbicides for a much longer period of time than the streams that supply the reservoirs (Stamer and Zelt, 1992). This can substantially affect the water quality of streams downstream from reservoirs. The length of time that reservoirs discharge water with elevated concentrations of herbicides depends on a number of factors including residence time of water in the reservoir, timing of inflow to the reservoir, land use and herbicide use in the contributing drainage area, and the timing and intensity of rainfall. Unregulated streams exhibit the flush effect (Thurman and others, 1991), which can produce high concentrations of herbicides for short periods of time. In contrast, peak concentrations of herbicides in streams regulated by reservoirs are much lower, but elevated concentrations (near or above MCLs) can persist for much longer periods of time. Stamer and Zelt (1992) have shown that atrazine concentrations in Perry Lake, Kans., remained near or above the MCL of 3 μg/L from March 1989 through October 1989 and above 1μg/L through February 1990, whereas atrazine concentrations in the principal tributary to Perry Lake exceeded the MCL for only a few months in late spring. However, atrazine concentrations in some of the samples from tributaries exceeded 10 μg/L during this period and much of the water in Perry Lake was replaced with containing these atrazine concentrations. Because little additional inflow to Perry Lake occurred after early summer, this "herbicide rich" water was stored in the reservoir until the next spring, when the cycle was repeated.

The process of storage and attenuation of herbicides documented in Perry Lake likely occurs in most other Midwestern reservoirs to greater or lesser degree depending on physical and hydrologic characteristics of the reservoirs and land use in the reservoir drainage basin. Atrazine concentrations in mid-winter samples during 1990-92 from several large reservoirs in Illinois, Iowa, Kansas, and Missouri are listed in table 1. Water samples from many of these reservoirs had atrazine concentrations of at least 2 μg/L during this time, which likely reflected the storage of herbicide-laden inflow originating from the "spring flush." In general, it appears that the larger the volume-to-drainage area ratio of the reservoir, the greater the atrazine concentration.

The way in which unregulated streams in the Midwest respond to the seasonal application of herbicides has been documented (Thurman and others, 1992; Goolsby and others, 1991). However, the temporal distribution of herbicides in streams regulated by reservoirs has not been examined. In addition, the process(es) by which physical, hydrologic, and land use characteristics of reservoirs and their contributing drainage areas interact to affect herbicide concentrations in the outflows from reservoirs has not been studied. In order to develop an understanding of these processes in reservoirs, a study was begun as part of the USGS's Toxic Substances Hydrology Program in April 1992. The study is still in progress at the present time (May 1993). The purpose of this paper is to describe the study plan and to summarize some of the preliminary study results.

141

Table 1.—Atrazine concentrations in water samples from selected midwestern reservoirs during winter months, 1990-92

[Vol/DA, volume to drainage area ratio; acre-ft, acre-feet; GC, gas chromatography; ELISA, immunoassay; µg/L, micrograms per liter, --, no data]

Reservoir	Sample date	Vol/DA (acre-ft/acre)	Atrazine concentration by GC (µg/L)	Atrazine concentration by ELISA (µg/L)
Illinois				
Carlyle Lake outflow	1- 3-92	0.14	--	2.3
Lake Decatur outflow	1- 8-92	.05	--	.2
Rend Lake Spillway	1- 2-92	.59	--	.6
Lake Shelbyville outflow	1- 8-92	.31	--	1.1
Lake Springfield at Sugar Creek	1-30-92	.34	--	2.5
Lake Springfield at Spaulding Dam	1-30-92	.34	--	4.0
Iowa				
Coralville Lake	2-21-92	0.01	--	.2
Corydon Reservoir	winter, 1992	--	--	10
Rathbun Reservoir	--12-90	.58	3.7	--
Rathbun Reservoir	2-20-92	.58	--	2.8
Red Rock Reservoir	2-12-92	.01	--	.2
Saylorville Lake	2-12-92	.02	--	.1
Kansas				
Perry Lake	2- 3-91	.34	3.9	--
Missouri				
Long Branch Reservoir	--12-90	.50	2.0	--
Smithville Reservoir	--12-90	1.06	3.6	--

(42

STUDY AREA AND PLAN OF INVESTIGATION

The study area (fig. 1) was defined as all hydrologic units in parts of 11 states (Illinois, Indiana, Iowa, Kansas, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin) that drain to the Ohio, Upper Mississippi, and Lower Missouri Rivers. This area comprises about 450,000 mi^2 and is virtually the same area covered by the 1989-90 reconnaissance for herbicides in streams (Thurman and others, 1991; 1992).

The primary objectives of the study are to (1) determine the occurrence and temporal distribution of selected herbicides and herbicide metabolites in the outflow from selected reservoirs in the upper Midwest, and (2) determine if the persistence of large concentrations (greater than about 1 µg/L) of herbicides in reservoir outflow can be quantified on the basis of reservoir and drainage-basin characteristics, hydrology, land use, herbicide use, and climate. Some specific hypotheses to be tested are--

1. Herbicides will be detected in Midwestern reservoirs for a longer period of time than in unregulated streams, but peak concentrations will be lower in the reservoirs than in these streams.
2. The duration of herbicide concentrations in reservoir outflow above a threshold value can be explained (statistical model) by reservoir and drainage-basin characteristics, land use, herbicide use, rainfall (intensity, timing and amount), and stability (half-lives) of individual herbicides. Consequently, the probability that a herbicide such as atrazine will persist in a reservoir all year above a specified concentration can be predicted.
3. The occurrence and concentrations of herbicides and herbicide metabolites in the anoxic hypolimnia of reservoirs during summer stratification differ from those in the aerobic epilimnia.

Reservoirs for study were selected from the reservoir data base compiled by Ruddy and others (1990). The principal criterion for selection of reservoirs was that data on reservoir volume and reservoir discharge must be obtainable so that the residence time of water in the reservoir and the timing of outflow can be determined. In addition, the reservoir outflow must be accessible for sampling. The reservoir data base was screened to determine which reservoirs met these criteria. As a result of this screening, 74 of the 440 reservoirs in the reservoir data base were selected for sampling. Two additional reservoirs, Lakes Monona and Waubesa in Wisconsin, which form a chain of reservoirs receiving outflow from Lake Mendota, also were selected. These three reservoirs will be treated as a single unit. Locations of these 76 reservoirs are shown in figure 1.

The outflow from each reservoir was sampled six times (approximately bimonthly) from April 1992 through March 1993, and a seventh time in mid-summer 1993. Samples are collected near the centroid of flow or other outflow point by methods that provide a representative sample of dissolved herbicides and nutrients in the outflow from the reservoir. During August 1992, herbicide samples, dissolved oxygen profiles, and temperature profiles were collected near the deepest point in 19 selected reservoirs to examine the effect, if any, of chemical stratification on herbicide concentrations. Herbicide samples were collected near the surface and near the bottom of each reservoir.

143

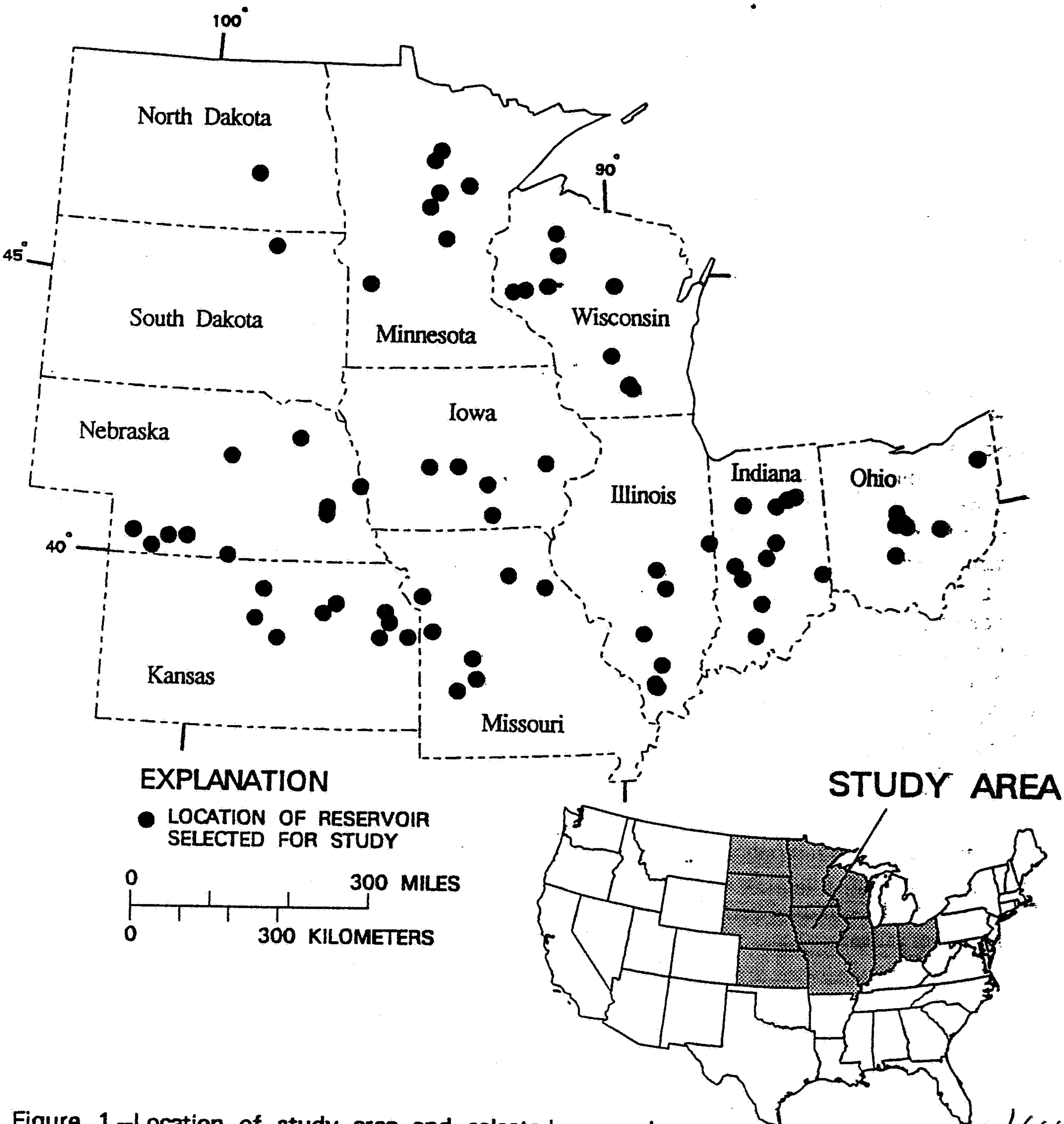

Figure 1.--Location of study area and selected reservoirs.

144

All samples are analyzed for 11 herbicides (alachlor, atrazine, ametryn, cyanazine, metolachlor, metribuzin, propazine, prometon, prometryn, simazine, and terbutryn) and at least 5 herbicide metabolites (desethylatrazine, desisopropylatrazine, deethylcyanazine, cyanazine amide, and deethylcyanazine amide) by gas chromatography/mass spectrometry (GC/MS). A metabolite of alachlor, [(2,6-diethylphenyl)(methoxymethyl) amino-2-oxoethane sulfonic acid], (ESA) is analyzed by immunoassay following isolation on C_{18} cartridges (Diana S. Aga, U.S. Geological Survey, written commun., 1993). Selected ESA samples are confirmed by high-performance liquid chromatography. Samples are also analyzed for nitrite, nitrate, ammonia, orthophosphate, and silica.

Ancillary data including land use, herbicide use, rainfall, and reservoir characteristics, are obtained from the following sources and stored in a geographic information system (GIS):

Data Type	Source
Land Use	1987 Census of Agriculture data.
Herbicide Use	Gianessi and Puffer, 1990.
Rainfall	National Weather Service.
Reservoir characteristics	U.S. Geological Survey and Corps of Engineers data bases.

PRELIMINARY RESULTS AND DISCUSSION

Analytical results from samples collected during the first four sampling periods, during April through November 1992 indicate that a number of herbicides and/or their metabolites, are present in many Midwestern reservoirs for long periods of time. The four sampling periods include pre-planting (late April-early May), post-planting (late June-early July), late summer (late August-mid-September), and fall (mid October-early November). Herbicides were detected in 82 to 92 percent of the 76 reservoirs during all four sampling periods. Four compounds (atrazine, desethylatrazine, desisopropylatrazine, and metolachlor) were detected in more than half the reservoirs during the fall (October-November sampling; table 2), whereas only atrazine was detected in more than one half the streams sampled in the fall of 1989 (table 2). One of the most notable differences between the occurrence of herbicides in reservoirs and streams is the much higher frequency of detection of cyanazine and desisopropylatrazine in reservoirs. A possible explanation (hypothesis) for this observation is that these two compounds are much more stable in the water column of lake and streams than in soil, where organic matter and microorganisms promote rapid biodegradation. Consequently, late spring and summer runoff can flush large amounts of these two compounds into reservoirs, where they can persist in the water column for long periods of time. Neither cyanazine nor desisopropylatrazine was detected in streams during the fall (table 2) because these compounds are no longer present in significant amounts on the agricultural fields where they were applied. This hypothesis points to the need for data on the half-lives of herbicides and insecticides in water. Virtually all available data on the half lives of herbicides are for soils. Water-column-half lives are particularly important with regard to the persistence of herbicides in reservoirs, lakes, and estuarine systems.

The spatial distribution of the detections of herbicides and metabolites in the 76 reservoirs is shown in figures 2 and 3 for the four sampling periods. These figures also show which reservoirs contained herbicides in concentrations that exceeded MCL's and/or health advisories

Table 2. - Herbicides analyzed and percent detections in Midwestern reservoirs during 1992, and in Midwestern streams during 1989.
[µg/L, micrograms per liter; ESA, ethanesulfonic acid metabolite of alachlor;; --, no data <, less than; N, number of samples]

		Percentage of detections greater than reporting limit:						
		76 Midwestern reservoirs in 1992				Midwestern streams in 1989		
Herbicide	Reporting limit (µg/L)	late April-mid-May	late June-early July	late August-early September	late October-early November	pre-application (N=55)	post-application (N=132)	fall low-flow (N=145)
alachlor	0.05	36	48	26	16	18	86	12
ametryn	.05	0	1	3	1	0	0	0
atrazine	.05	72	92	86	80	91	98	76
cyanazine	.05	49	65	56	46	--	--	--
	[1]0.2	25	40	33	26	5	63	0
desethyl-atrazine	.05	63	78	74	70	54	86	47
desisopropyl-atrazine	.05	58	70	63	62	9	54	0
metolachlor	.05	46	62	52	51	34	83	44
metribuzin	.05	12	9	5	0	2	53	0
prometon	.05	5	14	15	14	0	23	6
propazine	.05	2	10	5	1	0	40	<1
ESA	.1	72	79	77	64	--	--	--

[1]Reporting limit for Midwestern streams in 1989 was 0.2 µg/L. Percent detections for both reporting limits are given for data from 76 Midwestern reservoirs.

146

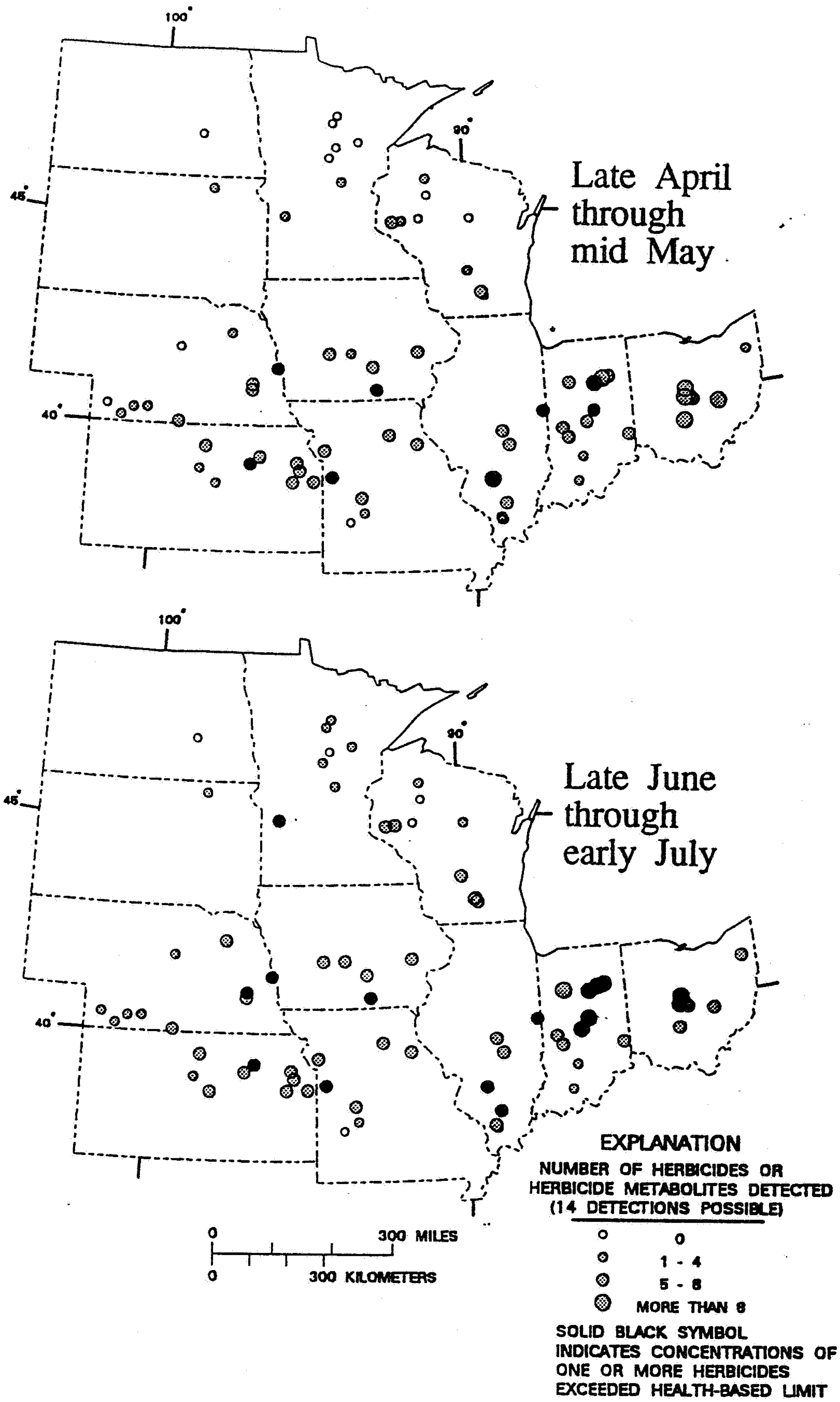

Figure 2.–Generalized distribution of herbicide detections in Midwestern reservoirs and reservoirs in which concentrations of one or more herbicides exceeded a U.S. Environmental Protection Agency maximum contaminant level or health-advisory level for drinking water during late April through mid May and late June through early July, 1992.

147

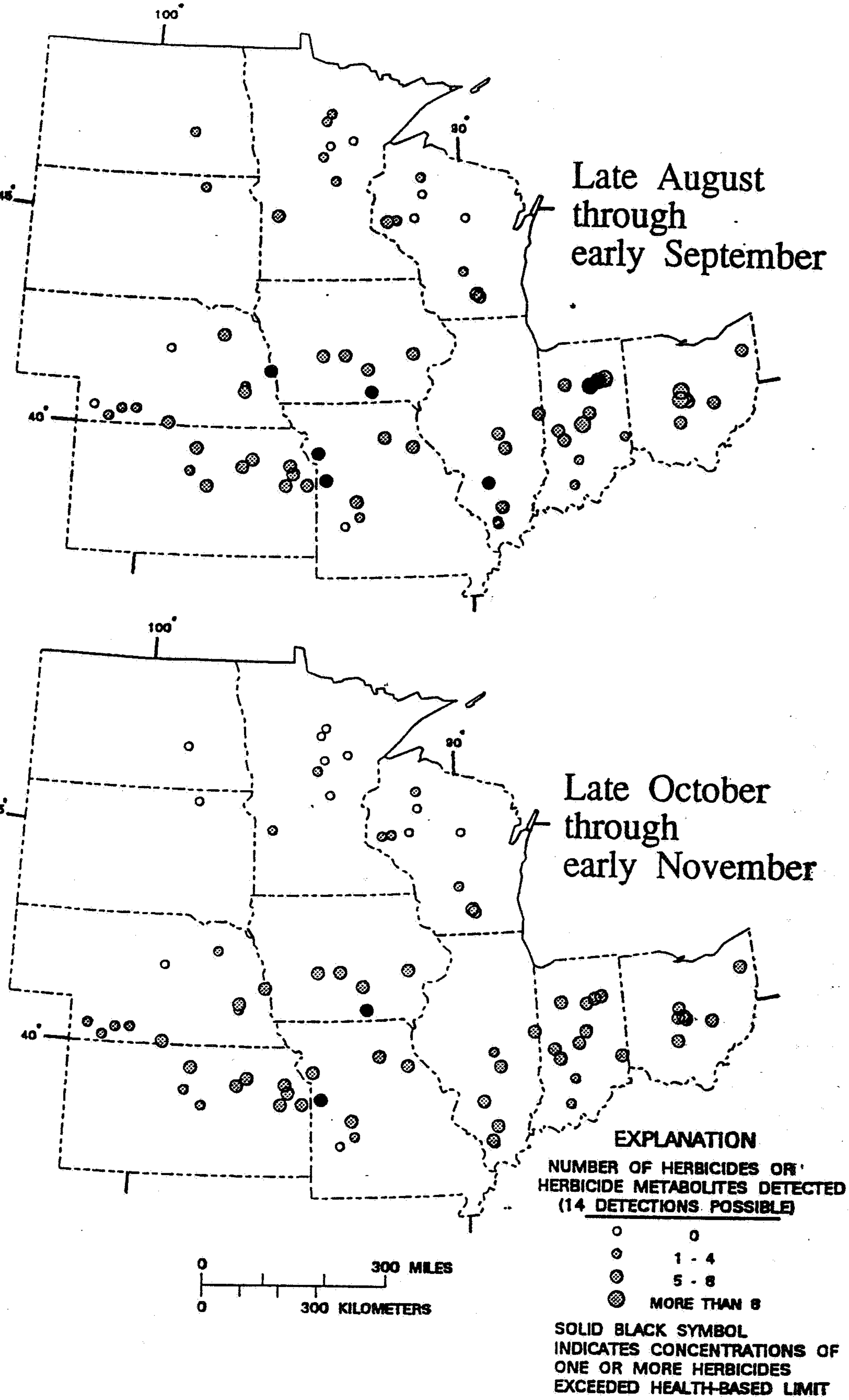

Figure 3.–Generalized distribution of herbicide detections in Midwestern reservoirs and reservoirs in which concentrations of one or more herbicides exceeded a U.S. Environmental Protection Agency maximum contaminant level or health-advisory level for drinking water during late August through early September and late October through early November, 1992.

148

(HA's) for drinking water. MCL's apply to average annual concentrations and are legally enforceable under the 1986 Safe Drinking Water Act, whereas HA's are not enforceable. Exceedence of MCL's or HA's is of concern because many Midwestern reservoirs are used for public water supply. Concentrations of one or more herbicides exceeded MCL's or HA's in 8 reservoirs during the first sampling period, in 16 reservoirs during the second sampling period (fig. 2), in 7 reservoirs in the third sampling period, and in 2 reservoirs during the fourth sampling period (fig. 3). More herbicides and metabolites were detected in reservoirs in areas where use of herbicides is most intense--that is, the area from eastern Kansas and Nebraska to Ohio (figs. 2 and 3).

One of the most significant findings from this study to date is the abundance and persistence of herbicide metabolites in reservoirs. Data are presently available from this study on two metabolites of atrazine (desethylatrazine and desisopropylatrazine) and one metabolite of alachlor, ethanesulfonic acid (ESA). The occurrence of atrazine metabolites in streams and their use as indicators of surface-water/ground-water interaction has been reported previously by Thurman and others (1991, 1992). The presence of ESA in ground water was recently reported by Baker and others (1993) and Kolpin and others (1993). However, the present reservoir study is believed to be the first systematic effort to investigate ESA in surface water. The frequency of detection was greatest for atrazine, followed by three metabolites, ESA, desethylatrazine, and desisopropylatrazine in the 76 reservoirs during the four sampling periods (table 2). The overall median concentrations of these four compounds followed the same order. Cyanazine, metolachlor, and alachlor were fifth, sixth, and seventh, respectively with respect to frequency of detection and median concentration. Previous studies have shown that the herbicide, alachlor is not very persistent in streams (Thurman and others, 1991, 1992; Goolsby and others, 1991) or in ground water (Kolpin and others, 1993). However, this does not appear to be the case for one of its metabolites, ESA, which apparently is both mobile and relatively persistent (stable) in surface water.

The temporal distribution of atrazine, alachlor, and three metabolites during the four reservoir sampling periods is shown in figure 4. Also shown for comparison purposes is the temporal distribution of these compounds (except ESA) during the 1989 reconnaissance of Midwestern streams (Thurman and others 1991, 1992). These results indicate that concentrations of atrazine and its metabolites in streams shortly after herbicide application are higher than in reservoirs. However, at other times of the year, concentrations are somewhat higher in the reservoirs, particularly concentrations of the two metabolites of atrazine. Desisopropylatrazine was detected infrequently in streams prior to application and not at all in the fall of the year (fig. 4). In contrast, this metabolite of atrazine was detected in 58 to 70 percent of all samples collected during the four reservoir-sampling periods. As hypothesized previously, the reason for this large difference in frequency of detection is probably the short half life for desisopropylatrazine in soil combined with its much longer half life in the water column, and long-term storage of this compound in the water mass within reservoirs.

With regard to alachlor there appears to be little difference between concentrations in streams and reservoirs except shortly after application when concentrations in streams are higher (fig. 4). Alachlor disappears rather quickly in streamflow and in reservoirs, consistent with data reported for Perry Lake in Kansas (Stamer and others, 1993). ESA appears to be a major soil

149

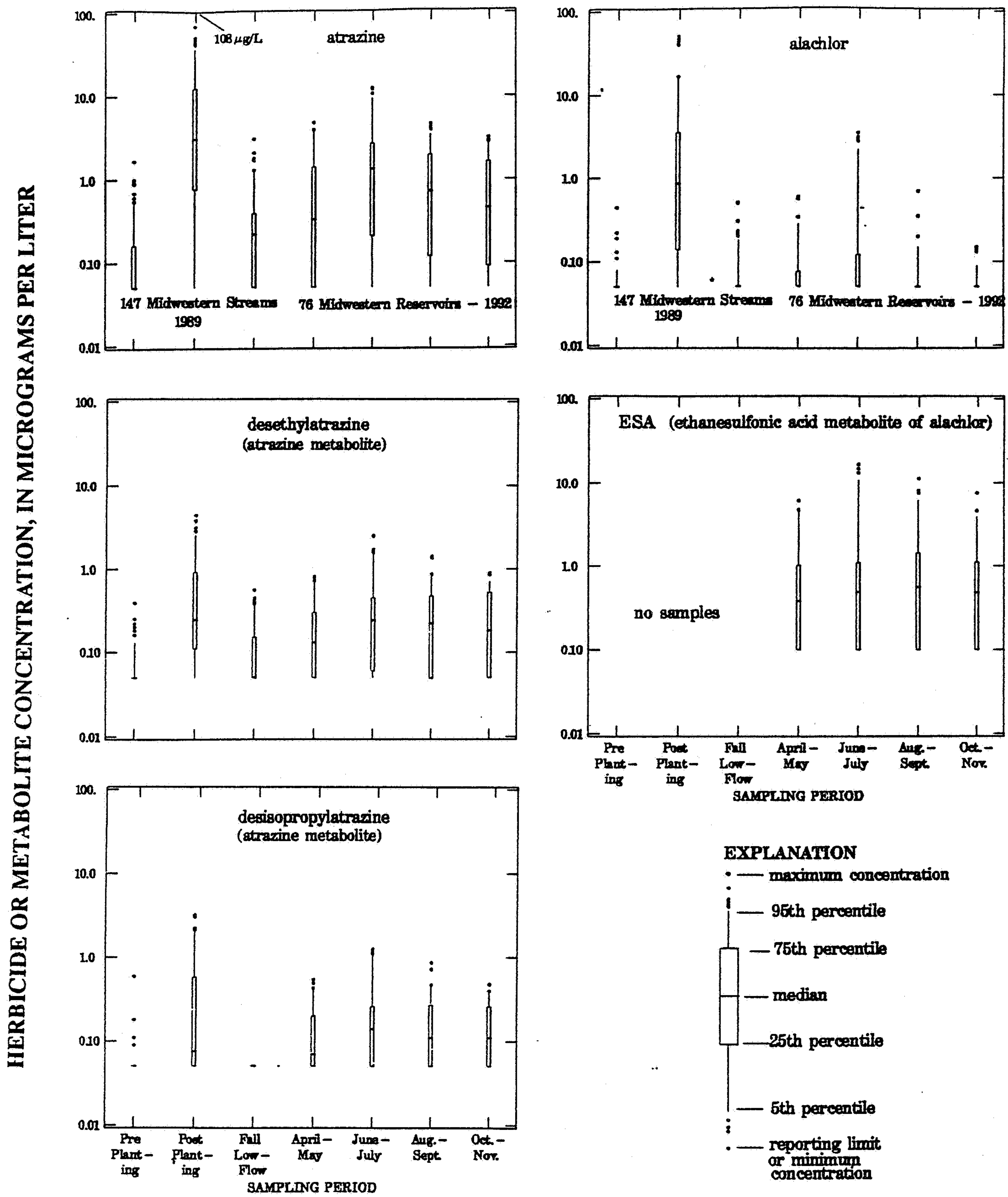

Figure 4.--Temporal distribution of atrazine, alachlor, and three metabolites in midwestern reservoirs during 1992 and in midwestern streams during 1989

150

metabolite of alachlor (Baker and others, 1993); however, it is not known whether significant degradation of alachlor to ESA occurs in the water column of streams and reservoirs. The ESA concentrations in reservoirs were similar during all four sampling periods (fig. 4).

Data on herbicide and nutrient concentrations, reservoir inflow and outflow (residence time), rainfall-patterns, pesticide use and land use will be available upon the completion of this study.

151

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152