

Ground-Water Quality and Vulnerability to Contamination in Selected Agricultural Areas of Southeastern Michigan, Northwestern Ohio, and Northeastern Indiana

Water-Resources Investigations Report 00-4146



U.S. Department of the Interior
U.S. Geological Survey

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By Mary Ann Thomas

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U.S. Department of the Interior
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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square mile	2.590	square kilometer
acre	0.4047	square hectometer (hectare)
ton	0.4536	kilogram
gallon per minute (gal/min)	3.785	liter per minute
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second
cubic foot per day (ft ³ /d)	0.02832	cubic meter per day
million gallons per day (Mgal/d)	0.04381	cubic meter per second

Temperature: Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$^{\circ}\text{F} = 1.8 (^{\circ}\text{C}) + 32$$

Abbreviated water-quality units used in this report: Chemical concentrations and water temperature are given in metric units. Chemical concentration in water is given in milligrams per liter (mg/L), micrograms per liter (µg/L), or milliequivalents per liter (meq/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is approximately the same as for concentrations in parts per million. Milliequivalents per liter is derived from the concentration in milligrams per liter, multiplied by the reciprocals of the combining weights of the ions of interest.

Concentration of organic carbon in till is given in milligrams of constituent per kilogram of sample (mg/kg).

Radioactivity is expressed in picocuries per liter (pCi/L). A picocurie is one-trillionth (1×10^{-12}) the amount of radioactivity represented by a curie (Ci). A curie is the amount of radioactivity that yields 3.7×10^{10} radioactive disintegrations per second. A picocurie yields 2.22 disintegrations per minute. Tritium concentration is expressed in tritium units (TU). One tritium unit is equal to one tritium atom per 10^{18} hydrogen atoms; in terms of radioactivity, it is equivalent to 3.24 picocuries per liter.

Ground-water quality and vulnerability to contamination in selected agricultural areas of southeastern Michigan, northwestern Ohio, and northeastern Indiana

by Mary Ann Thomas

Abstract

Ground-water quality was assessed in the north-eastern part of the Corn Belt, where tile-drained row crops are underlain by fractured glacial till. Data were collected from 30 shallow monitor wells and 18 co-located domestic wells as part of the U.S. Geological Survey's National Water-Quality Assessment in the Lake Erie-Lake St. Clair Basin.

Pesticides or pesticide degradates were detected in 41 percent of the monitor wells and 6 percent of the domestic wells. The pesticides detected closely correspond to those most heavily applied—herbicides used on corn and soybeans. Pesticide degradates were detected three times more frequently, and at higher concentrations, than were parent compounds. No pesticide concentration exceeded a USEPA Maximum Contaminant Level (MCL), but MCL's have not been established for 9 of the 11 compounds detected.

Thirty-seven percent of monitor-well samples had nitrate concentrations indicative of human influences such as fertilizer, manure or septic systems. Nitrate was the only chemical constituent detected at a concentration greater than an MCL. The MCL was exceeded in 7 percent of samples from monitor wells which were too shallow to be used as a source of drinking water.

Pesticide and nitrate concentrations in the study area are low relative to other agricultural areas of the Nation. Several authors have suggested that ground water in parts of the Upper Midwest is minimally contaminated because it is protected by the surficial glacial till or tile drains. These ideas are examined in light of the relations between concentration, well depth, and ground-water age in the study area.

Most of the shallow ground water is hydraulically connected to the land surface, based on the observations that 83 percent of waters from monitor wells were recharged after 1953, and 57 percent contained a pesticide or an elevated nitrate concentration. Fractures or sand-and-gravel stringers within the till are the probable pathways.

In some areas, deeper parts of the ground-water-flow system are also hydraulically connected to the land surface. Almost half the waters from wells 50 to 100 feet deep were recharged after 1953. Anthropogenic constituents were detected in samples from three domestic wells 60 to 121 feet deep, in areas where the till is relatively coarse-grained.

The hydrogeologic system has several geochemical characteristics conducive to transformations or sorption of nitrate or pesticides: (1) the till is clay-rich, has a high organic-carbon content, and contains an abundance of pyrite-rich shale fragments, (2) the ground water has low dissolved-oxygen concentrations, and (3) iron and

manganese oxides and oxyhydroxides line the faces of fractures in the unsaturated zone.

Although the aquifer system appears to be protected from contamination in some areas, the fact that the surficial till is heterogeneous and of variable thickness suggests that the protection is not uniform. The protection can be breached by fractures or sand-and-gravel stringers, which are apparent in core samples but not noted on domestic-well logs.

Introduction

The effects of agricultural land use on water quality have been investigated as part of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) program. The Lake Erie-Lake St. Clair Basin is the focus of one of these NAWQA studies. The northwestern part of the basin (fig. 1) includes part of the midwestern Corn Belt, where rates of fertilizer and pesticide use are among the highest in the country (Mueller and Helsel, 1996; Barbash and others, 1999). In this area, the potential for agrichemicals to affect ground-water quality is a concern because domestic wells are the primary source of drinking water. Although heavy use of agrichemicals is a logical basis for concern, preliminary data from NAWQA studies throughout the country indicate that ground water in parts of the Upper Midwest is minimally contaminated by nitrate and pesticides, presumably because ground water is protected by the surficial glacial till and (or) widespread tile drainage (Mueller and others, 1995; Mueller and Helsel, 1996; Barbash and others, 1999; U.S. Geological Survey, 1999).

This report is based on data from two NAWQA studies done in the Lake Erie-Lake St. Clair Basin in 1998. The report has three goals. The first is to describe ground-water quality at a range of depths and locations within an agricultural area underlain by till. The focus is on comparing ground-water quality to U.S. Environmental Protection Agency (USEPA) drinking-water standards and to state well-depth requirements.

The second goal is to present evidence as to whether the study area is linked to those parts of the Upper Midwest where the ground water is minimally contaminated by agrichemicals. This will be accomplished by comparing nitrate and pesticide detection

frequencies in the study area to those of comparable studies in other agricultural areas.

The third goal is to use the relations between concentration, well depth, and ground-water age to refine our understanding of how vulnerable ground water is to the effects of agricultural land use.

Study design and methods

Water quality was assessed in shallow ground water from monitor wells and in deeper ground water from domestic wells. NAWQA guidelines were followed for defining the extent of the study area (Gilliom and others, 1995); selecting sampling sites within the study area (Scott, 1990); installing monitor wells (Lapham and others, 1995); and collecting water-quality, quality-control, and ancillary data (Koterba and others, 1995).

Agricultural land-use study

The goal of a NAWQA agricultural land-use study is to determine how agricultural land use affects shallow ground-water quality. NAWQA guidelines state that land-use studies should be located in areas that are relatively homogenous in terms of factors that affect water quality. In the northwestern part of the Lake Erie-Lake St. Clair Basin, those factors were judged to be land use, surficial geology, and bedrock geology. Therefore, the extent of the study was limited to areas that meet all of the following criteria: (1) the land use is predominantly agricultural, and the primary crops are corn and soybeans (fig. 2A), (2) the glacial sediment is more than 100 ft thick, and consists of till at the land surface (fig. 2B), and (3) the underlying bedrock is interbedded shale and sandstone of Mississippian age (fig. 2C). These criteria are met in a noncontiguous, 1,647-mi² area of southeastern Michigan, northwestern Ohio, and northeastern Indiana.

Within the study area as defined, sites were randomly selected for installation of monitor wells. At each potential well site, field reconnaissance verified that the land use was predominantly agricultural, and domestic well logs were used to verify that the surficial sediment was till.

A network of 30 monitor wells was installed during the summer of 1997. The goal was to screen the wells just below the water table. To accomplish this,

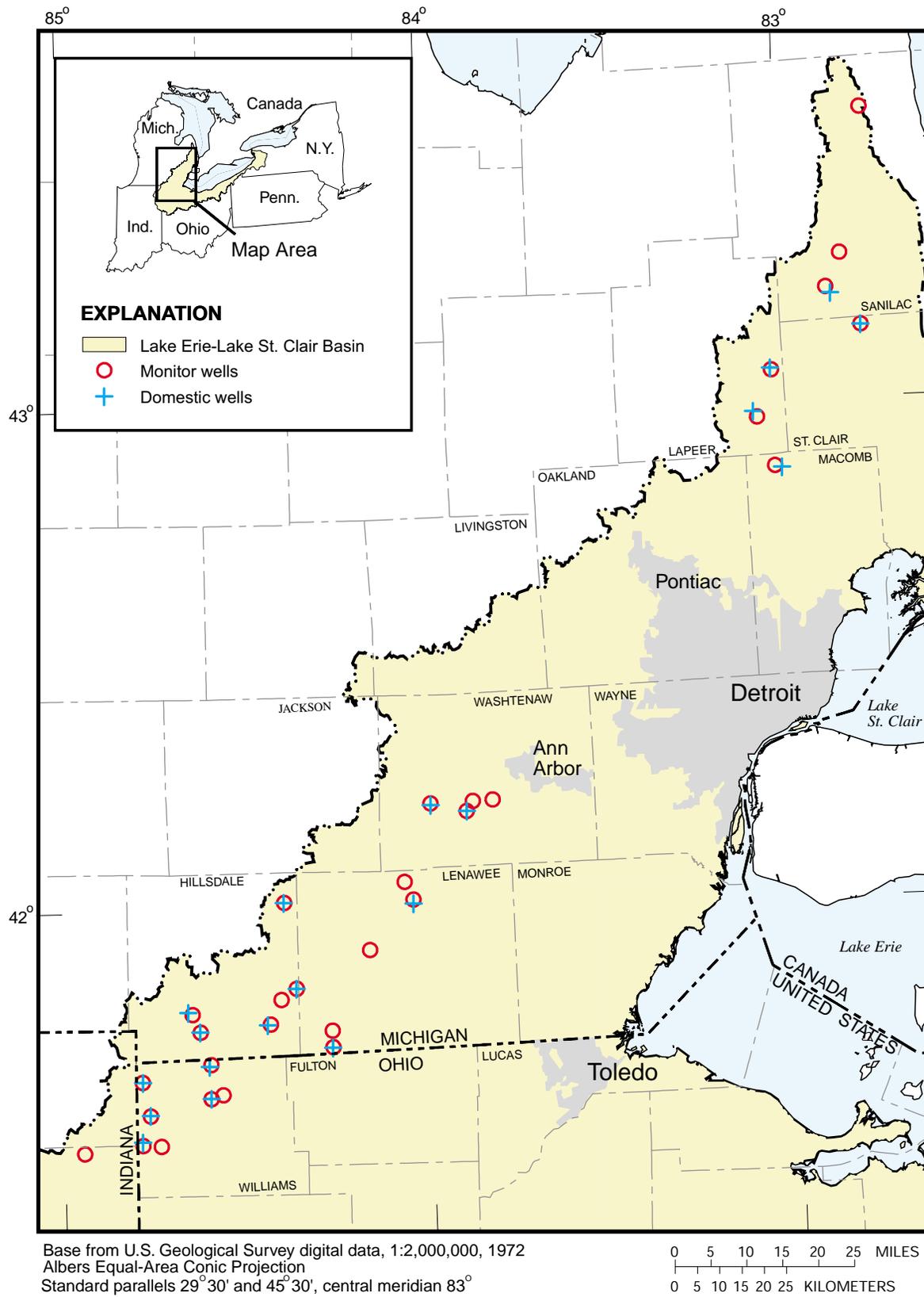


Figure 1. Location of NAWQA well networks in agricultural areas of the Lake Erie-Lake St. Clair Basin

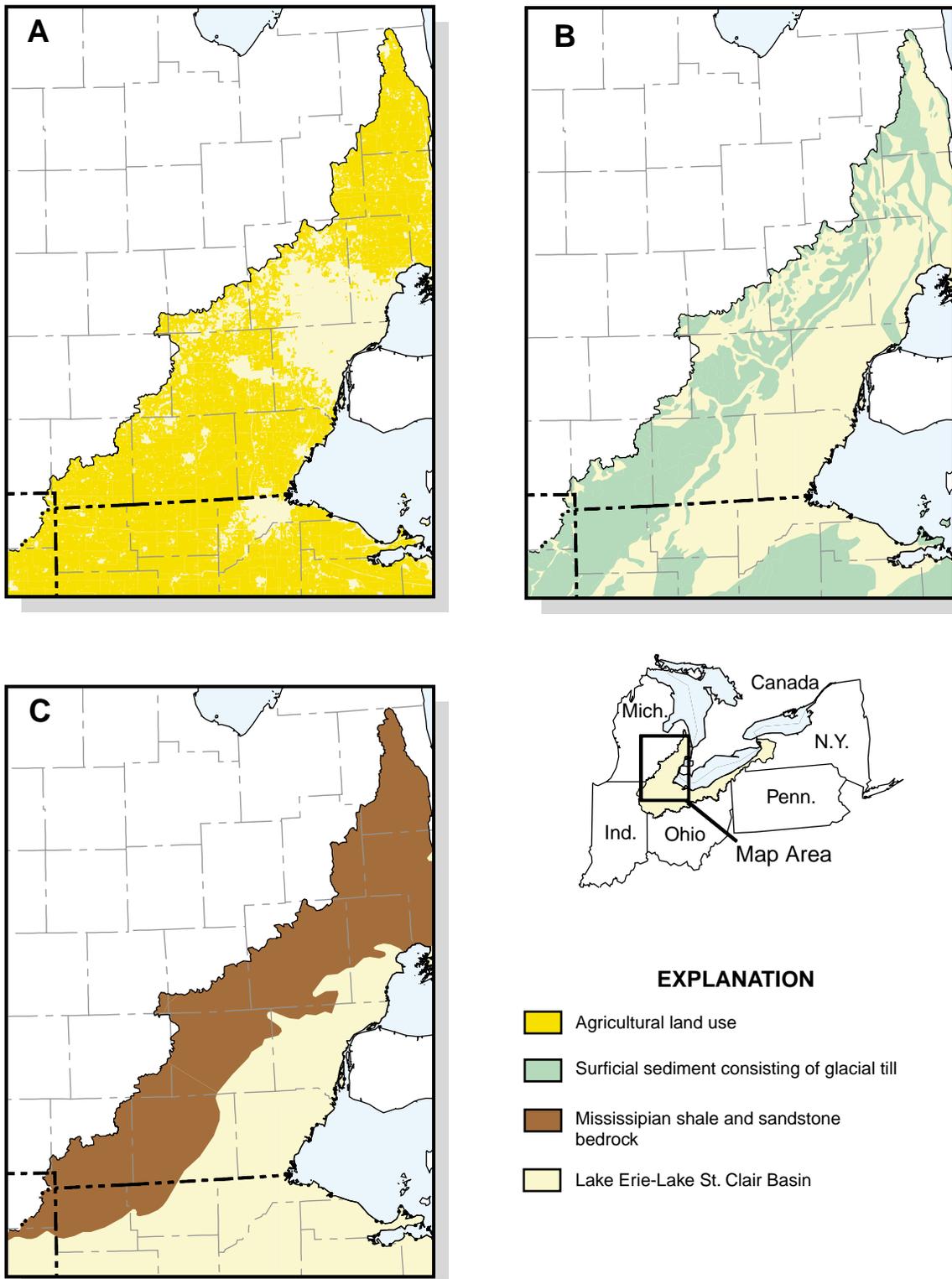


Figure 2. Factors used to define agricultural land-use study area: (A) land use, (B) surficial geology, and (C) bedrock geology.

boreholes were drilled through the unsaturated surficial till, and well screens were set in the shallowest saturated sand-and-gravel stringer estimated to be capable of producing a volume of water sufficient for sampling. These coarse-grained stringers were commonly only a few inches thick and were not identified on domestic well logs. At all sites, a thin stringer of sand and (or) gravel was present less than 20 ft below the top of the saturated zone. The median depth of the 30 monitor wells is 18 ft, and the range is 9 to 34 ft (table 1). Sediment cores were collected during well installation. Four-inch-diameter cores were retrieved

from depths of 4 ft below land surface to the bottom of the well. Lithology was described, and representative samples were analyzed for organic carbon content.

Three casing volumes were purged from the wells before sampling. Approximately two-thirds of the wells were slow to recharge; therefore, these wells were purged on a series of visits spaced over a period of several weeks or months. In addition, at least one casing volume was purged immediately before sampling. The well network was sampled in the early summer of 1998. Samples were analyzed for major ions,

Table 1. Characteristics of ground-water-quality studies and wells in the northwestern part of the Lake Erie-Lake St. Clair Basin, 1998 [ft, feet; VOC's, volatile organic compounds; PVC, polyvinyl chloride]

Agricultural land-use study		Domestic wells from agricultural areas of the subunit survey
Study characteristics		
Goal of study	Assess how agricultural land use affects shallow ground-water quality.	Assess the quality of ground water used for drinking water in an agricultural area.
Sampling network	30 monitor wells installed by USGS following NAWQA protocols (Lapham and others, 1995).	18 domestic wells co-located with the monitor wells sampled for the Agricultural Land-Use Study.
Depth of wells	Median: 18 ft Range: 9 to 34 ft	Median: 90 ft Range: 31 to 158 ft
Horizon sampled	Shallowest saturated sand-and-gravel stringer within glacial till.	Sand-and-gravel aquifer overlain by glacial till.
Sampling date	May to July 1998	May to August 1998
Sample collection	Collected with submersible pump. Followed NAWQA protocols for collection, filtration, and preservation (Koterba and others, 1995).	Collected from outside tap before water softener. Followed NAWQA protocols for collection, filtration, and preservation (Koterba and others, 1995).
Laboratory, analyses, and analytical methods	USGS National Water Quality Laboratory: <ul style="list-style-type: none"> – Major ions (Fishman and Friedman, 1989) – Nutrients (Fishman and Friedman, 1989) – Pesticides (Zaugg and others, 1995; Werner and others, 1996) – Tritium (Ostland and Dorsey, 1977) – Dissolved organic carbon (Brenton and Arnett, 1993) USGS Organic Chemistry Lab: <ul style="list-style-type: none"> – Pesticides and degradates (Zimmerman and Thurman, 1999; Hostetler and Thurman, 2000) 	USGS National Water Quality Laboratory: <ul style="list-style-type: none"> – Major ions (Fishman and Friedman, 1989) – Nutrients (Fishman and Friedman, 1989) – Pesticides (Zaugg and others, 1995) – Tritium (Ostland and Dorsey, 1977) – Dissolved organic carbon (Brenton and Arnett, 1993) – VOC's (Connor and others, 1998) – Radon (American Society for Testing and Materials, 1996) USGS Organic Chemistry Lab: <ul style="list-style-type: none"> – Pesticides and degradates (Zimmerman and Thurman, 1999; Hostetler and Thurman, 2000)
Well characteristics		
Year of construction	1997	1969-98
Length of screen	5 ft	3 to 8 ft
Casing material	PVC	PVC (14); galvanized steel (4)
Grouted?	Yes	Yes (11); no (7)

nutrients, tritium, dissolved organic carbon, pesticides, and pesticide degradates (tables 1 and 2).

Subunit survey

The goal of a NAWQA subunit survey (SUS) is to assess the water quality of an aquifer that is an important source of drinking water. In the northwestern part of the Lake Erie-Lake St. Clair Basin, thick lenses or layers of sand and gravel within the glacial deposits are the primary source of water to domestic wells.

The SUS sampling network consists of 28 domestic wells. The study area for the SUS was defined to coincide with that of the agricultural land-use study in terms of surficial sediment (fig. 2B) and bedrock geology (fig. 2C). Land use was not a factor used to define the extent of the SUS; however, approximately two-thirds of the SUS study area consists of row-crop agriculture. In agricultural areas, the SUS domestic wells were co-located with the randomly selected monitor wells installed for the agricultural land-use study. Of the 28 domestic wells sampled, 18 are co-located with monitor wells in agricultural areas (fig. 1, fig. 3).

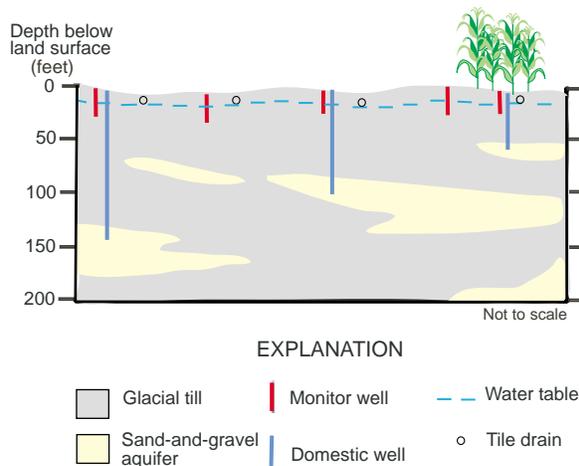


Figure 3. Simplified section showing relation of monitor and domestic wells to hydrogeologic setting.

The domestic wells were sampled during the summer of 1998. A minimum of three casing volumes were purged from the wells immediately prior to sampling. Samples of untreated water were collected and analyzed for major ions, nutrients, tritium, dissolved organic carbon, pesticides, pesticide degradates, volatile organic compounds (VOC's), and radon (tables 1 and 2).

Description of study area

The study area is part of the Eastern Lake Section of the Central Lowlands Physiographic Province, where the topography ranges from nearly flat-lying land to low-relief rolling hills (Casey and others, 1997). Mean annual air temperature is approximately 45 to 48°F, and mean annual precipitation is approximately 28 to 38 in. (Casey and others, 1997). Precipitation is highest in May, June, and July and lowest in January and February (Casey and others, 1997).

Land use

The predominant land use is row-crop agriculture, and the predominant crops are corn, soybeans and small grains, which are planted in rotation. Small, scattered herds of livestock, farmhouses, rural homes, and small towns also occur in the study area.

Almost all of the cultivated land is artificially drained by a widespread, long-standing network of tile drains and ditches. Subsurface tile drains, typically set about 3 ft deep, discharge to streams or drainage ditches. Some of the natural streams are managed as agricultural drainage ditches.

Hydrogeology

Domestic wells are typically 50 to 150 ft deep and produce water from discontinuous layers of sand and gravel that are present at various depths within the glacial till (fig. 3). Collectively, these layers of sand and gravel are considered to be an aquifer system that is variably confined (Fleming, 1994). The aquifer system is recharged primarily by infiltration of precipitation. Ground water discharges to wells, tile drains, agricultural ditches, streams, wetlands, and small lakes. Regional ground-water discharge is to major rivers and ultimately to Lake Erie.

The aquifer system is overlain by till, an unsorted glacial deposit. The study area includes tills from two glacial lobes; Erie Lobe tills are typically clayey, and those of the Saginaw Lobe can be sandy or contain small lenses of sand and gravel (Fleming and others, 1994). At most of the monitor-well sites (24 of 30), the till consists of a dense mixture of silt, clay, and gravel interspersed with one or more thin stringers of sand and gravel. The surficial till is saturated at depths of approximately 5 to 15 ft below land surface, and the unsaturated till contains fractures, root traces, and

Table 2. Pesticides analyzed in samples from monitor and domestic wells, northwestern part of the Lake Erie-Lake St. Clair Basin, 1998

[MDL, Method detection limit in micrograms per liter; degradates are in italics]

Compound	MDL	Compound	MDL	Compound	MDL
Pesticides, monitor and domestic wells					
USGS National Water Quality Laboratory:					
Acetochlor	0.002	Eptam	0.002	Pendimethalin	0.004
Alachlor	.002	Ethalfuralin	.004	Permethrin	.005
Atrazine	.001	Ethoprop	.003	Phorate	.002
Benfluralin	.002	Fonofos	.003	Prometon	.018
Butylate	.002	<i>HCH, alpha</i>	.002	Pronamide	.003
Carbaryl	.003	Lindane	.004	Propachlor	.007
Carbofuran	.003	Linuron	.002	Propanil	.004
Chlorpyrifos	.004	Malathion	.005	Propargite	.013
Cyanazine	.004	Methyl azinphos	.001	Simazine	.005
Dacthal	.002	Methyl parathion	.001	Tebuthiuron	.01
<i>DDE</i>	.006	Metolachlor	.006	Terbacil	.007
<i>Deethylatrazine</i>	.002	Metribuzin	.002	Terbufos	.013
Diazinon	.002	Molinate	.004	Thiobencarb	.002
Dieldrin	.001	Napropamide	.004	Triallate	.001
<i>Diethylaniline, 2'6-</i>	.003	Parathion	.003	Trifluralin	.002
Disulfoton	.017	Pebulate	.004		
USGS Organic Chemistry Laboratory:					
Acetochlor	0.05	<i>Deethylatrazine</i>	0.05	Metribuzin	0.05
<i>Acetochlor ESA</i>	.20	<i>Deisopropylatrazine</i>	.05	Prometon	.05
<i>Acetochlor OA</i>	.20	<i>Hydroxyatrazine</i>	.05	Prometryn	.05
Alachlor	.05	Cyanazine	.20	Propachlor	.05
<i>Alachlor ESA</i>	.20	Cyanazine amide4	.05	Propazine	.05
<i>Alachlor OA</i>	.20	Metolachlor	.05	Simazine	.05
Amethryn	.05	<i>Metolachlor ESA</i>	.20	Terbutryn	.05
Atrazine	.05	<i>Metolachlor OA</i>	.20		
Additional pesticides, monitor wells only					
USGS National Water Quality Laboratory:					
2,4,5-T	0.035	Clopyralid	0.05	Methiocarb	0.026
2,4-D	.035	Dacthal, MA	.017	Methomyl	.017
2,4-DB	.035	Dicamba	.035	<i>1-Naphthol</i>	.007
Acifluorfen	.035	Dichlobenil	.02	Neburon	.015
Aldicarb	.016	Dichlorprop	.032	Norflurazon	.024
<i>Aldicarb sulfone</i>	.016	Dinoseb	.035	Oryzalin	.019
<i>Aldicarb sulfoxide</i>	.021	Diuron	.02	Oxamyl	.018
Bentazon	.014	DNOC	.035	Picloram	.05
Bromacil	.035	Esfenvalerate	.019	Propham	.035
Bromoxynil	.035	Fenuron	.013	Propoxur	.035
<i>Carbofuran, 3-hyd</i>	.014	Fluometuron	.035	Silvex	.021
Chloramben	.011	MCPA	.05	Triclopyr	.05
Chlorothalonil	.035	MCPB	.035		

horizontal partings. At 6 of the 30 sites, the till is visibly more coarse grained, and fractures in the unsaturated zone were not observed in 4-in.-diameter cores.

Recharge to the aquifer system occurs through the surficial till by (1) migration along near-vertical fractures, (2) diffusion through the till matrix, (3) migration through sand-and-gravel deposits hydraulically connected to the land surface, or (4) any combination of these processes. Characteristics of the till influence the chemistry of the water and the efficiency of the hydraulic connection between the land surface and ground water.

Drillers' logs from co-located domestic and monitor wells in Williams County, Ohio, are shown in figure 4. The domestic well is screened in a thick layer of gravel at a depth of 57 ft (fig. 4A). The monitor well is screened in a sand-and-gravel stringer within the till at a depth of 30 ft (fig. 4B).

Figure 4C is a description of the sediment from a 4-in.-diameter core retrieved during installation of the monitor well. The characteristics of the glacial till at this site are representative of the till at most of the sites in the study area (24 of 30). In addition, the till is similar to that in southwestern Ontario (Ruland and others, 1991), northeastern Indiana (Fleming, 1994), and western Ohio (Strobel, 1993).

The upper part of the till is weathered. Below the soil zone, the till matrix is light orangeish brown. In southwestern Ontario, this color has been attributed to the alteration of chlorite (Ruland and others, 1991). Near-vertical fractures are prominent and are lined with a pale-gray alteration halo described as a calcareous material (Ruland and others, 1991), gypsum (A.H. Fleming, Indiana Geological Survey, oral commun., 1997), and caliche (Strobel, 1993).

At a depth of 7 ft, the till is slightly moist, and the matrix color is darker than above. Iron oxyhydroxides occur on the gray alteration haloes lining the fractures. Oxidized iron also is present along root traces and horizontal partings, and within the matrix as mottling. At a depth of approximately 11 ft, the matrix is grayish brown, and the gray alteration haloes are less distinct. Black, dendritic manganese oxides and two shades of iron oxyhydroxides are visible on the fracture faces.

The top of the unweathered zone occurs at approximately 12 ft. Below this depth, the till matrix is dark gray, sticky, and dense, and it shows no evidence of fracturing or mineralization. Fragments of black shale are a common component of the tills except in

the extreme northern part of the study area. The fragments are presumably derived from the pyrite-rich Antrim Shale that subcrops along the eastern boundary of the study area (Fleming, 1994).

Ruland and others (1991), Strobel (1993), and Fleming (1994) used hydraulic data to demonstrate that (1) hydraulically active fractures are present in the unweathered zone despite the fact that they are not visible in cores, (2) fractures are interconnected, either directly, or by intersection with sand-and-gravel stringers, (3) a zone of active ground-water flow extends from the land surface to depths of 15-35 ft, and the flow direction is predominantly horizontal, and (4) fracture density decreases with depth below the land surface. Ruland and others (1991) concluded that less densely spaced fractures that are hydraulically active may extend deeper than 30 ft in some cases and that ground-water flow in these deeper, more isolated fractures may be mainly vertical in response to seasonal changes in hydraulic gradient.

The hydrogeology is complex because of several factors: (1) heterogeneity of the aquifer system, (2) heterogeneity of the till, (3) fracturing in the surficial till, and (4) the network of tile drains that affects ground-water recharge and discharge. The influence of each factor, and the interaction between factors, is not completely understood.

Ground-water quality

The complete data sets from the agricultural land-use study (30 monitor wells) and the subunit survey (28 domestic wells) are published elsewhere (Shindel and others, 1999). The pages that follow focus on data from the 30 monitor wells and the subset of 18 domestic wells located in agricultural areas. The goal is to describe ground-water quality at a range of depths and locations within an agricultural area underlain by glacial till. No assumptions are made regarding the hydraulic connection between the co-located monitor and domestic wells; well pairs are not assumed to lie along the same ground-water flowpaths. It is assumed, however, that the monitor wells were recharged in agricultural areas, an assumption that is consistent with the study design for NAWQA land-use studies.

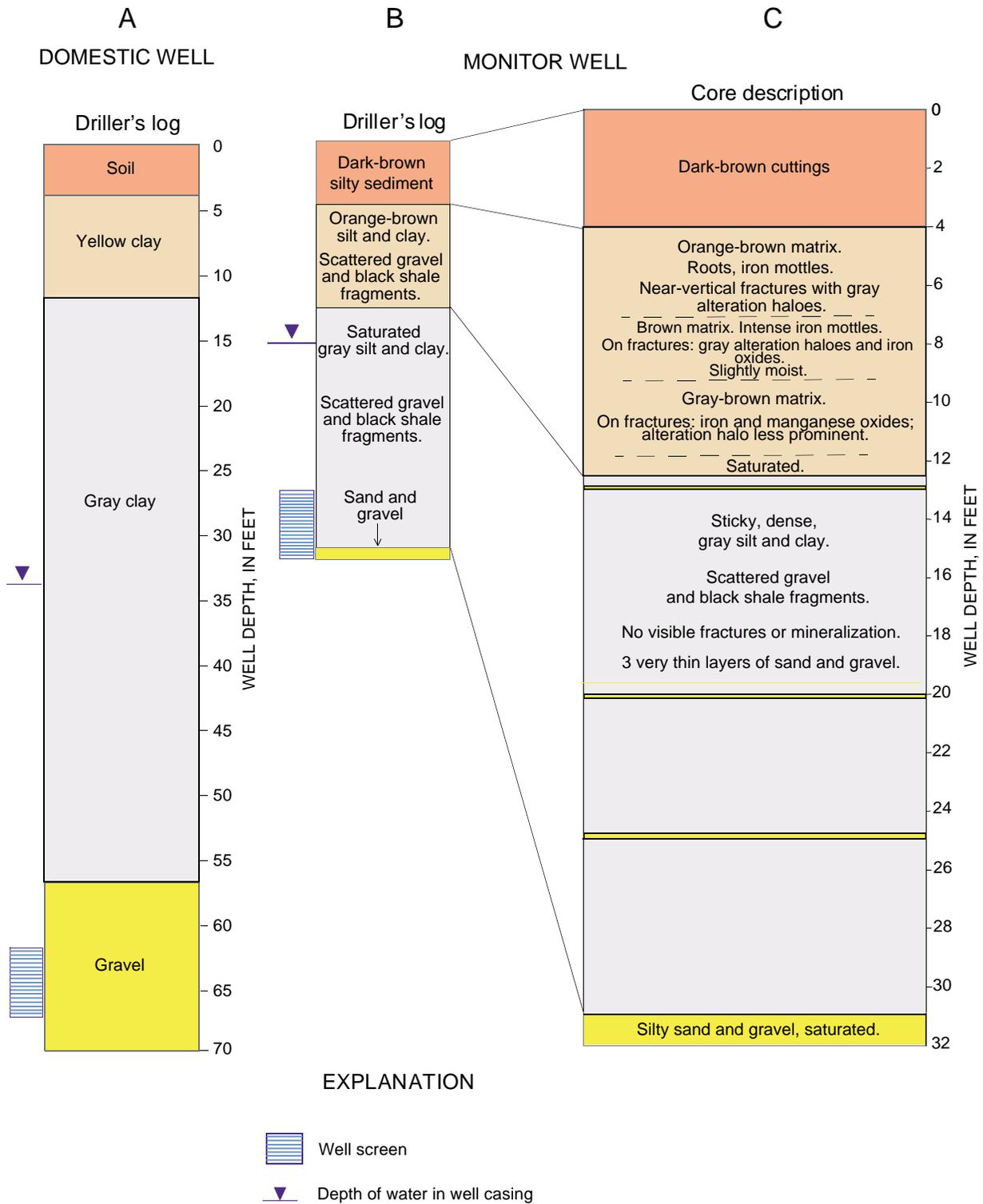


Figure 4. Drillers' logs and core description from the domestic and monitor wells co-located at a site in Williams County, Ohio.

Ground-water age

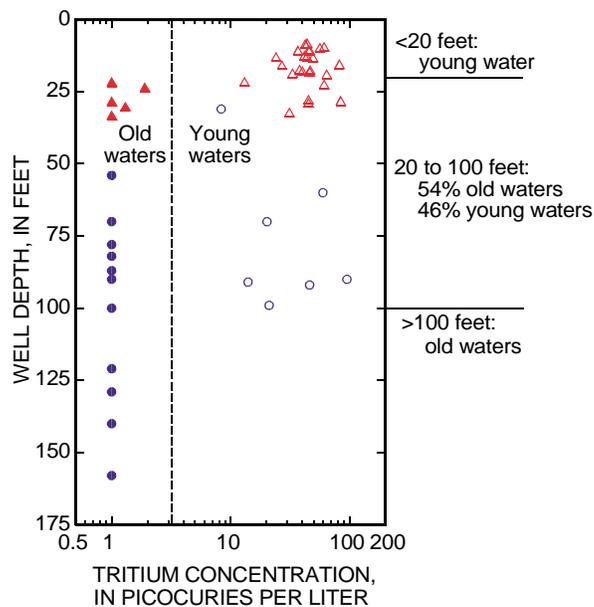
The age of the ground water was estimated by means of tritium age-dating, which is based on the fact that tritium concentrations in precipitation increased after 1953 because of atmospheric testing of atomic weapons (Plummer and others, 1993). Waters with tritium concentrations of less than 1 Tritium Unit (TU, equivalent to 3.2 picocuries per liter) are interpreted to have been recharged before 1953 and are hereafter referred to as “old waters.” Waters with tritium concentrations greater than or equal to 1 TU are interpreted to have been recharged after 1953, and are hereafter referred to as “young waters.” This is a simplification of the real system, where young and old ground waters can mix in the subsurface. Nonetheless, waters with more than 1 TU are assumed to contain some fraction of young water.

The relation between ground-water age and well depth is shown in figure 5. All of the samples from wells less than 20 ft deep were young waters. All samples from wells greater than 100 ft deep were old waters. Samples from wells between 20 and 99 ft deep were 46 percent young and 54 percent old.

Water type

The relative proportions of major ions in samples from domestic and monitor wells are illustrated in figure 6. Samples from domestic wells have a median dissolved solids (DS) concentration of 387 mg/L, and most samples are calcium-magnesium-bicarbonate-type waters. Relatively dilute calcium-magnesium-bicarbonate-type waters are characteristic of recently recharged ground water in the humid East (Back and others, 1993). Domestic-well samples with higher than median dissolved solids concentrations are enriched in chloride or sulfate or both.

Monitor-well samples have a significantly higher median dissolved solids concentration (500 mg/L) than domestic-well samples. Samples from monitor and domestic wells are similar in that (1) samples with low dissolved solids concentrations are calcium-magnesium-bicarbonate-type waters, and (2) samples with high dissolved solids concentrations are enriched in chloride or sulfate or both. Possible sources of chloride and sulfate are discussed in a later section.



EXPLANATION

- Domestic well
- △ Monitor well
- Solid symbol: old water
- Open symbol: young water
- Tritium concentration used to differentiate between waters recharged before and after 1953 (3.2 picocuries per liter = 1 Tritium Unit)

Figure 5. Relation of tritium concentrations to well depth in the northwestern part of the Lake Erie-Lake St. Clair Basin, 1998.

Pesticides and pesticide degradates

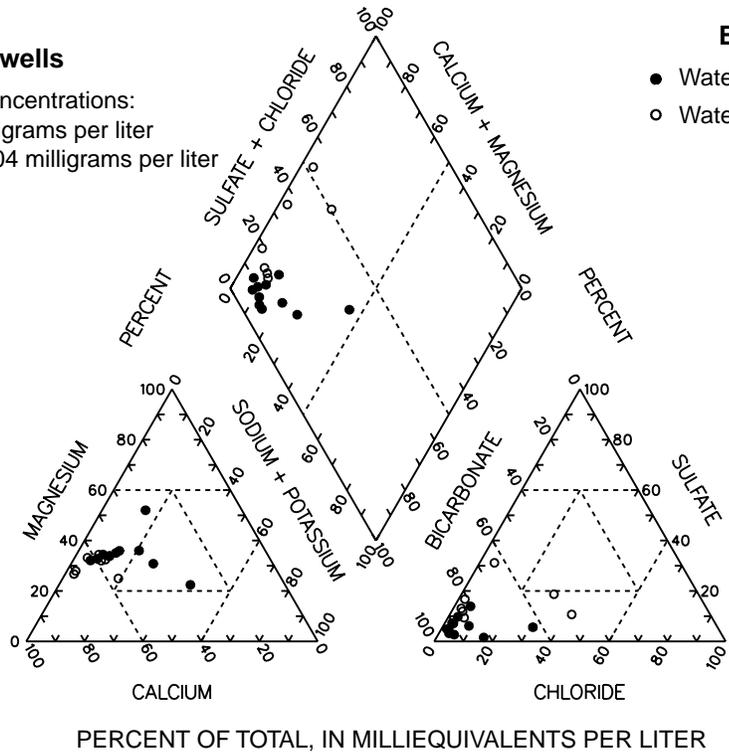
Rates of pesticide use in the study area are among the highest in the country (Barbash and others, 1999; U.S. Geological Survey, 1999). The five most heavily used pesticides in the Lake Erie Basin during 1994-95 were metolachlor, atrazine, cyanazine, acetochlor, and alachlor (Brody and others, 1998). All are herbicides used on corn and soybeans (Theelin, 1998). Samples from monitor and domestic wells were analyzed for parent compounds (the original active ingredient) and selected degradates (breakdown products) (table 2). Hereafter in this report, the term “pesticide” refers to either a parent compound or a degradate.

Pesticides detected in the ground water closely correspond to those most heavily used in the Lake Erie

Domestic wells
 Dissolved solids concentrations:
 Median: 316 milligrams per liter
 Range: 250 to 404 milligrams per liter

EXPLANATION

- Waters recharged before 1953
- Waters recharged after 1953



Monitor wells
 Dissolved solids concentrations:
 Median: 466 milligrams per liter
 Range: 82 to 1840 milligrams per liter

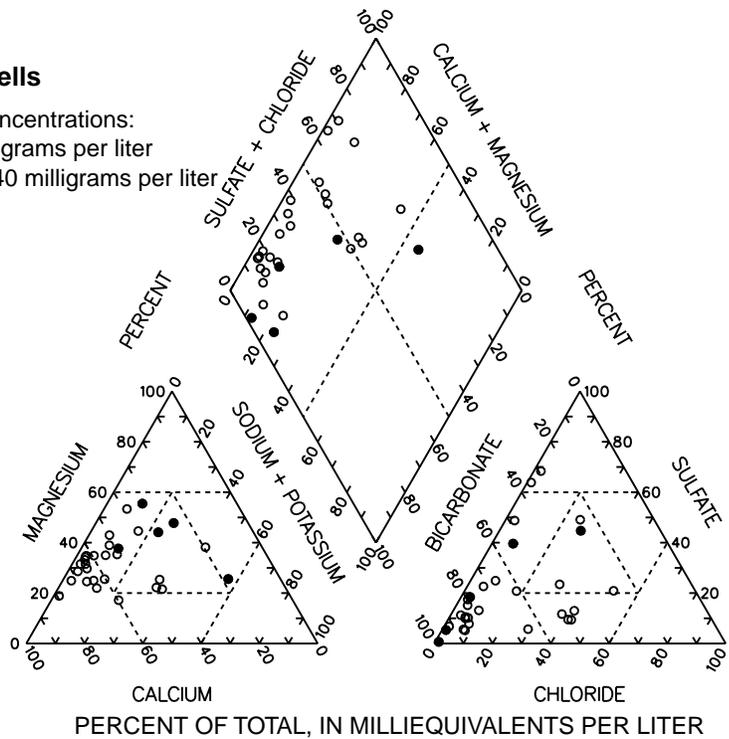


Figure 6. Piper diagrams of waters from domestic and monitor wells, northwestern part of the Lake Erie-Lake St. Clair Basin, 1998.

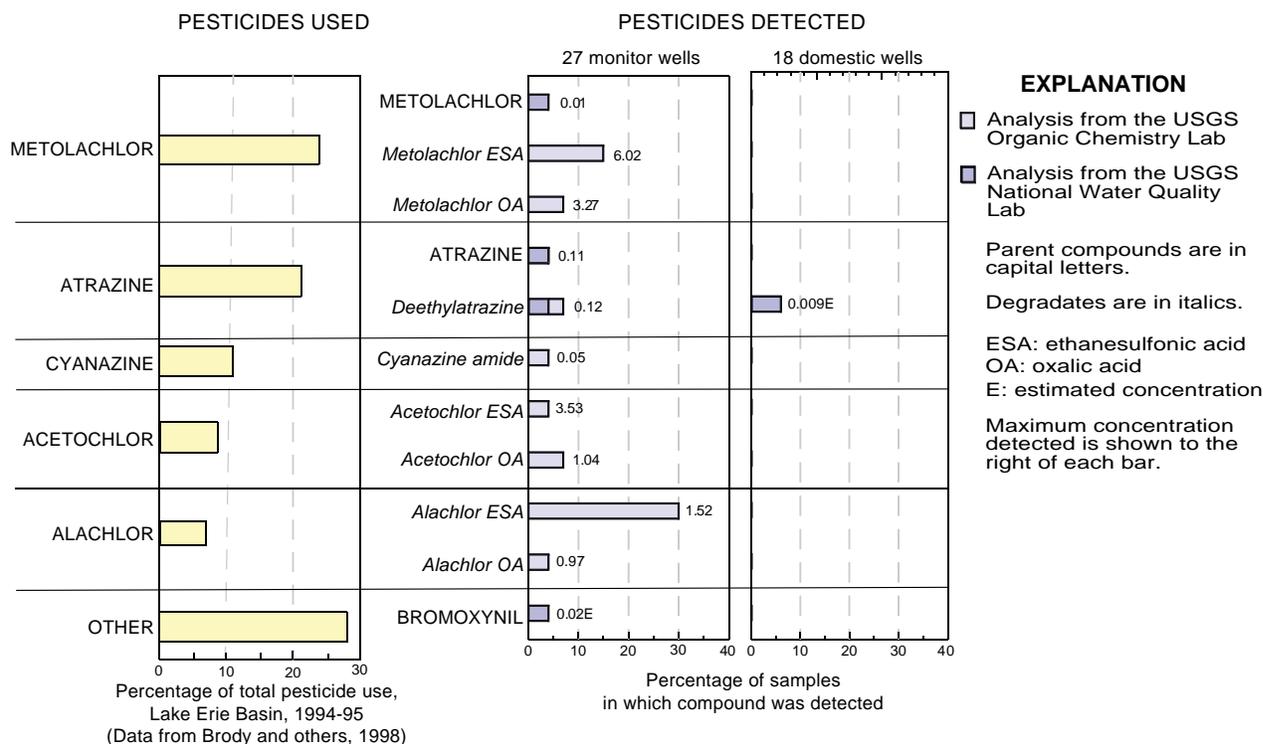


Figure 7. Pesticides most heavily applied in the Lake Erie Basin relative to those detected in ground water, northwestern part of the Lake Erie-Lake St. Clair Basin, 1998.

Basin (fig. 7). Six pesticides were detected in the study area—metolachlor, atrazine, cyanazine, acetochlor, alachlor, and bromoxynil. All are herbicides used on corn; metolachlor and alachlor are also used on soybeans, and bromoxynil is also used on wheat and other small grains (Thelin, 1998). Five of the six pesticides were the most heavily applied pesticides in the Lake Erie Basin during 1994-95 (Brody and others, 1998). Samples were not analyzed for glyphosate, which ranked sixth in terms of the amount applied in the Lake Erie Basin during 1994-95 (Brody and others, 1998).

Pesticides were detected in 41 percent (11 of 27) of the monitor wells and 6 percent (1 of 18) of the domestic wells. In monitor wells, degradates were detected three times more frequently, and at higher concentrations, than were parent compounds (fig. 7; table 3). Metolachlor ESA (ethanesulfonic acid) was the compound that was detected in the highest concentrations (1.1 to 6.0 µg/L). Alachlor ESA was the most frequently detected compound in the study area, even though it ranked fifth in terms of use during 1994-95.

The discrepancy may be due to heavier use of alachlor in the past; for example, alachlor was ranked second in terms of use during 1989-90 in Williams County, Ohio (Battaglin and Goolsby, 1994).

No pesticide was detected at a concentration greater than a USEPA Maximum Contaminant Level (MCL), which is an enforceable drinking-water standard based on health criteria. However, MCL's have not been established for 9 of the 11 compounds detected in the study area.

Mixtures of two or more pesticides were found in half of the wells with a pesticide detection (6 of 12). One sample contained a mixture of five pesticides. The health effect of mixtures of pesticides is unknown (U.S. Geological Survey, 1999).

Relations between pesticide detections, well depth, and ground-water age are shown in figure 8. Most of the pesticide detections (75 percent) were in young waters from monitor wells less than 25 ft deep, the minimum casing-depth required for wells in Michigan (Part 127, Public Act 368, 1978, revised 1994) and Ohio (Ohio Department of Health, 2000). Two

Table 3. Pesticide detection frequencies and maximum concentrations in ground-water samples, northwestern part of the Lake Erie-Lake St. Clair Basin, 1998

[Detection frequencies are based on varied minimum reporting limits; $\mu\text{g/L}$, micrograms per liter; E, estimated concentration]

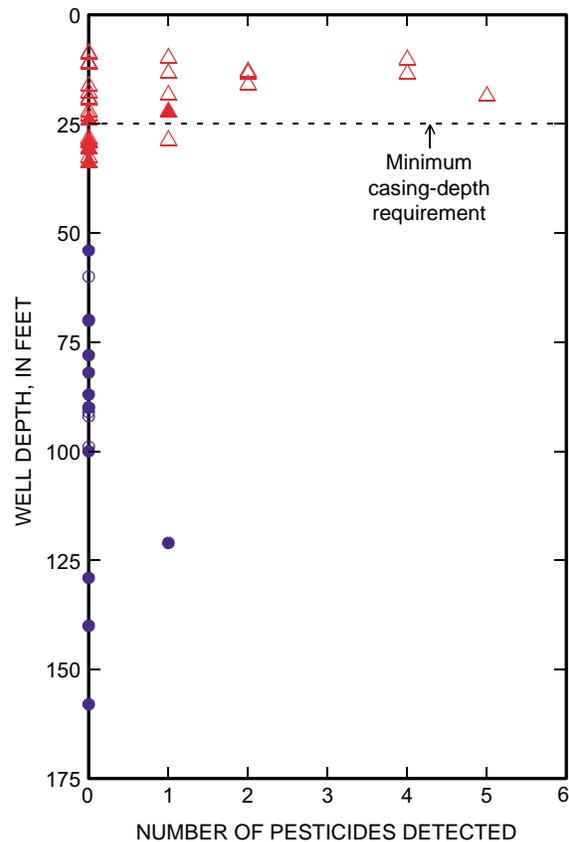
Summary statistic	27 monitor wells	18 domestic wells
Pesticide parent compounds:		
Detection frequency (%)	11	0
Maximum concentration ($\mu\text{g/L}$)	0.11	N/A
Pesticide degradates:		
Detection frequency (%)	33	6
Maximum concentration ($\mu\text{g/L}$)	6.02	0.009E
Pesticide parent compounds or degradates:		
Detection frequency (%)	41	6

samples containing pesticides were from wells greater than 25 ft deep. One was a 121-ft-deep domestic well that produced old water with an estimated deethylatrazine (DEA) concentration of 0.009 $\mu\text{g/L}$. DEA is a degradate of atrazine that is more mobile than its parent compound (Barbash and Resek, 1996). This sample also contained the maximum concentrations of ammonia (0.46 mg/L) and nitrite (0.11 mg/L) detected in any domestic well. The well is in an area where the till is unusually coarse grained relative to most other parts of the study area.

Trace concentrations of degradates of pesticides introduced after 1953 (atrazine and metolachlor) were detected in two waters classified as old. This finding indicates that these samples are actually a mixture of old and young waters (Kolpin and others, 1995).

Nitrate

Nitrogen occurs naturally in soil organic matter and the atmosphere. Anthropogenic sources of nitrogen include chemical fertilizers, manure, septic-system effluent, and fossil-fuel combustion products. In the study area, fertilizer application rates are reported to be among the highest in the country (Mueller and Helsel, 1996); therefore, agricultural fertilizers are assumed to be the major source of nitrogen to the ground water. Nitrate is the form of nitrogen that causes human-health concerns in drinking water and is therefore the focus of this report. The term “nitrate” is used as shorthand for “nitrate plus nitrite, reported as nitrogen.”



EXPLANATION

- Domestic well
- △ Monitor well
- Solid symbol: old water
- Open symbol: young water

Figure 8. Relation of pesticide detections to well depth and ground-water age in the northwestern part of the Lake Erie-Lake St. Clair Basin, 1998.

Detection frequencies and concentrations of nitrate in monitor and domestic wells are summarized in table 4. In monitor wells, the median nitrate concentration was 0.17 mg/L, and the maximum value was 14.8 mg/L. In domestic wells, nitrate concentrations were significantly lower. In 17 of 18 domestic wells, nitrate was not detected with a minimum reporting level of 0.05 mg/L. In one domestic-well sample, the nitrate concentration was 1.56 mg/L.

In ground water, nitrate concentrations greater than 2 mg/L are considered to be the result of human influence (U.S. Geological Survey, 1999). Thirty-seven percent of samples from monitor wells (11 of

Table 4. Nitrate detection frequencies and concentrations in ground-water samples, northwestern part of the Lake Erie-Lake St. Clair Basin, 1998

[mg/L, milligrams per liter; detection frequencies are based on a minimum reporting limit of 0.05 ug/L]

Summary statistic	30 Monitor wells	18 Domestic wells
Percentage of samples with concentration >2 mg/L ^a	37	0
Percentage of samples with concentration >10 mg/L ^b	7	0
Median concentration (mg/L)	0.17	<0.05
Maximum concentration (mg/L)	14.8	1.56

^a 2 mg/L is background concentration for ground water (U.S. Geological Survey, 1999)

^b 10 mg/L is the U.S. Environmental Protection Agency Maximum Contaminant Level

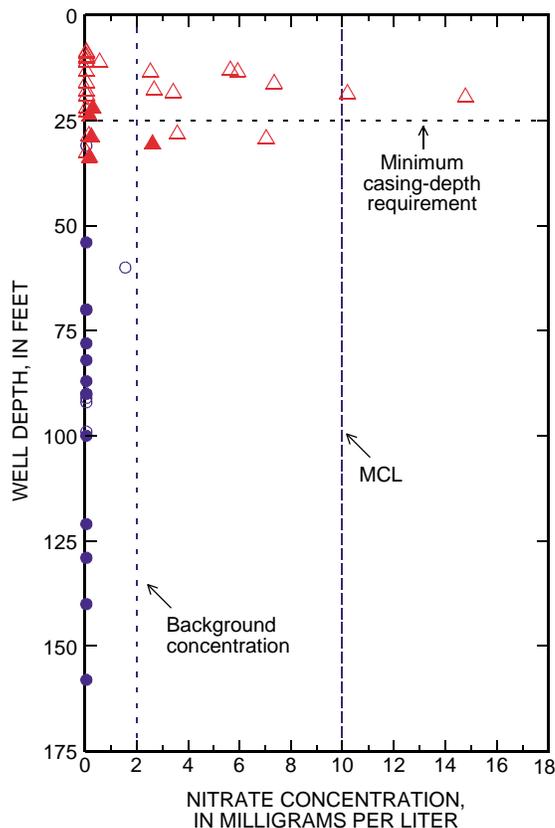
30) had nitrate concentrations greater than 2 mg/L. In this report, the term “elevated nitrate concentration” is used as shorthand for “nitrate concentration greater than the estimated background concentration of 2 mg/L”.

Nitrate was the only constituent detected at a concentration greater than an MCL. The MCL for nitrate, 10 mg/L, was exceeded in samples from 7 percent of the monitor wells (2 of 30) but in none of the samples from domestic wells.

The relations between nitrate concentration, well depth, and ground-water age are shown in figure 9. The two exceedances of the MCL were in samples from monitor wells 19 to 20 ft deep. The MCL was not exceeded in wells deeper than the minimum well-depth requirement; however, elevated nitrate concentrations indicative of human activities were detected in samples from three monitor wells 28 to 31 ft deep. Nitrate was detected in one domestic-well sample at a concentration of 1.56 mg/L, a concentration that is probably high enough to be the result of human activities. This sample was from a 60-ft-deep well in an area where the surficial till is clayey but is only 20 ft thick. Between depths of 21 and 60 ft, the sediment is predominantly sand and gravel.

Constituents that exceeded secondary drinking-water standards

USEPA Secondary Maximum Contaminant Levels (SMCL's) are non-enforceable drinking-water standards based on esthetic criteria such as taste, odor, and staining. SMCL's were exceeded with respect to



EXPLANATION

- Domestic well
- △ Monitor well
- Solid symbol: old water
- Open symbol: young water
- MCL—Maximum Contaminant Level (U.S. Environmental Protection Agency)

Figure 9. Relation of nitrate concentrations to well depth and ground-water age in the northwestern part of the Lake Erie-Lake St. Clair Basin, 1998.

five inorganic constituents: chloride, sulfate, dissolved solids, iron, and manganese (fig. 10). Chloride concentrations greater than the SMCL are interpreted to be the result of human activities. In contrast, iron concentrations greater than the SMCL are probably largely due to natural factors. High concentrations of sulfate, dissolved solids, and manganese could be due to either natural sources, human activities, or both.

Chloride. Chloride concentrations in young, shallow waters were significantly higher than those in old, deep waters, according to the results of a rank-sum test with a 95-percent confidence level. The SMCL for chloride (250 mg/L) was exceeded in samples from 10 percent of the monitor wells (3 of 30).

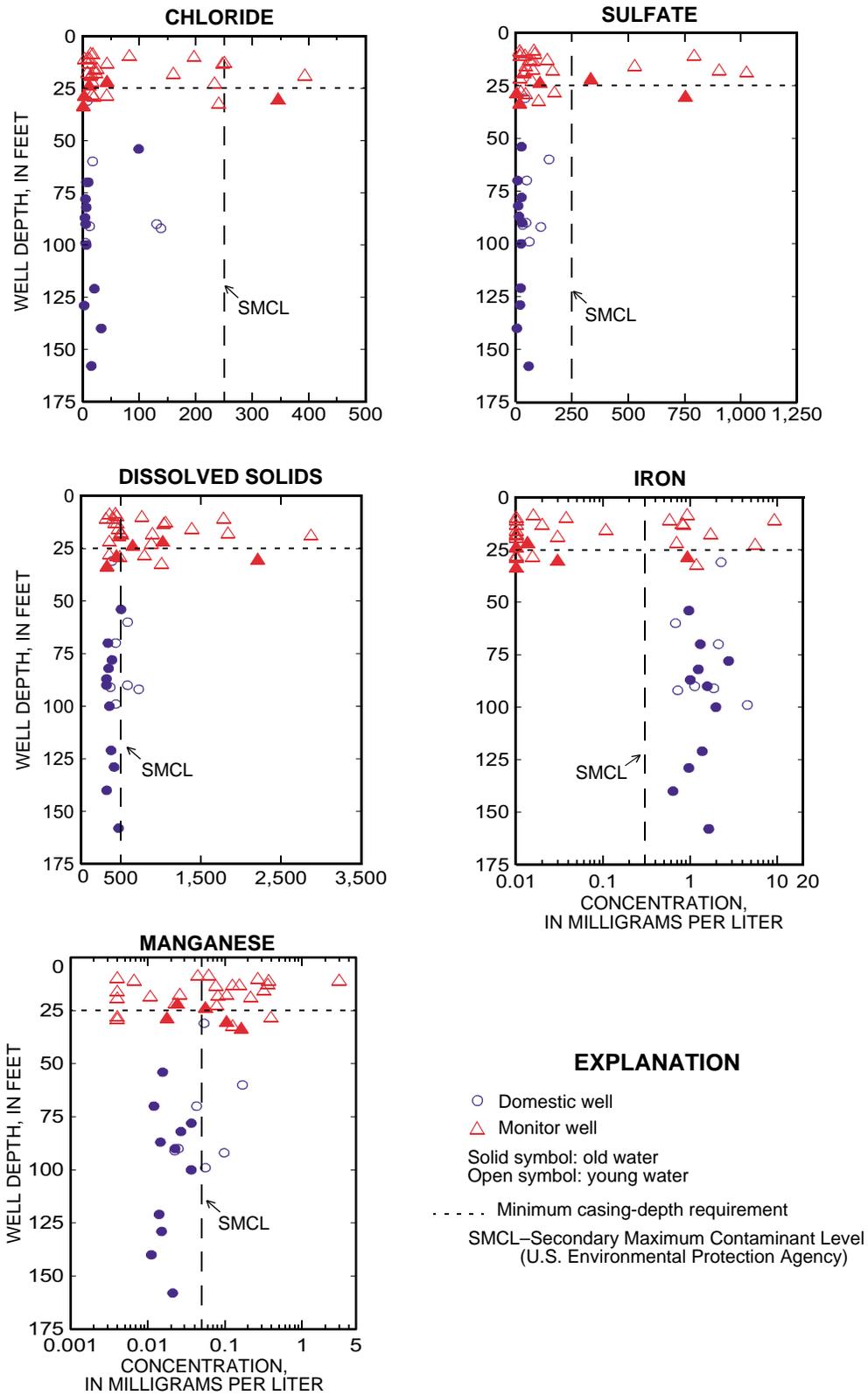


Figure 10. Relation of concentrations of constituents that exceeded SMCL's to well depth and ground-water age, northwestern part of the Lake Erie-Lake St. Clair Basin, 1998.

Possible sources of elevated chloride concentrations are anthropogenic (potash fertilizer, road salt, septic-system effluent) and natural (upward migration of deep-seated brine, dissolution of halite). In the study area, it is unlikely that elevated chloride concentrations are from natural sources because (1) relations between concentration, well-depth and ground-water age are not consistent with upward migration of old, deep, high-chloride waters (brine), and (2) halite has not been identified in the glacial sediment or near-surface bedrock (Mozola, 1953; Coen, 1989; Fleming and others, 1994). Therefore, elevated chloride concentrations are likely to be from human activities.

One sample from a 92-foot-deep domestic well had a chloride concentration of 138 mg/L and a chloride/bromide ratio of 1,056. In a nearby study area, similar values were interpreted to be an indication of human influence (Thomas, 2000). This well is in an area where the till is coarse grained relative to the study area as a whole.

Sulfate. Sulfate concentrations are significantly higher in young, shallow waters than in old, deep waters, according to the results of a rank-sum test (95-percent confidence level). The SMCL for sulfate (250 mg/L) was exceeded in 6 of 30 monitor wells. In domestic-well samples, none of the sulfate concentrations were greater than the SMCL, but concentrations in young waters were higher than those in old waters at similar depths. In general, the relations between concentration, well depth, and ground-water age are consistent with a source of sulfate at or near the land surface (fig. 10).

Possible sources of sulfate are anthropogenic (fertilizer, coal combustion) and natural (mineral reactions, organic matter in soil). In the study area, fertilizer is one possible source of sulfate in shallow ground water; ammonium sulfate was the second most heavily used form of nitrogen fertilizer in Michigan during spring 1997 (R. Pigg, Michigan Department of Agriculture, written commun., 1998). Potassium sulfate, potassium-magnesium sulfate, and calcium sulfate (gypsum) also were used as fertilizer in Michigan (R. Pigg, written commun., 1998).

Mineral reactions in the shallow subsurface are another possible source of high sulfate concentrations in shallow ground water. Sulfides (for example, pyrite) present in the till at the time of deposition can be oxidized to soluble forms of sulfur (for example, gypsum) in the upper weathered zone of the till (Hendry and

Wassenaar, 2000). Dissolution of gypsum can also increase sulfate concentrations in ground water.

On the basis of data from the current study, it is not possible to differentiate between the three possible sources of sulfate—fertilizer, pyrite oxidation, and gypsum dissolution. The statistical correlation between sulfate and calcium (Kendall's tau = 0.60) is one of the strongest between any two chemical constituents in the study. However, this correlation could be due to either gypsum dissolution or pyrite oxidation (Kolle and others, 1985). In addition, the correlation between sulfate and calcium does not disprove ammonium sulfate fertilizer as a source of sulfate in the shallow ground water.

Dissolved solids. Concentrations of dissolved solids are significantly higher in young, shallow waters than in old, deep waters, according to the results of a rank-sum test (95-percent confidence level). The SMCL for dissolved solids (500 mg/L) was exceeded in 50 percent of the monitor wells and 17 percent of the domestic wells (fig. 10). Concentrations of dissolved solids are correlated with calcium, sulfate, magnesium, or chloride concentrations.

Iron. In contrast to chloride, sulfate, and dissolved solids, concentrations of iron are significantly lower in young, shallow waters than in old, deep waters, according to the results of a rank-sum test (95-percent confidence level). The SMCL for iron (0.3 mg/L) was exceeded in 33 percent of the monitor wells and 100 percent of the domestic wells.

Iron solubility is related to the oxidation-reduction potential and pH of ground water (Hem, 1985). All waters from domestic wells had low concentrations of dissolved oxygen (the median was 0.14 mg/L and the maximum was 0.8 mg/L). Therefore, high iron concentrations in domestic-well samples may be the result of reductive dissolution of iron oxyhydroxides or iron-rich silicate minerals. Another possible source is corrosion of steel well casings (Hem, 1985), but samples from the four domestic wells with steel casings did not have unusually high iron concentrations.

In samples from monitor wells, possible additional sources of dissolved iron are (1) oxidation of iron-rich clay minerals such as chlorite (Ruland and others, 1991), (2) oxidation of pyrite-rich black shale fragments, or (3) reductive dissolution of iron oxyhydroxides that occur along fractures, as mottles within the till matrix, or on the surface of mineral grains. In fig. 4C, the two different shades of iron oxyhydroxides just above the saturated zone could be evidence of sev-

eral episodes of reduction and oxidation in response to fluctuating water levels.

Manganese. The results of a rank-sum test (95-percent confidence level) indicate that manganese concentrations in young, shallow waters are not significantly different from those in old, deep waters. The SMCL for manganese (0.05 mg/L) was exceeded in samples from 60 percent of monitor wells and 22 percent of domestic wells (fig. 10).

Manganese is a component of some fertilizers that are applied in relatively small amounts in Michigan (R. Pigg, written commun., 1998). Another possible source of dissolved manganese is mineral reactions. Manganese exchanges with iron, magnesium, or calcium in lattices of silicate minerals (Hem, 1985). Manganese solubility is sensitive to oxidation-reduction potentials, but less so than iron (Hem, 1985). Mineral reactions that could increase dissolved manganese concentrations in shallow ground water are (1) oxidation of pyrite, clays, or other minerals containing reduced manganese species or (2) reductive dissolution of manganese oxides, including those that occur just above the water table on the faces of the fractures (fig. 4C).

Vulnerability of ground water to contamination

National synthesis of data from NAWQA water-quality studies done during 1993-95 indicates that ground water in parts of the Upper Midwest is minimally contaminated by nitrate and pesticides, despite high rates of agrichemical use (U.S. Geological Survey, 1999). Data from the current study are consistent with this conclusion. As table 5 shows, detection frequencies and median concentrations of nitrate and pesticides from the current study are low when compared to the Midwest as a whole (Kolpin and others, 1996) and to the Nation as a whole (Mueller and Helsel, 1996; U.S. Geological Survey, 1999). Ground water in the study area appears to be protected, to some degree, from the effects of agricultural land use. Several authors have suggested that ground water in parts of the Upper Midwest is protected by the surficial glacial till and (or) tile drains (Mueller and others, 1995; Mueller and Helsel, 1996; Nolan and others, 1997; Barbash and others, 1999; U.S. Geological Survey, 1999). Presumably, the surficial layer of glacial till could protect the ground water by (1) physically impeding movement of water and solutes from the land surface, (2) facilitating biogeochemical processes that convert nitrate and pes-

ticides to other compounds, or (3) both. Presumably, tile drains could (1) intercept water and solutes before they reach the water table, (2) facilitate the discharge of water and solutes from the shallow ground water and thereby prevent them from migrating to deeper parts of the ground-water-flow system, or (3) both. Data from the current study do not confirm or disprove any of these hypotheses. However, inferences about the vulnerability of ground water in the study area can be based on the relations between concentration of anthropogenic constituents, well depth, and ground-water age.

Hydraulic connection to the land surface

Shallow ground water. Movement of water or solutes from the land surface to the shallow ground water is not completely impeded, as indicated by the observations that 83 percent of the waters from monitor wells were recharged after 1953, and 57 percent contained either a pesticide or an elevated nitrate concentration. These data support the conclusions of hydraulic studies in nearby fractured tills—that an active ground-water-flow system exists between the land surface and depths of 15 to 35 ft (Ruland and others, 1991; Strobel, 1993; Fleming, 1994; Fleming and others, 1994). Moreover, Fleming and others (1994) concluded that, in northern Indiana, shallow ground water in the upper part of fractured, clayey till is one of the hydrogeologic settings most vulnerable to contamination.

Tile drains are typically installed at a depth of 3 ft, and pesticides or elevated nitrate concentrations were detected in monitor wells 10 to 31 ft deep. Therefore, tile drains do not intercept all agrichemicals before they reach the water table. Over most of the study area, the surficial till contains near-vertical fractures that provide a direct pathway from the land surface to the water table. The possibility that tile drains would intercept agrichemicals before they reach the water table seems most likely (1) where tile drains intersect fractures or (2) where the till is relatively coarse-grained and therefore unfractured. Over most of the study area, tile drains probably function as a network of small discharge areas, thereby exacerbating the shallow nature of the local ground-water-flow system. Presumably, contaminants enter the shallow ground water but then discharge through tile drains rather than migrate to deeper parts of the ground-water-flow system.

Table 5. Nitrate and pesticide results from the northwestern part of the Lake Erie-Lake St. Clair Basin relative to those of comparable ground-water studies

[NWQL, USGS National Water Quality Laboratory; OCL, USGS Organic Chemistry Laboratory; mg/L, milligrams per liter; -, no data]

Constituent	Summary statistic	Results		
		Current study	Midwest Pesticide Study, 1992 ^a	NAWQA Studies, 1993-95 ^b
Shallow ground water from monitor wells				
Nitrate	Percentage of samples with concentration >10 mg/L	7	-	15
	Median concentration (mg/L)	0.17	-	>3
Pesticides	Percentage of samples with at least one pesticide based on pesticides analyzed at NWQL (table 2)	10		59
Ground water from domestic-supply wells				
Nitrate	Percentage of samples with concentration >10 mg/L	0	8	12
	Percentage of samples with concentration >3 mg/L	0	33	-
	Median concentration (mg/L)	<0.05	-	2
Pesticides	Percentage of samples with at least one pesticide based on pesticides analyzed at NWQL and OCL (table 2)	6	62	-
	Percentage of samples with at least one pesticide based on pesticides analyzed at NWQL (table 2)	6	-	33 ^c

^a Midwest Pesticide Study, 1992 (Kolpin and others, 1994); includes water-quality data from shallow aquifers in agricultural areas of 12 Midwest states.

^b NAWQA studies, 1993-95 include data from agricultural areas of 20 Study Units throughout the country (Mueller and Helsel, 1996; U.S. Geological Survey, 1999).

^c Statistic is from areas of mixed land use.

Deep ground water. The hydraulic connection between the shallow, dynamic ground-water-flow system in fractured till and the underlying aquifer system is not well understood. Fleming and others (1994) speculated that the shallow and deep ground-water-flow systems in northern Indiana are not well connected, if at all. Ruland and others (1991) concluded that hydraulically isolated fractures could extend beyond a depth of 30 ft in southwestern Ontario. In western Ohio, the potential for fracture flow exists to depths of at least 60 ft (M.L. Strobel, U.S. Geological Survey, written commun., 2000).

In the current study, almost half (6 of 13) of the waters between depths of 50 and 100 ft were recharged after 1953 (fig. 5). In addition, anthropogenic constituents were detected in domestic wells at depths of 121 ft (pesticide metabolite), 92 ft (elevated chloride concentration and chloride/bromide ratio), and 60 ft (elevated nitrate concentration). These wells are in areas where the till is relatively coarse grained, or the surfi-

cial till is clayey but thin. These observations indicate that parts of the aquifer system are hydraulically connected to the land surface.

In the study area, the minimum casing depth for water-supply wells is 25 ft. If active ground-water flow extends to depths of 25 to 35 ft, water in some of the shallowest domestic wells could be vulnerable to the effects of land use.

Geochemical properties of the till.

The observations that pesticides were detected in the ground water, but that most were degradates rather than parent compounds, indicates that pesticides can physically reach the shallow ground water but that they are chemically broken down somewhere along the way. The clay-rich tills have several properties conducive to the transformation of nitrate or pesticides to other compounds:

- Clays, which have a negative surface charge, promote sorption of pesticides.
- Organic carbon also sorbs pesticides. In addition, organic carbon is used as a substrate for microbes that mediate processes that chemically transform nitrogen and pesticides. Sediment collected from monitor-well cores had fairly high organic-carbon content; the median organic carbon content was 10 mg/kg, and the range was 5 to 27 mg/kg.
- Low dissolved-oxygen concentrations promote denitrification. Dissolved-oxygen concentrations less than 1 mg/L were detected in samples from 100 percent of the domestic wells and 43 percent of the monitor wells.
- Iron and manganese oxides, which occur along fractures in the weathered till, are chemically reactive with organic compounds and nitrate.
- Reduced sulfur compounds (pyrite or organic sulfur) in unweathered till can serve as the electron donor for denitrification (Kolle and others, 1985; Korom, 1992; Robertson and others, 1996). Kolle and others (1985) documented that nitrate was reduced by pyrite oxidation in a reaction mediated by *Thiobacillus denitrificans*. The reaction products were gaseous nitrogen, sulfate, and dissolved iron.

Heterogeneity of the till

The presence of coarse-grained sediment in the till is likely to increase the vulnerability of ground water to contamination. This assumption is supported by the observation that domestic-well samples containing anthropogenic constituents were from areas where the till is relatively coarse grained. Presumably, the coarser grained sediment could increase the hydraulic connection to land surface, decrease biogeochemical transformations, or both.

A sequence of till studied by Hendry and Wasenaar (2000) was chosen to be a homogeneous, clay-rich till without stringers of sand and gravel. Age dating indicated that waters deeper than 60 ft were thousands of years old. In the study area, by contrast, waters from similar depths were substantially younger; 6 of 13 samples from wells 50 to 100 ft deep were recharged after 1953. The striking difference in the age of waters between the two areas could be partly due to the fact that till in the study area is heterogeneous and contains numerous sand stringers that are potential pathways for the migration of young waters.

Although the aquifer system may be protected from contamination in some areas, the fact that the surficial till is heterogeneous and of varied thickness suggests that protection is not uniform. Moreover, it is not always possible to predict where the ground water is protected and where it is not. Thin sand-and-gravel stringers or fractures are rarely noted on driller's logs, partly because they are not always visible in well cuttings. In Figure 4, for example, the driller's log for the domestic well shows that the aquifer is overlain by more than 50 ft of homogeneous clay. From this description, one might assume that the underlying aquifer system is not vulnerable to contamination. However, the core from the monitor well shows potential pathways for contaminants: (1) near-vertical fractures that are visible from the land surface to the water table, but that probably extend to deeper depths (Ruland, 1991; Strobel, 1993; Fleming, 1994), and (2) at least four sand stringers that extend for unknown distances. Indeed, the sand and gravel at a depth of 31 ft contained concentrations of nitrate (2.6 mg/L) and chloride (350 mg/L) indicative of human influence, and the water in the aquifer was recharged after 1953.

Summary and conclusions

Ground-water quality was assessed in the northeastern part of the Corn Belt, where rates of pesticide and fertilizer use are among the highest in the country. Data were collected from 30 shallow monitor wells and 18 co-located domestic wells in areas where tile-drained row crops are underlain by glacial till. The study was part of the U.S. Geological Survey's National Water-Quality Assessment of the Lake Erie drainage basin.

Pesticides or pesticide degradates were detected in samples from 41 percent of the monitor wells and 6 percent of the domestic wells. The pesticides detected closely correspond to those most heavily applied in the Lake Erie-Lake St. Clair Basin—herbicides used on corn, soybeans, or wheat. Degradates were detected more frequently, and at much higher concentrations, than parent compounds. Concentrations were generally low; no pesticide was detected at a concentration greater than a USEPA Maximum Contaminant Level (MCL). However, MCL's do not exist for 9 of the 11 pesticide compounds detected.

Nitrate was the only chemical constituent detected at a concentration greater than an MCL. The MCL was exceeded in 7 percent of samples from monitor wells. In 37 percent of monitor-well samples,

nitrate was detected at concentrations greater than 2 mg/L, a level indicative of human influence. The primary source of nitrate is probably agricultural fertilizer, but other possible sources are manure and septic-system effluent.

Secondary MCL's, which are based on esthetic criteria, were exceeded with respect to chloride, sulfate, dissolved solids, iron, and manganese. High concentrations of chloride are interpreted to be the result of human inputs; possible sources are potash fertilizer, road salt, and septic-system effluent. In contrast, high concentrations of iron are interpreted to be from mineral reactions. High concentrations of sulfate, dissolved solids, and manganese could be due to either human activities or mineral reactions in the shallow subsurface.

Detection frequencies of nitrate and pesticides are low in comparison to the Midwest as a whole and the Nation as a whole. Preliminary data from NAWQA studies indicates that ground water in parts of the Upper Midwest is minimally contaminated by pesticides and fertilizers, presumably because it is protected by the surficial glacial till and (or) tile drains.

In the study area, most of the shallow ground water is hydraulically connected to the land surface, as indicated by the observations that 83 percent of waters from monitor wells were recharged after 1953, and 57 percent contained a pesticide or an elevated nitrate concentration. Potential pathways are provided by near-vertical fractures and (or) sand-and-gravel stringers within the till. Water-quality data from the current study are consistent with hydraulic data from other studies that indicate a dynamic local flow system to depths of 25 to 35 ft. The minimum casing depth for water-supply wells is 25 ft, therefore, water in some of the shallowest domestic wells could be vulnerable to the effects of land use.

In some areas, deeper parts of the ground-water-flow system are also hydraulically connected to the land surface. Almost half the waters from wells 50 to 100 ft deep were recharged after 1953. Anthropogenic constituents were detected in samples from three domestic wells 60 to 121 ft deep. These three wells are in areas where the till is coarse grained relative to the study area as a whole.

Over most of the study area, tile drains do not intercept all agrichemicals before they reach the water table. Near-vertical fractures in the till provide a direct pathway for migration of solutes from the land surface to the water table. Presumably, tile drains could facili-

tate the discharge of agrichemicals from the shallow ground water and thereby prevent their migration to deeper parts of the ground-water-flow system.

The hydrogeologic system has several geochemical characteristics conducive to transformations or sorption of nitrate or pesticides: (1) the till is clay-rich, has a high organic-carbon content, and contains an abundance of pyrite, (2) the ground water has low dissolved-oxygen concentrations, and (3) iron and manganese oxides and oxyhydroxides occur on fractures in the unsaturated zone.

The aquifer system appears to be protected from contamination relative to aquifers beneath most other agricultural areas of the country. The nature of the protection may be both physical and geochemical. However, the surficial glacial till is heterogeneous, and therefore the protection is not likely to be uniform.

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