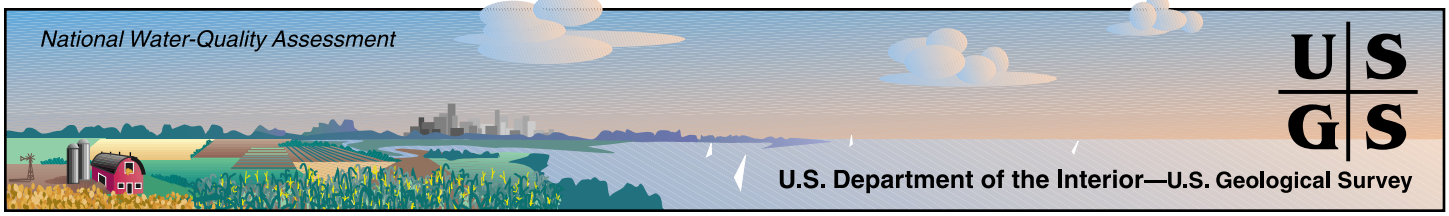
Fact Sheet FS-192-96



Pesticides in Ground Water in the Western Lake Michigan Drainages, Wisconsin and Michigan, 1983–1995

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Introduction

In 1991, the U.S. Geological Survey (USGS) began implementation of the National Water-Quality Assessment (NAWQA) Program. The long-term goals of the NAWQA Program are to describe the status and trends in the quality of a large, representative part of the Nation's surface- and ground-water resources, and to identify, describe, and explain, if possible, the major factors that affect the observed water quality (Hirsch and others, 1988). The program consists of study-unit investigations that include parts of most major river basins and aquifer systems in the country. The Western Lake Michigan Drainages study unit encompasses a 20,000-square-mile area in eastern Wisconsin and the Upper Peninsula of Michigan that drains to Lake Michigan and Green Bay (figure 1).

An important component of the NAWQA Program is the retrospective analysis of available water-quality data. One of the primary concerns in the Western Lake Michigan Drainages study unit is the effect of pesticides on ground-water quality. This fact sheet summarizes 32,064 synthetic-organic pesticide analyses and detections for ground-water samples collected from 4,155 wells in the study unit between 1983 and 1995 (figure 1 and table 1). The term pesticide in this fact sheet refers to both the parent product and its breakdown products, and includes herbicides, insecticides, and fungicides.

SUMMARY

- 32,064 pesticide analyses, including 117 different pesticides, were performed on ground-water samples collected from 4,155 wells in the Western Lake Michigan Drainages study unit between 1983 and 1995.
- In 29 percent of sampled wells, at least one pesticide was detected.
- Only 28 of 117 pesticides were detected.
- Of the 28 pesticides detected, 18 were found in less than 3 percent of the wells in which they were sampled.
- The triazine class of herbicides, which includes atrazine, atrazine breakdown products, cyanazine, simazine, and triazine screen results, were some of the most commonly analyzed for and detected pesticides.
- Other commonly sampled for and detected pesticides include alachlor and metolachlor (acetanilide herbicides).
- Detected pesticides generally were present in low concentrations.
- Of the pesticides with a drinking-water standard, only atrazine, atrazine breakdown products, and triazines (as determined by a triazine screen) exceeded a standard in more than 2 percent of the sampled wells.
- The highest triazine and acetanilide concentrations were generally observed in ground-water samples from the southwestern part of the study unit, which is predominated by agricultural land use and permeable surficial deposits.
- Limited analyses of pesticide breakdown products likely has resulted in underestimating the occurrence of pesticides in ground water in the study unit.

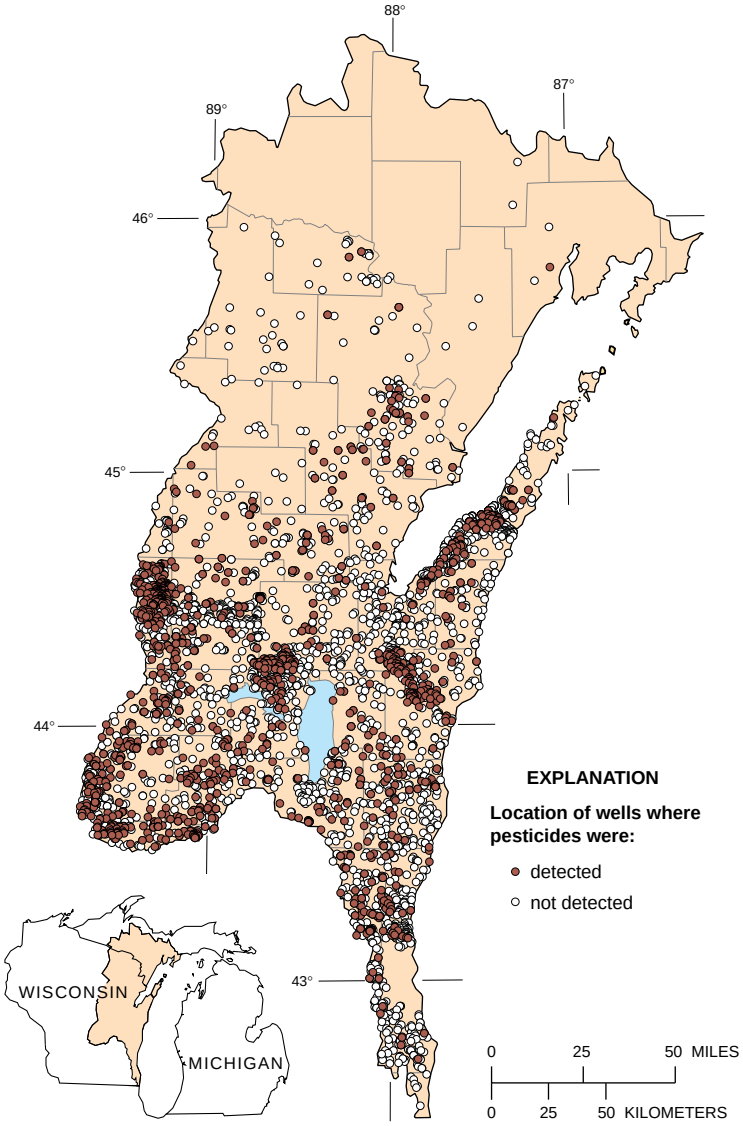

Figure 1. Location of the Western Lake Michigan Drainages NAWQA study unit and locations of wells sampled for pesticides.

Background

The total amounts and numbers of pesticides used in agricultural and nonagricultural settings in the United States have steadily increased since the early 1960's (Barbash and Resek, 1996). Pesticides have been detected throughout the hydrologic system and have been found in ground water in more than 43 states during the last two decades. They are commonly found in ground water below agricultural areas, but they have also been detected below nonagricultural areas, such as golf courses and residential areas.

Ground-water contamination by pesticides is a concern because ground water is used for drinking water by about 50 percent of the nation's population. Until the mid-1970's, it was generally assumed that the soil provided a barrier to pesticide contamination (Barbash and Resek, 1996), and this

perception was supported for many years by a lack of detections in sampled ground water. More recently, however, data from more than 300 studies nationwide show that pesticides from every major chemical class have been detected in ground water (Barbash and Resek, 1996). The increase in detections is likely due to improved analytical methods.

Numerous factors influence the susceptibility of ground water to contamination. For example, contamination is more likely in areas of high pesticide use, high ground-water recharge, high soil permeability, unconfined or unconsolidated aquifers, dug or driven wells, and wells with faulty construction.

Pesticides in Ground Water in the Western Lake Michigan Drainages

Synthetic-organic pesticides have been used extensively in the study unit for more than 30 years; application of herbicides to corn and soybeans have accounted for most of the use. Pesticides were first identified as a problem near the west-central part of the study unit in 1980 when aldicarb was detected in ground water near Stevens Point, Wisconsin (Wisconsin Department of Natural Resources, 1992). Since 1983, pesticide samples collected by the Wisconsin Department of Natural Resources (WDNR) and the Wisconsin Department of Agriculture, Trade and Consumer Protection (DATCP) have included analyses for aldicarb, in addition to many other pesticides. Historical pesticides in ground water data for the Western Lake Michigan Drainages study unit were obtained from three sources: WDNR, DATCP, and the USGS. The USGS data are from studies done as part of the NAWQA program and from an assessment of near-surface aquifers of the Midwestern U.S. (Kolpin and others 1996). The NAWQA ground-water data are from two agricultural land-use studies and a study of the Cambrian-Ordovician aquifer in the study unit.

During the period from 1983 to 1995, the number of wells sampled and the number of different pesticides analyzed for have steadily increased. A total of 117 pesticides have been analyzed in ground-water samples from the study unit, however, most were analyzed only a limited number of times and in a limited area. Only 28 of the 117 pesticides were detected in ground-water samples.

Most of the 28 pesticides detected in ground water in the study unit are herbicides used on corn, beans, cereal grains, and potatoes. Three of the detected pesticides—aldicarb, carbofuran, and terbufos—are insecticides. One of the detected breakdown products, p,p'-DDE, comes from the insecticide DDT which has been banned in the United States since 1972.

A triazine screen was the most common pesticide analysis in the study unit. It was performed on ground-water samples from about 71 percent (2,934 of 4,155) of the wells and accounted for about 12 percent (3,878 of 32,064) of all pesticide analyses. The triazine screen used for these samples uses the principle of enzyme-linked immunosorbent assay (ELISA) to determine the concentration of triazine herbicides such as atrazine, cyanazine, and simazine in a water sample. Results of the ELISA-analyzed samples will be referred to as triazines. Some other common pesticide analyses include alachlor, atrazine, atrazine breakdown products, cyanazine, metolachlor, and simazine. Historically, these have also been some of the most used pesticides in the study unit (Wisconsin Agricultural Statistical Service, 1986 and 1991).

Most of the pesticides listed in table 1 were not detected in any wells. Those detected were found in only a small percentage of the sampled wells and usually at low concentrations. Of the pesticides analyzed in samples from more than 100 wells, atrazine, deethyl atrazine (an atrazine breakdown product), prometon, and triazines were the only pesticides detected in more than 10 percent of sampled wells (table 2).

Drinking-water standards for some of the detected pesticides have been set by the U.S. Environmental Protection Agency (EPA) or by the State of

Table 1. Pesticides analyzed in ground water from sampled wells in the Western Lake Michigan Drainage Basin, 1983-1995. (Pesticides in red were detected in at least one well; —, no data)

Pesticide name Breakdown product	No. Wells	No. Analyses
2,4-D	493	557
2,4,5-T	100	100
2,4-DB	88	88
Acetochlor	88	88
Acifluorfen	88	88
Alachlor[1]	993	1,063
Alachor, -ESA [1]	1	1
Diethylaniline,2,6'-	88	88
Aldicarb	491	493
Aldicarb Sulfone	479	493
Aldicarb Sulfoxide	478	492
Aldrin[1]	403	425
Atrazine[1]	1,008	1,195
Atrazine, deethyl- [1]	1,300	2,800
Atrazine, deisopropyl- [1,2]	1,071	2,528
Atrazine, diamino- [1]	36	45
Benfluralin[1]	88	88
Bentazone	88	88
BHC, Alpha-[1]	94	94
BHC, Beta-	6	6
BHC, Delta-	6	6
BHC, Gamma-	393	418
Bromacil	88	88
Bromoxynil	88	88
Butachlor	389	410
Butylate[1]	106	109
Captan	2	2
Carbam	6	6
Carbaryl	483	498
Carbofuran	483	499
Carbofuran, 3-hydroxy-	88	88
Chloramben	92	92
Chlordane[1]	391	414
Chlordane, Alpha-	376	396
Chlordene[1]	—	—
Chlorothalonil[1]	94	94
Chlorpyrifos[1]	88	88
Clopyralid	88	88
Cyanazine[1]	416	493
Dacthal (DCPA)[1]	89	89
Dalapon	390	406
DDT[1]	8	8
DDD, p,p'-	6	6
DDE, p,p'-	94	94
Diazinon[1]	93	93
Dicamba	513	538
Dichlobenil[1]	88	88
Dichlorprop	88	88
Dieldrin[1]	501	537
Dimethoate[1]	1	1
Dinoseb	484	503
Disulfoton[1]	88	88
Diuron	88	88
DNOC	88	88
Endosulfan, Alpha[1]	6	6
Endosulfan Sulfate	6	6
Endothal	173	180
Endrin[1]	392	418
Endrin Ketone	13	13
Eptam[1] (EPTC)	109	114
Esfenvalerate	88	88
Ethalfluralin	88	88
Ethoprop	88	88
Fenuron	88	88
Fluometuron	88	88
Fonofos[1]	88	88
HCB[1]	395	417
Heptachlor[1]	392	418
Heptachlor -epoxide [1]	392	418
Imidan	2	2
Lindane[1]	95	95
Linuron[1]	92	92
Malathion[1]	88	88
MCPA	88	88
MCPB	89	89
Methamidaphos[1]	—	—
Methiocarb	89	89
Methomyl	495	513
Methoxychlor[1]	392	418
Metolachlor[1]	920	1,042
Metribuzin[1]	471	489
Molinate	88	88
1-Naphthol	88	88
Napropamide	88	88
Neburon	88	88
Norflurazon	88	88
Oryzalin	88	88
Oxamyl	480	494
Parathion[1]	1	1
Parathion, ethyl-	88	88
Parathion, methyl- [1]	88	88
PCNB[1]	—	—
Pebulate	88	88
Pendimethalin[1]	93	93
Pentachlorophenal (PCP)	391	409
Permethrin, cis-	88	88
Phorate[1]	91	91
Phthalates[1]	—	—
Picloram (Tordon)	481	511
Prometon[1]	111	119
Pronamide	88	88
Propachlor	88	88
Propanil	88	88
Propargite	88	88
Propham	88	88
Propoxur	89	89
Silvex	489	508
Simazine[1]	547	588
Tebuthiuron	88	88
Terbacil	89	89
Terbufos[1]	89	89
Thiobencarb	88	88
Toxaphene	392	410
Triallate	88	88
Triazines	2,934	3,878
Triclopyr	88	88
Trifluralin[1]	88	88
Total	**4,155**	**32,064**

[1] The number of wells sampled and number of analyses performed does not include results of samples analyzed by DATCP and WDNR gas chromatography analyses for which the pesticide was not deteded; therefore, additional samples may have been collected and additional analyses performed which are not accounted for here.

[2] Deisopropyl atrazine can be a breakdown product of atrazine, cyanazine, or simazine.

Table 2. Pesticides detected in water from sampled wells in the Western Lake Michigan Drainages, 1983–1995. (na, not applicable; —, no data; µg/L, micrograms per liter; PAL, Preventive Action Limit; ES, Enforcement Standard)

Pesticide or breakdown product (Number of wells for which samples were analyzed for the pesticide)	Percent of wells with detects	PAL (µg/L)	Percent of wells with detects above PAL	ES (µg/L)	Percent of wells with detects above ES	Maximum concentr-ation detected (µg/L)
Total number of wells (4,155)	29	na	na	na	na	1,000
Alachlor[1] (993)	3.4	.2	0.9	2.0	0.9	70
Alachlor -ESA[1] (1)	100	—	—	—	—	4.0
Diethylaniline, 2,6'- (88)	1.1	—	—	—	—	.003
Aldicarb (491)	.2	2	0	10	0	1.7
Atrazine[1] (1,008)	19	.3	10	3.0	2.7	1,000
Atrazine, deethyl-[1] (1,300)	11	.3	6.9	3.0	.4	1 1
Atrazine, deisopropyl-[1] (1,071)	2.1	.3	1.0	3.0	0	1.4
Atrazine, diamino-[1] (36)	8.3	.3	8.3	3.0	0	1.1
Butylate[1] (106)	.9	6.7	0	67	0	2.9
Carbofuran (483)	.4	8	0	40	0	.012
Cyanazine[1] (416)	2.2	1.5	1.7	12.5	.2	1 10
Dacthal[1] (89)	1.1	—	—	—	—	.001
DDE p,'p- (94)	6.4	—	—	—	—	.002
Dicamba (513)	1.4	60	0.4	300	0.2	360
Dichlobenil[1] (88)	1.1	—	—	—	—	.06
Eptam[1] (109)	.9	50	0	250	0	2.7
Linuron[1] (92)	2.2	—	—	—	—	34
Metolachlor[1] (920)	3.0	1.5	1.0	15	.2	24
Metribuzin[1] (471)	1.3	50	0	250	0	.54
Picloram (481)	.2	100	0	500	0	1.3
Prometon[1] (111)	18.9	—	—	—	—	4.8
Silvex (489)	2.3	10	0	10	0	.1
Simazine[1] (547)	3.2	.4	.6	4.0	0	1.2
Tebuthiuron (88)	1.1	—	—	—	—	.019
Terbacil (89)	1.1	—	—	—	—	1.5
Terbufos[1] (89)	1.1	—	—	—	—	52
Triallate (88)	2.3	—	—	—	—	.002
Triazines (2,934)	29	.3	8.0	3.0	.7	24

[1] Percentage of wells with detects may be less than indicated because the number of wells sampled does not include results of gas chromatography analyses by DATCP and WDNR for which the pesticide was not detected.

Wisconsin, or both. Wisconsin drinking-water Preventive Action Limits (PAL) and Enforcement Standards (ES) are included in table 2 because most of the data from the study unit are from samples collected in Wisconsin. Wisconsin also provides a more extensive list of standards than does the EPA. Atrazine, several atrazine breakdown products, and triazines (using the drinking-water standards for atrazine), were the only pesticides that exceeded a drinking-water standard in more than two percent of sampled wells. Atrazine had the highest percentage of exceedances for the PAL (10 percent) and the ES (2.7 percent), as well as the highest measured concentration [1,000 µg/L (micrograms per liter)] of all the detected pesticides.

Triazine-screen analyses were performed on water samples from much of the study unit and provided semi-quantitative information about where some of the most commonly used pesticides were detected in ground water. Triazines were detected predominately in the southern half of the study unit (fig. 2), where there is a large percentage of agricultural land. Concentrations greater than 0.3 µg/L were detected in many parts of the study unit; however, concentrations greater than 3.0 µg/L were detected primarily in the southwest, where agriculture predominates and surficial deposits are very permeable.

Some of the most commonly used non-triazine pesticides in the study unit are the acetanilide herbicides, which include alachlor and metolachlor. Wells with detectable alachlor and metolachlor are located predominately in the southern half of the study unit, with the highest concentrations generally located in the southwest (fig. 3), similar to the spatial distribution of triazines.

Data from the Western Lake Michigan Drainages show similar pesticides detected and percent of samples with detections as the study of near-surface aquifers in the Midwestern United States (Kolpin and others, 1996). Percentages of detections for alachlor, cyanazine, and simazine in the near-surface Midwestern aquifers were within one percent of those for the Western Lake Michigan Drainages. Atrazine detections in the two study areas were within four percent.

Pesticide breakdown products often are found in ground water (Kolpin and others, 1996). Breakdown products from alachlor, atrazine, cyanazine, and dacthal were detected in the near-surface aquifer study ground-water samples more often than the parent pesticides (Kolpin and others, 1996). For example, alachlor was detected in only about 3 percent of water samples from near-surface aquifers, yet alachlor-ESA, a breakdown product of alachlor, was detected in about 46 percent of samples. Additionally, the maximum concentration of alachlor-ESA was nearly twice as high as the highest concentration of alachlor. Alachlor has been one of the most widely used pesticides in the Western Lake Michigan Drainages, and was detected in 2.3 percent of the wells for which it was analyzed, yet alachlor-ESA was rarely analyzed. Some breakdown products are structurally and toxicologically similar to the parent pesticides and they should also be considered important for their environmen-

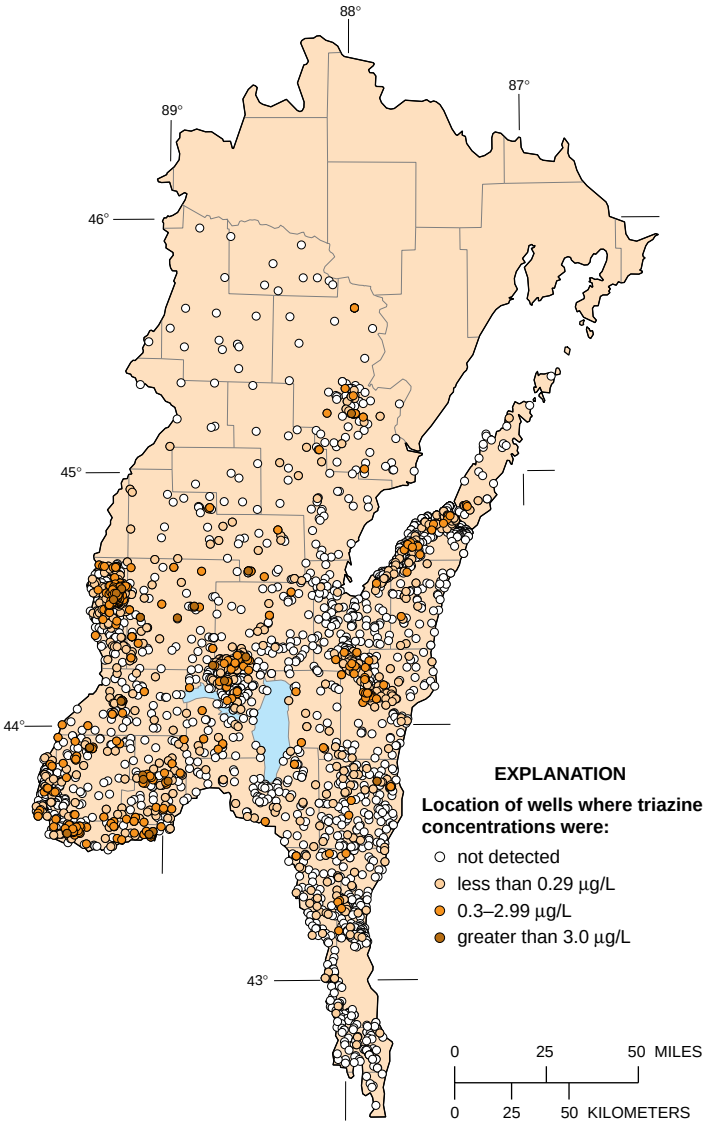

Figure 2. Spatial distribution of triazine concentrations in ground water from sampled wells in the study unit (if a well had multiple triazine analyses, only the highest concentration is shown).

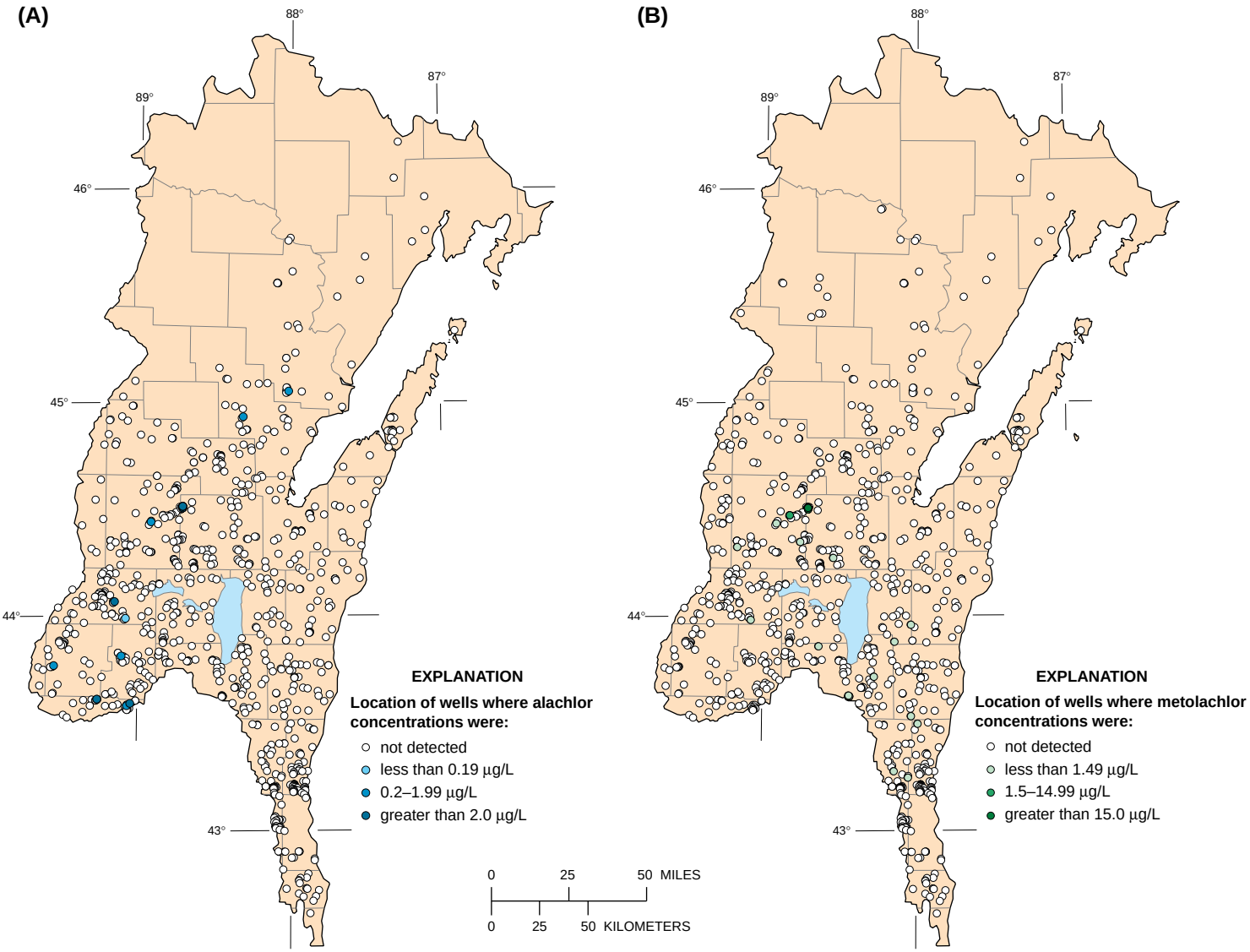

Figure 3. Spatial distribution of (A) alachlor and (B) metolachlor concentrations in ground water from sampled wells in the study unit (if a well had multiple alachlor or metolachlor analyses, only the highest concentration is shown).

tal occurrence (Kolpin and others 1996). Because samples have rarely been analyzed for breakdown products, pesticide occurrences in ground water have likely been underestimated in the study unit in the past. As more is learned about the toxicity of these compounds and their effects, and as detection methods become more refined, our ability to assess pesticide effects on ground-water quality will improve.

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