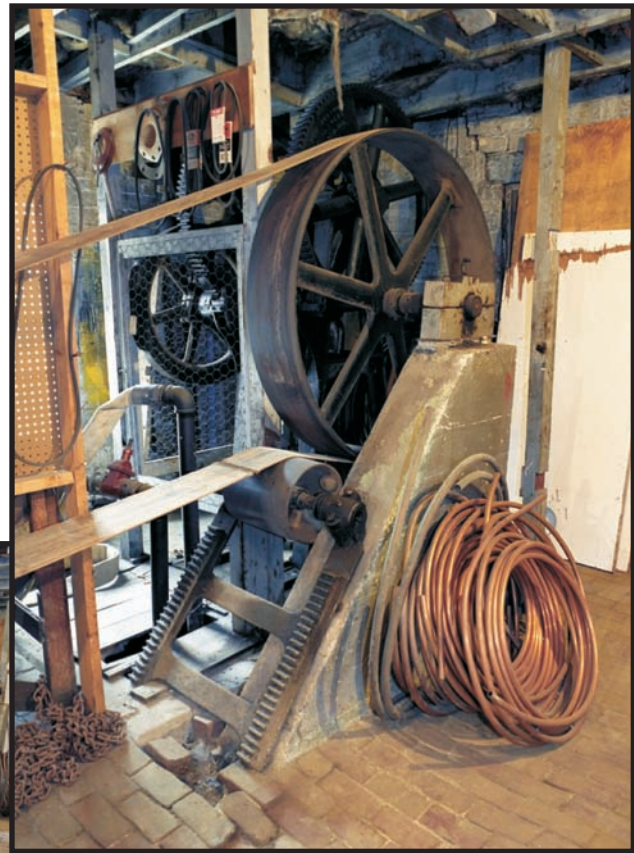


In cooperation with the Illinois Environmental Protection Agency

Herbicides and Their Transformation Products in Source-Water Aquifers Tapped by Public-Supply Wells in Illinois, 2001-02



Water-Resources Investigations Report 03-4226

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By Patrick C. Mills (U.S. Geological Survey) and William D. McMillan
(Illinois Environmental Protection Agency)

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Water-Resources Investigations Report 03-4226

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Cover photographs: Suction-lift pump, dating from about 1924, standby well 11561, Franklin Grove, Ill. (Photographs courtesy of Kelly Mills, Atlanta, Georgia. Reproduced with permission.)

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Conversion Factors, Vertical Datums, and Abbreviated Water-Quality Units

Multiply	By	To obtain
Length		
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi ²)	2.590	square kilometer (km ²)
Flow rate		
gallon per minute (gal/min)	3.785	liter per minute (L/m)
Mass		
pound (lb)	0.4536	kilogram (kg)
Yield		
gallon per day per square mile (gal/d/mi ²)	0.00144	cubic meter per day per square kilometer

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

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

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD27).

Abbreviated water-quality units used in this report: Organic- and inorganic-constituent concentrations, water temperature, and other water-quality measures are given in metric units. Constituent concentrations are given in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter are considered equivalent to parts per million at the reported concentrations. Micrograms per liter are considered equivalent to parts per billion at the reported concentrations.

Specific conductance (SC) of water is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C). The unit is equivalent to micromhos per centimeter at 25 °C (µmho/cm), formerly used by the U.S. Geological Survey.

Turbidity is not quantified; determined from visual inspection of water clarity.

pH of water is given in standard units.

Additional abbreviations: milliliter (ml), millimeter (mm).

Herbicides and Their Transformation Products in Source-Water Aquifers Tapped by Public-Supply Wells in Illinois, 2001-02

By Patrick C. Mills (U.S. Geological Survey) and William D. McMillan (Illinois Environmental Protection Agency)

Abstract

During 2001-02, ground-water samples were collected from 117 public-supply wells distributed throughout Illinois to evaluate the occurrence of herbicides and their transformation products in the State's source-water aquifers. Wells were selected using a stratified-random method to ensure representation of the major types of source-water aquifers in the State. Samples were analyzed for 18 herbicides and 18 transformation products, including 3 triazine and 14 chloroacetanilide products. Herbicide compounds (field-applied parent herbicides and their transformation products) were detected in 34 percent of samples. A subset of samples was collected unfiltered to determine if analytical results for herbicides in unfiltered samples are similar to those in paired filtered samples and, thus, can be considered equally representative of herbicide concentrations in ground water supplied to the public. The study by the U.S. Geological Survey was done in cooperation with the Illinois Environmental Protection Agency.

Parent herbicides were detected in only 4 percent of all samples. The six most frequently detected herbicide compounds (from 5 to 28 percent of samples) were chloroacetanilide transformation products. The frequent occurrence of transformation products and their higher concentrations relative to those of most parent herbicides confirm the importance of obtaining information on transformation products to understand the mobility and fate of herbicides in ground-water systems. No sample concentrations determined during this study exceeded current (2003) Federal or State drinking-water standards; however, standards are established for only seven parent herbicides.

Factors related to the occurrence of herbicide compounds in the State's source-water aquifers include unconsolidated and unconfined conditions, various hydrogeologic characteristics and well-construction aspects at shallow depths, and proximity to streams. Generally, the closer an aquifer (or well location) is to a recharge area and (or) the stronger the hydraulic connection between an aquifer and a recharge area, the younger the ground water and the more vulnerable the aquifer will be to contamination by herbicide compounds. The weak relation between current (2001) statewide application rates of herbicides and current (2001-02) occurrence of herbicide compounds in source-water aquifers indicates that additional factors must be considered when relating herbicide-application rates to occurrence. These factors include historical application rates and the mobility and persistence of the various herbicide compounds in ground-water systems. Frequency of detection and concentrations of herbicides compounds in the State's source-water aquifers are indicated to be highest during the spring, when crops are planted and herbicides primarily are applied. Excess nitrate (concentrations of nitrate, as nitrogen, higher than 3 milligrams per liter) in ground water strongly indicates the co-occurrence of herbicide compounds. However, nitrate concentrations are not a reliable indicator of herbicide-compound concentrations. The inverse relation found between current use of land for corn and soybean production and current occurrence of herbicide compounds in underlying aquifers indicates that various factors, along with current agricultural land use, contribute to herbicide occurrence. These factors include, among others, land-use history, ground-water age, ground-water-flow patterns, geology, soil microbiology, and chemistry and persistence of the herbicide compounds. Detection of agriculture-

specific herbicide compounds in 71 percent of samples from urban areas with no current or recent agricultural land use near the sampled wells indicates that recharge to certain high-capacity supply wells may originate at considerable distances (up to about 10 miles) from the wells. Essentially no difference was found between the analytical results for herbicides in paired unfiltered and filtered samples, although additional study of this issue is warranted.

Introduction

Herbicides are used extensively in agricultural regions of the United States for control of competing grass and broadleaf weeds. Substantial advances in agricultural production during the past 35 years are associated directly with the increased use of herbicides. However, this increased use of herbicides has introduced concerns about their occurrence in water resources and their possible adverse effect on human health and the environment. Numerous studies have documented the occurrence of herbicides in ground water at the State (Detroy and others, 1988; Risch, 1994; Mehnert and others, 1995; Kolpin and others, 1997, 1998b, 2000b; Kalkhoff and others, 1998; Dana W. Kolpin, U.S. Geological Survey, written commun., 2004), regional (Kolpin and others, 1994, 1995, 1996, 1998a), and national (U.S. Environmental Protection Agency, 1990, 1992; Holden and others, 1992; Kolpin and others, 2000a, 2002) scales. Concerns about ground-water contamination by herbicides are high in many agricultural regions, particularly in Midwestern States, where ground water typically is the principal source of drinking water. The toxic effects of herbicides on humans and animals, and the disruption of reproductive cycles and food chains have been documented in various studies (Blaustein and Wake, 1990; Carbonell and other, 1995; Nemes-Kosa and Cserhati, 1995; Bain and LeBlanc, 1996; Longley and Sotherton, 1997; Ribas and others, 1997; Russell and others, 1997; Spawn and others, 1997; Andersen and others, 2002; Anderson and others, 2002; Crump and others, 2002; Sinclair and Boxall, 2003).

Despite the number of studies regarding the occurrence of herbicides in ground water, there remains an incomplete understanding of the factors that affect their distribution. Additionally, study of herbicide transformation products (also referred to as degradates, metabo-

lites, or breakdown products) in ground water is comparatively limited. These transformation products result from microbial, physical, and chemical processes that alter the field-applied (parent) herbicides and commonly the products occur more frequently and at higher concentrations in ground water than their parent compounds (Kolpin and others, 1998b). Transformation products can, in some cases, have toxicity similar to their parent herbicide compounds (Belfroid and others, 1998; Tessier and Clark, 1995; Tixier and others, 2001), particularly if their chemical structure remains chlorinated.

Because herbicides are used heavily in Illinois corn and soybean production, various statewide studies have been conducted that evaluate the occurrence of herbicides and, in some cases, their transformation products in ground water (Mehnert and others, 1995; Kelly L. Warner and William S. Morrow, U.S. Geological Survey, written commun., 2003; Dana W. Kolpin, U.S. Geological Survey, written commun., 2004). However, none of these studies specifically address herbicide occurrence in the State's source-water aquifers – that is, aquifers that provide untreated water that is used to supply private wells and public drinking water (U.S. Environmental Protection Agency, 2003a) (figs. 1, 2). In an attempt to better understand the occurrence of herbicides in Illinois' source-water aquifers and the factors that affect their occurrence, 117 public-supply wells distributed throughout the State (figs. 1, 3) were sampled by the U.S. Geological Survey (USGS) from October 2001 through September 2002. The study, done in cooperation with the Illinois Environmental Protection Agency (IEPA), was part of an ongoing IEPA program to assess ambient ground-water quality in the State's source-water aquifers tapped for public supply (Illinois Environmental Protection Agency, 2003a). Since 1998, IEPA periodically has collected samples from a subset of the 360 public-supply wells in its ambient ground-water-quality network for analysis of selected triazine and chloroacetanilide herbicides. These analyses do not include every herbicide reportedly (U.S. Department of Agriculture, 2003) used in Illinois, including heavily used glyphosate (the active ingredient in Roundup), nor their transformation products. The present USGS-IEPA study provides analyses of all herbicides reportedly used in Illinois corn and soybean production during the past decade (1991-2001) (U.S. Department of Agriculture, 2003), some herbicides that may not have been used, and various transformation products of these herbicides.

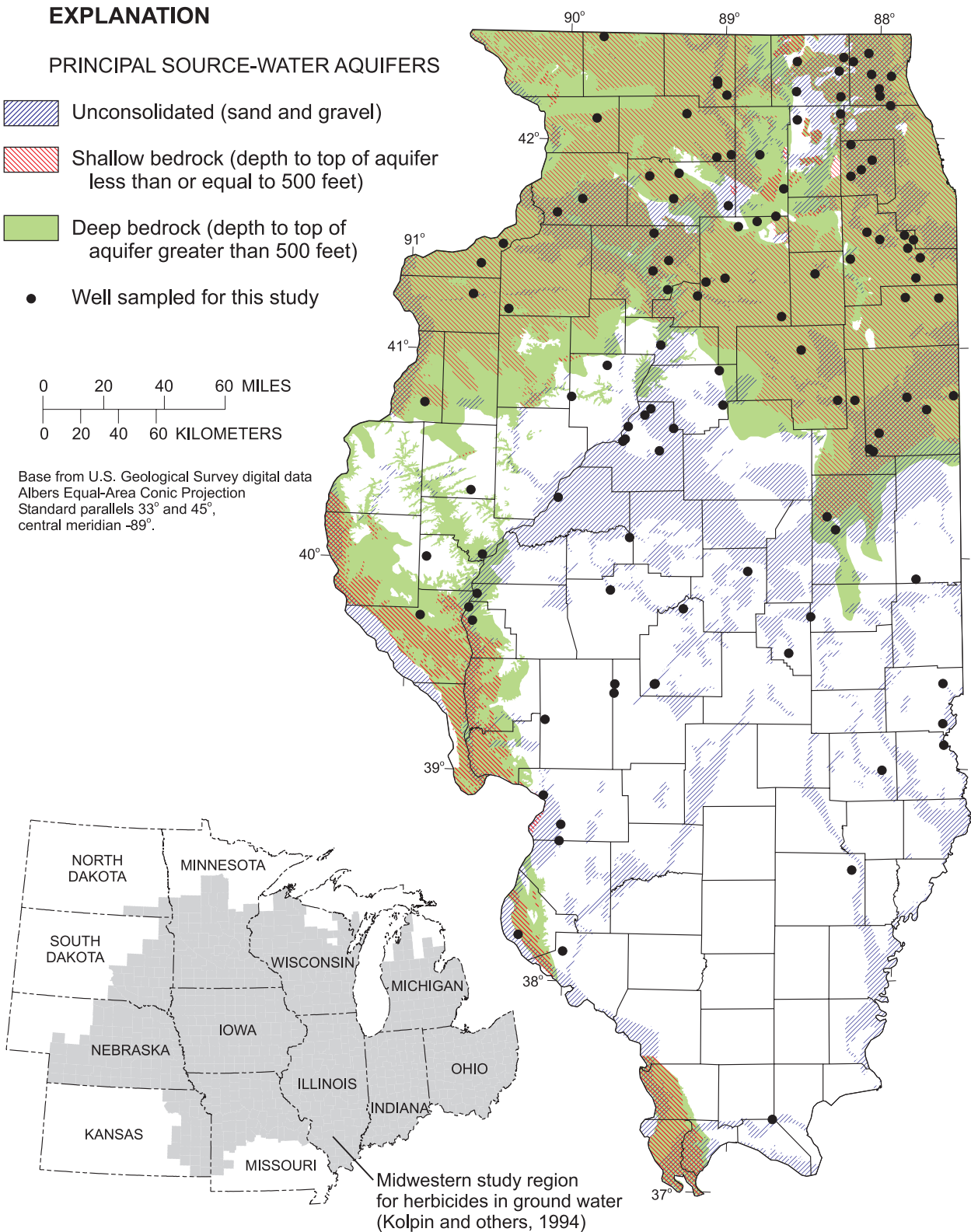


Figure 1. Locations of principal source-water aquifers tapped by most public-supply wells in Illinois (modified from O’Hearn and Schock,1984, fig. 1 and Joseph Konczyk, Illinois Environmental Protection Agency, written commun., 2003).

SYSTEM	SERIES	LITHO-STRATIGRAPHIC UNIT	HYDROSTRATIGRAPHIC UNIT	PRINCIPAL AQUIFER TYPE	LOG	DESCRIPTION	
Quaternary	Pleistocene	Undifferentiated	Sand and gravel	Unconsolidated		Unconsolidated glacial deposits--pebbly clay (till) silt, and gravel. Loess (windblown silt), and alluvial silts, sands and gravels.	
Tertiary and Cretaceous	Undifferentiated	Undifferentiated	Aquifer or confining unit	Shallow bedrock		Sand and silt.	
Pennsylvanian	Undifferentiated	Undifferentiated	Pennsylvanian aquifer or confining unit			Mainly shale and thin sandstone, limestone, and coal beds.	
Mississippian	Valmeyeran	St. Louis Ls. Salem Ls. Warsaw Ls. Keokuk Ls. Burlington Ls.	Mississippian aquifer		St. Louis-Salem aquifer		Limestone; cherty limestone; green, brown, and black shale; silty dolomite.
		Aquifer or confining unit			Keokuk-Burlington aquifer		
	Kinderhookian	Undifferentiated			Aquifer or confining unit		
Devonian	Undifferentiated	Undifferentiated	Devonian aquifer		Silurian-Devonian aquifer		Shale, calcareous; limestone beds, thin.
Silurian	Niagaran	Port Byron Fm. Racine Fm. Waukesha Ls. Joliet Ls.	Silurian-Devonian aquifer		Silurian aquifer		Dolomite, silty at base, locally cherty.
	Alexandrian	Kankakee Ls. Edgewood Ls.					
Ordovician	Cincinnatian	Maquoketa Shale Group	Maquoketa confining unit			Shale, gray or brown; locally dolomite and/or limestone, argillaceous.	
	Mohawkian	Galena Group Decorah Subgroup Platteville Group	Galena-Platteville aquifer or confining unit			Dolomite and/or limestone, cherty. Dolomite, shale partings, speckled. Dolomite and/or limestone, cherty, sandy at base.	
			Glenwood Fm.	Ancell aquifer			
	Chazyan	St. Peter Sandstone				Sandstone, fine- and coarse-grained; little dolomite; shale at top. Sandstone, fine- to medium-grained; locally cherty red shale at base.	
	Canadian	Prairie du Chien Group	Shakopee Dol. New Richmond Ss. Oneota Dol. Gunter Ss.	Cambrian-Ordovician aquifer	Middle confining unit		Dolomite, sandy, cherty (oolitic), sandstone. Sandstone, interbedded with dolomite. Dolomite, white to pink, coarse-grained, cherty (oolitic), sandy at base.
Cambrian	St. Croixian	Jordan Ss. Eminence Fm.-Potosi Dol.				Dolomite, white, fine-grained, geodic quartz, sandy at base.	
		Franconia Fm.	Franconia				
		Ironton Ss.	Ironton-Galesville aquifer				
		Galesville Ss.					
		Eau Claire Fm.	Eau Claire aquifer or confining unit				
		Mt. Simon Fm.	Elmhurst-Mt. Simon aquifer				
Pre-Cambrian						Granite and other crystalline rock.	

Dol. = Dolomite
 Fm. = Formation
 Gr. = Group
 Ls. = Limestone
 Ss. = Sandstone

Figure 2. General classification of lithostratigraphic and hydrostratigraphic units that compose source-water aquifers in Illinois (lithostratigraphic and hydrostratigraphic classifications generally follow the use of the Illinois State Geological Survey; modified from Visocky, 1997, fig. 2).

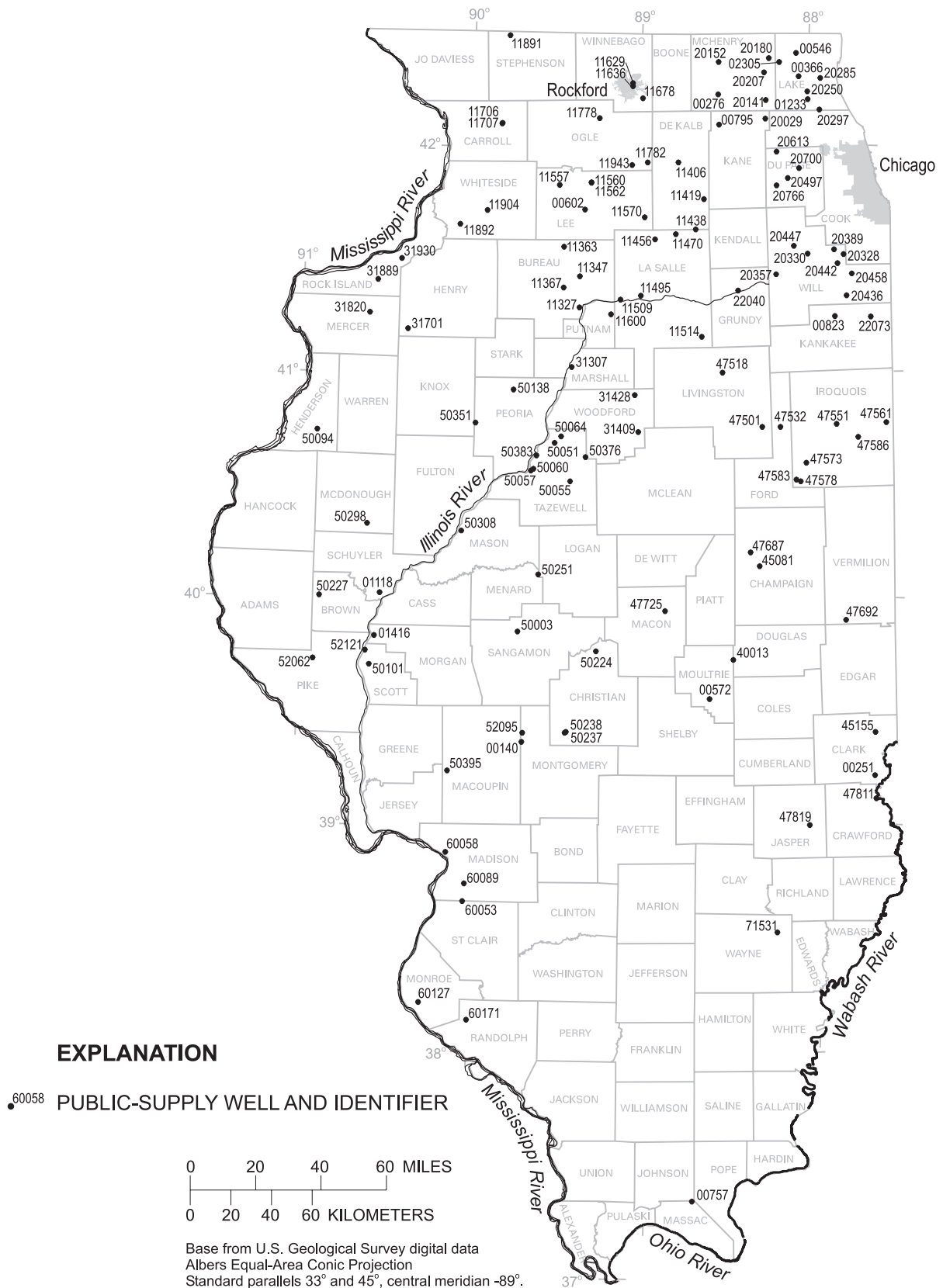


Figure 3. Locations of selected public-supply wells that tap source-water aquifers in Illinois.

Purpose and Scope

This report presents (1) analytical results for selected herbicides and their transformation products in samples collected from 117 public-supply wells in Illinois from October 2001 through September 2002, (2) analysis of selected factors that may relate to the occurrence of herbicides in the State's source-water aquifers or indicate their possible occurrence, and (3) results of herbicide analyses in paired unfiltered and filtered samples to determine if these two types of samples can be considered equally representative of herbicide concentrations in ground water supplied to the public. Analytical results are included for 18 herbicides and 18 transformation products, representing triazine, chloroacetanilide, and glyphosate compounds. Relational factors that were evaluated include herbicide use, hydrogeologic characteristics, well-construction aspects, land use, and occurrence of excess nitrate (concentrations of nitrate, as nitrogen, higher than 3 mg/L) in ground water.

Acknowledgments

Various persons and agencies are acknowledged for their contributions to the study. Wade Boring, Alan Fuhrmann, Laurie Moyer, Gregory White, Edward Wagner, Joseph Konczyk, and Matthew Campbell of the IEPA, Division of Public Water Supplies, scheduled sampling visits with well owners; provided location maps, routing instructions, well-construction details, and other study-related information; calibrated field water-quality meters; prepared wells for sampling; and collected ancillary water-quality data. Well operators and owners freely provided ancillary well information and access to the wells for sampling. Paul Terrio, Robert Kay, and Steven Stammer, USGS, Illinois District, assisted in collecting water samples.

Study Methods

The methods used for well selection, land-use determination, sample collection, laboratory analysis, quality assurance, and data analysis are described in the following sections of the report. Quality-assurance methods include on-site (sampling) and laboratory methods.

Well Selection and Land-Use Determination

Water samples collected in this study for analysis of herbicide compounds were obtained from wells selected by a stratified-random method (Illinois Environmental Protection Agency, 2003a). Criteria used for stratification included aquifer type, geologic-based vulnerability to contamination, and well depth. The selected wells tap major types of source-water aquifers in Illinois – that is, aquifers composed of sand and gravel or of Pennsylvanian- to Cambrian-age bedrock (generally classified as sand and gravel, Pennsylvanian, Mississippian, Silurian-Devonian, and Cambrian-Ordovician aquifers) (fig. 2). Most of the source-water aquifers tapped by the wells in this study (and other public-supply wells in this State) are principal aquifers, as classified by O'Hearn and Schock (1984) (fig. 1). These aquifers have a potential yield of 100,000 gal/d/mi², an area of at least 50 mi², and are categorized here as unconsolidated (sand and gravel), shallow bedrock (depth to top of aquifer is less than or equal to 500 ft), and deep bedrock (depth to top of aquifer is greater than 500 ft) aquifers (figs. 1, 2). The sand and gravel of the unconsolidated aquifers are deposits from glacial meltwater or streams. The bedrock aquifers generally consist of carbonate or sandstone. Fifty-four of the selected wells tap unconsolidated aquifers (well depths 28-404 ft), 54 tap shallow bedrock aquifers (well depths 71-1,870 ft), and 9 tap deep bedrock aquifers (well depths 820-2,591 ft).

As part of the study, extent of land use for corn and soybean (row-crop) production near the sampled wells was determined. On-site inspection, aerial photographs, and topographic maps were used to identify and estimate percentages of land used for row-crop production within radial distances of 1 and 2 mi of the wells. Trace percentages were estimated to be within the range from greater than 0 to 5 percent of land use. Other percentages were estimated within ranges of from greater than 5 to 25, greater than 25 to 50, greater than 50 to 75, and greater than 75 to 100 percent.

Sample Collection and Laboratory Analysis

Water samples for herbicide analysis were collected by USGS personnel using methods detailed in Kolpin and Burkart (1991) and Wilde and others (1997 to present). Prior to collection of these samples, the wells were purged and other water-quality samples, including

samples for nitrate analysis, were collected by IEPA personnel. Wells were purged through a raw-water tap (before chlorination or other chemical treatment) for 15 minutes or longer to remove water stored in the well casing and delivery piping (fig. 4). Using a calibrated field water-quality meter with an attached flow-through cell, values of water temperature, pH, specific conductance, and oxidation-reduction potential were monitored to ensure stabilization of these field water-quality characteristics and, thus, that the sample would be representative of aquifer water quality. Samples for herbicide analysis were passed through a 0.7 micron, baked, glass-fiber filter (fig. 5a) at a rate of 0.25 gal/min or less and collected in 125-ml, amber, baked-glass bottles (fig. 5b). To limit exposure of the sample to the atmosphere, the filtering equipment was connected directly to the sample tap at the well; more than 90 percent of the wells and sample taps were enclosed in a well house. The samples were shipped chilled (4° C or less) to the analytical laboratory within 2 days of collection.

The filtering equipment, including tubing, connectors, and filter plate, was constructed of Teflon or stainless steel to avoid leaching or adsorption of the organic

herbicides. Before sampling, all equipment was cleaned thoroughly with a mixture of laboratory-grade (non-phosphate) soap and tap water and rinsed with deionized water. The water, obtained from the USGS, Illinois District office, has been tested periodically and found free of herbicide compounds.

Selected samples were collected to evaluate the relation between herbicide analytical results for unfiltered and filtered samples. The sampling method used in most herbicide studies by the USGS, particularly projects assisted by the USGS Organic Geochemistry Research Group (OGRG) (Kolpin and Burkart, 1991; Zimmerman and Thurman, 1999), requires filtering to provide samples that essentially are free of particulates. Traditionally, the IEPA collects unfiltered samples that represent total concentrations of constituents (dissolved and undissolved fractions). The IEPA sampling method is dictated by one aspect of their mission -- to evaluate and regulate the quality of drinking water (Illinois Environmental Protection Agency, 2003b). Ground water supplied to the public generally is not processed to remove particulates. Because ground water withdrawn by public-supply wells typically is essentially



Figure 4. Monitoring of field water-quality characteristics (temperature, pH, specific conductance, oxidation-reduction potential) for stabilization of values prior to collection of ground-water samples.

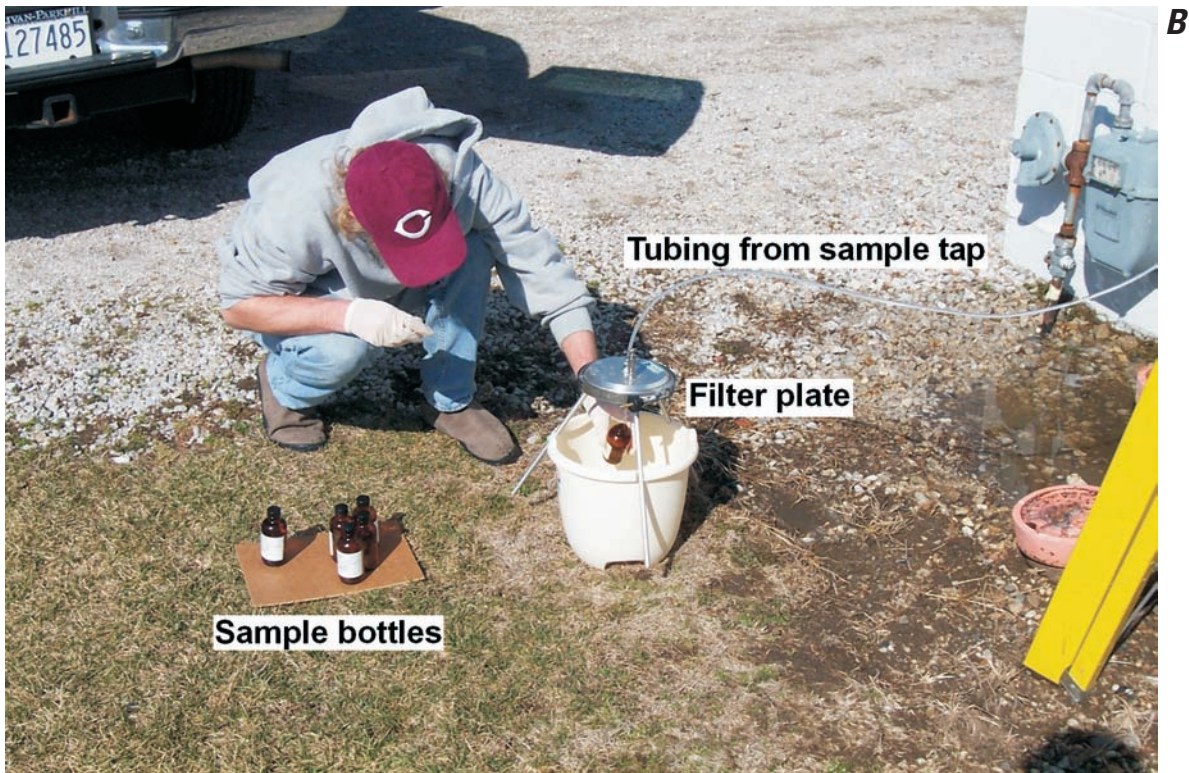
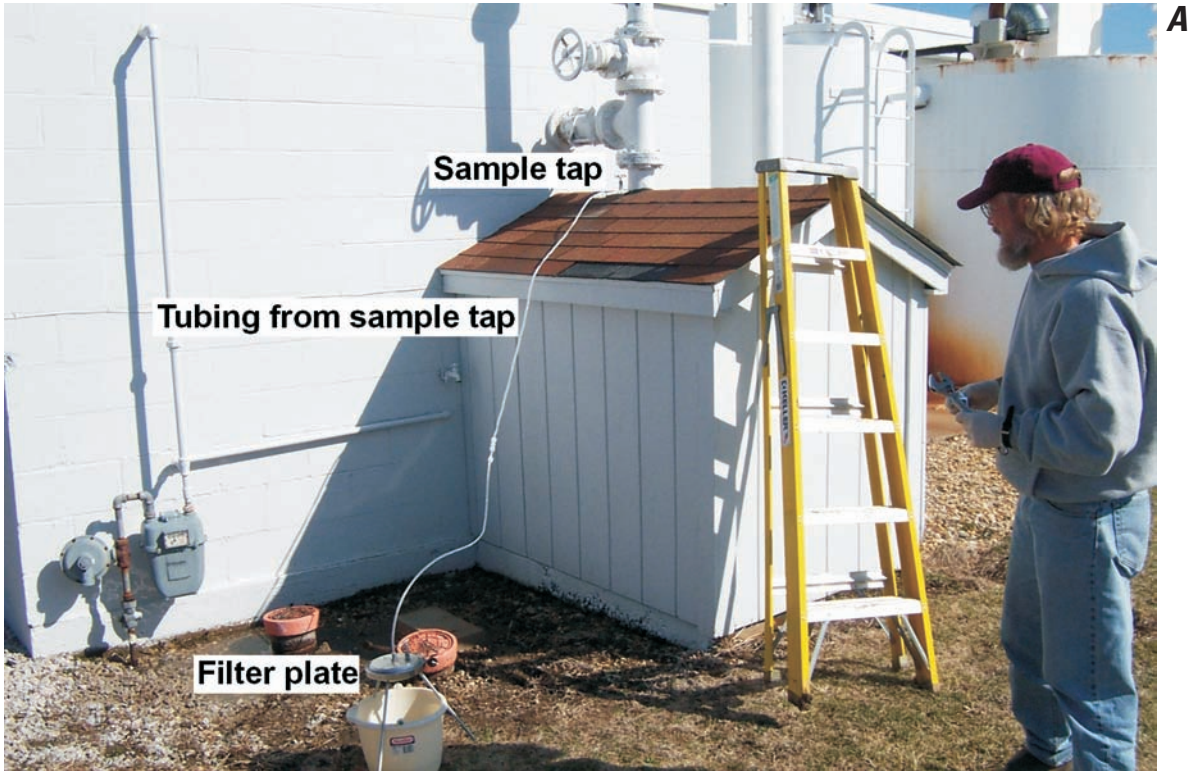


Figure 5. Ground-water sampling at well 47725, Oreana, Ill., for analysis of herbicide compounds: (A) routing of discharge from the well through Teflon tubing to a 0.7-micron, baked, glass-fiber filter enclosed in a stainless-steel filter plate, and (B) collection of samples in 125-milliliter, amber, baked-glass bottles (refer to figure 3, Macon Co., for well location; photographs by Steven E. Stammer, U.S. Geological Survey).

free of visible particulates, the following assumption was evaluated – herbicide-analytical results for unfiltered and filtered samples should be similar (cannot be differentiated statistically). If this assumption is valid, it would indicate that filtering is unnecessary for most samples collected from public-supply wells for herbicide analysis (assumed to be at least 95 percent of samples, as indicated by the samples collected during this study), because unfiltered-sample results can be considered as equally representative of herbicide concentrations as filtered-sample results in ground water supplied to the public. Elimination of filtering would (1) allow better comparison of herbicide-analytical results to those of other constituents from public-supply wells using IEPA methods and (2) substantially reduce the time and expense of sample collection.

Unfiltered samples were collected at 13 wells (11 percent of all samples) for comparison with the filtered samples that were collected routinely during the year-long study. Eleven of the wells were selected randomly. Two of the wells, including well 52095 and 50351 (fig. 3), were selected on the basis of field observations of

clay-sized particulates on the filter media following routine sample collection (fig. 6).

Thirty-six herbicide compounds were analyzed by the USGS OGRG laboratory in Lawrence, Kans. Samples were analyzed for 16 herbicides and 3 triazine transformation products by gas chromatography/mass spectrometry (GC/MS) following solid-phase extraction (Zimmerman and Thurman, 1999; Kish and others, 2000); 14 chloroacetanilide transformation products (6 ethane sulfonic (ESA), 6 oxanilic (OA), and 2 sulfynil acetic (SAA) acids) by high-performance liquid chromatography/mass spectrometry (HPLC/MS) following solid-phase extraction (Zimmerman and others, 2000; Lee and others, 2001); and glyphosate, its transformation product amino methyl phosphonic acid (AMPA), and glufosinate by HPLC/MS following solid-phase extraction (Lee and others, 2002). The reporting limit for most herbicides and transformation products was 0.05 $\mu\text{g/L}$; the limit for glyphosate and related compounds was 0.1 $\mu\text{g/L}$.



Figure 6. Examples of clay-sized particulates on filter media for samples collected from two public-supply wells that tap source-water aquifers in Illinois, 2001-02 (filter diameter is 142 millimeters—about 5.5 inches; refer to figure 3, Montgomery Co. and Peoria Co., respectively, for well locations).

Quality Assurance

The quality-assurance program for the data collected during this study are divided into two categories: on-site (sampling) methods and laboratory methods. Discussion of those methods and results of quality-assurance evaluations follows.

Differences in paired quality-assurance samples were evaluated by the relative percent difference (RPD) method (U.S. Environmental Protection Agency, 1989). For this method,

$$RPD = \frac{(C1 - C2) \times 100 \text{ percent}}{(C1 + C2) / 2} ,$$

where

C1 is the concentration of the field sample,

and

C2 is the concentration of the quality-assurance sample.

The method is used to assess the relative magnitude to which the analytical results of the sample pairs differ, and possible bias in the analytical results; that is, whether concentrations are typically over- or under-estimated for a particular sample type.

Quality-assurance methods used during sample collection are described in the previous section "Sample Collection and Laboratory Analysis" and in Kolpin and Burkart (1991) and Wilde and others (1997 to present). Other on-site methods consisted of collecting equipment (or field) blanks and sample duplicates for analysis. Each equipment blank was collected after cleaning the filtering equipment following sample collection. The blanks were collected, as if routine field samples, by pumping laboratory-certified, volatile-organic-free water through the filtering equipment using a peristaltic pump. Analytical results of equipment-blank samples are used to evaluate the effectiveness of routine equipment-cleaning methods and the possibility of atmospheric contamination of the filtering equipment. Twelve equipment blanks were collected (10 percent of field samples). A pseudo-random process was used to select blank-sample sites. Sites were weighted to ensure that blanks were collected (1) during the primary period of herbicide application in Illinois (March-May) (30 percent of blanks) and (2) by each sampler (representing from 5 percent of the sites visited by a sampler to 22 percent of the sites visited by a sampler).

No herbicide compounds were detected in any of the equipment blanks. Five of the field samples collected immediately prior to collection of the blank samples had detectable concentrations of three to seven herbicide compounds, with a maximum concentration of 1.59 µg/L. Thus, equipment-cleaning methods used in the study were determined to be effective.

Each duplicate sample was collected after its associated routinely scheduled field sample was collected and the filtering equipment was cleaned. Thus, the duplicate-sample site was treated as if had not been sampled previously. Analytical results of duplicates are used to evaluate the random variation of sampling. Five duplicates were collected (4 percent of field samples). A pseudo-random process was used to select duplicate-sample sites. Sites were weighted to ensure that duplicates were collected by each sampler; duplicates were collected from 2 percent of the sites visited by a sampler to 15 percent of the sites visited by a sampler.

No herbicide compounds were detected in three of the paired field and duplicate samples. Two of the field samples had detectable concentrations of one to three herbicide compounds. RPD's for the detectable concentrations in the paired samples ranged from -15 to +8 percent. The RPD's are exaggerated by the low herbicide concentrations (0.06-0.41 µg/L). No difference in concentration between individual analyte pairs was greater than 0.02 µg/L. The measured differences in concentrations were at or near the expected variance of the analytical methods (Zimmerman and Thurman, 1999; Zimmerman and others, 2000). With minimal random variation associated with sample collection, the analytical results were determined to accurately represent ground-water quality at the sample sites.

Laboratory quality-assurance samples are used for evaluation of laboratory-analytical methods, which include guidelines for sample-holding times, quantitation-reporting limits, instrument calibration, sample preparation, and sample analysis. Laboratory quality-assurance methods consisted of collecting laboratory duplicates and spikes for analysis. Specific methods for selecting and preparing laboratory quality-assurance samples can be obtained from the OGRL laboratory, on request. Laboratory duplicates were prepared and evaluated for 15 samples analyzed primarily for parent triazine and chloroacetanilide herbicides by GC/MS, 12 samples analyzed for glyphosate and related compounds

by HPLC/MS, and 15 samples analyzed for chloroacetanilide transformation products by HPLC/MS.

No parent triazine, chloroacetanilide, or glyphosate-related herbicides were detected in any of the paired laboratory duplicates. Three of the paired field and laboratory-duplicate samples had detectable concentrations of one to three chloroacetanilide transformation products. RPD's for the detectable concentrations in the paired samples ranged from -13 to +15 percent. The RPD's are exaggerated by the low herbicide concentrations (0.06-0.18 $\mu\text{g/L}$). No difference in concentration between individual analyte pairs was greater than 0.01 $\mu\text{g/L}$. The measured differences in concentrations were within the expected variance of the analytical methods (Zimmerman and Thurman, 1999; Zimmerman and others, 2000). With minimal variability associated with sample preparation and analysis, the analytical results were determined to accurately represent ground-water quality at the sample sites.

Data Analysis

Selected factors that may relate to the occurrence of herbicide compounds in the source-water aquifers of the State or indicate their possible occurrence were analyzed graphically and statistically. Relational factors included herbicide use, hydrogeologic characteristics, well-construction aspects, land use, and occurrence of excess nitrate. Most of the factors have been identified in other studies of herbicides in ground water. Among these studies is a regional study of the Midwestern corn-belt States (fig. 1), including Illinois, conducted during 1991-94 (Kolpin and others, 1994, 1995, 1996, 1998a). The factors were reexamined in this study to determine whether the relations were consistent at a scale smaller than the Midwestern study and, in particular, whether they were consistent with hydrogeologic conditions specific to Illinois.

The correlation between frequency of detection (representing occurrence) of herbicide compounds in the State's source-water aquifers and the selected relational factors was examined using the Pearson's r method (Helsel and Hirsch, 1995). The method provides the degree of linear relation (from -1 to +1) between selected variables. A correlation of +1 indicates a perfect positive linear (but not causal) relation between two variables (for example, frequency of herbicide detection and confining-unit thickness). For the correlations, rank values

were used to represent selected ranges of the measurable factors. For example, for the factor confining-unit thickness, ranks of 1 to 5 were used to represent the following intervals of increasing thickness: 0-10, 11-20, 21-50, 51-100, and greater than 100 ft. Examination of the histograms used to graphically evaluate the correlation between herbicide occurrence and the various relational factors verifies the linear relation between these variables and, thus, the use of the Pearson's r method. The Spearman's rank test was used to determine the covariance (degree of linear relation from -1 to +1) between nitrate and herbicide-compound concentrations; that is, whether, as nitrate concentrations increase, herbicide-compound concentrations tend to increase or decrease.

The difference in concentration of herbicide compounds determined from paired unfiltered and filtered samples was evaluated, in part, using the RPD method (U.S. Environmental Protection Agency, 1989). As described in the section "Quality Assurance", the method is used to assess the relative magnitude to which the analytical results of sample pairs differ. For the evaluation of unfiltered and filtered sample pairs, concentration C1 represents the unfiltered sample and C2 represents the filtered sample. It was assumed that if concentrations of the paired samples differ, concentrations of the unfiltered sample likely would be higher than those of the filtered sample.

Concentrations of herbicide compounds determined from paired unfiltered and filtered samples also were evaluated to determine if the resultant populations were statistically different. Various statistical tests were used, including the sign test, Wilcoxon signed-ranks test, and paired Student's t -test (Helsel and Hirsch, 1995). These tests were considered appropriate because the differences between values (concentrations) in the data pairs, although typically nonparametric (not distributed normally), can be considered symmetric. For paired data, the sign test determines whether values from one data set generally are larger, smaller, or different than values from its paired data set. This test may be used regardless of the distribution of the differences and, thus, is fully nonparametric. The Wilcoxon signed-ranks test determines whether the median difference between paired values is significantly different than zero. That is, do the paired data sets represent different populations? For this test, the distribution of the difference in paired values need not be normal but is assumed to be symmetric. The paired Student's t -test determines whether mean differ-

ence between paired values is significantly different than zero. For this test, the distribution of the difference in paired values is assumed to be normal.

A significance level of 0.05 was used for all statistical evaluations. This probability of error ($\rho=0.05$) means that there is 1 chance in 20 that the statistical test reported a significant difference between the paired data when there was not a significant difference. The smaller the ρ value, the greater is the certainty that a reported statistical difference is real.

Occurrence of Herbicides and Transformation Products

Analytical results for the study of herbicides and herbicide transformation products in source-water aquifers tapped for public supply in Illinois are presented in this section. Frequencies of detection and representative concentrations of the herbicide compounds are described and considered with respect to the results of other studies conducted in Illinois and elsewhere of herbicides in ground water. The analytical results, representing samples collected from October 2001 through September 2002, are summarized in table 1 and presented in full in appendixes 1 and 2. Location and construction information for the sampled wells and their field-measured characteristics of water quality also are presented in appendix 1.

Frequencies of Detection and Concentrations

Herbicide compounds were prevalent in Illinois' source-water aquifers, as indicated by the frequency (table 1) and spatial distribution of detected herbicides and (or) transformation products (fig. 7). Parent herbicides (atrazine and metolachlor) were detected in 4 percent of all samples, and parent herbicides and transformation products were detected in 34 percent of samples. Multiple herbicide compounds were detected in 70 percent of samples, with a median of three and a maximum of eight compounds in samples in which more than one compound was detected. Of the 11 detected compounds, 9 were transformation products (table 1; fig. 8). Six chloroacetanilide transformation products, including alachlor ESA (28 percent), metolachlor ESA (26 percent), metolachlor OA (14 percent), and acetochlor ESA (9 percent), were the most frequently detected

compounds. Detection frequencies of ESA compounds consistently exceeded those of OA compounds for all chloroacetanilides (for example, alachlor ESA, 28 percent; alachlor OA, 6 percent).

Concentrations of detected herbicide compounds ranged from the reporting limit of 0.05 $\mu\text{g/L}$ to 7.24 $\mu\text{g/L}$ (metolachlor ESA), with concentrations of parent herbicides substantially lower than those of their transformation products (table 1; fig. 9). The median concentration of detected parent herbicides was 0.07 $\mu\text{g/L}$, whereas the median concentration of all detected herbicide compounds, including transformation products, was 0.16 $\mu\text{g/L}$. The highest concentration of a parent herbicide (atrazine) was 0.22 $\mu\text{g/L}$, whereas concentrations of the chloroacetanilide transformation products in seven samples (including metolachlor ESA in four samples) exceeded 1 $\mu\text{g/L}$. Concentrations (maximum, mean, and usually median) of ESA compounds exceeded those of OSA compounds and both exceeded the concentrations of their parent compounds. As indicated by these findings, the frequency of detection and the concentration greatly increase for most herbicides when their transformation products also are considered (table 1; figs. 8, 9).

No concentrations exceeded Federal maximum contaminant levels (MCL's) or health advisory levels (U.S. Environmental Protection Agency, 2003b) (table 1) or Illinois standards (Illinois Pollution Control Board, 2003) established for the protection of public-water supplies. However, these levels have been established for only seven herbicides and have not been established for any transformation products. In addition, no regulatory levels consider the toxicity or aquatic effect of multiple compounds in water. The concentration of alachlor ESA in one sample exceeded the MCL (2 $\mu\text{g/L}$) of its parent compound. S-metolachlor was not analyzed for in this study. Recorded use of this herbicide began in 2000 with about 3 million pounds applied in that year and 4 million pounds applied in 2001 (U.S. Department of Agriculture, 2001). These herbicide-application rates rank fourth and third, respectively, in those years. S-metolachlor reportedly requires only 65 percent of the application rate of metolachlor, thus less active ingredient than that of metolachlor may be available for leaching to ground water (Ecologic-IPM, 2003).

Deethylatrazine, deisopropylatrazine, and cyanazine amide were the only transformation products of triazine herbicides analyzed for in this study. Other triazine transformation products that previously have been

Table 1. Summary statistics for herbicides and their transformation products in ground-water samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001–September 2002.

[µg/L, micrograms per liter; na, not applicable]

Analyzed for but not detected: acetochlor sulfinil acetic acid (SAA), alachlor SAA, ametryn, flufenacet, flufenacet ethanesulfonic acid (ESA), flufenacet oxanilic acid (OA), glufosinate, AMPA, pendimethalin, prometon, prometryn, propazine, and terbutryn; SAA, ESA, and OA are transformation products (TP) of the associated herbicides; AMPA is a transformation product of glyphosate. Reporting limit for most herbicide compounds was 0.05 µg/L; reporting limit for glyphosate, amino methyl phosphonic acid (AMPA), and glufosinate was 0.10 µg/L.

Maximum contaminant levels (MCL)¹ for atrazine, alachlor, simazine, and glyphosate are 3, 2, 4, and 700 µg/L, respectively; health advisory levels¹ for cyanazine, metolachlor, and metribuzin are 1, 100, and 200 µg/L, respectively.

Herbicide compound	Detection frequency, in percent	Median detected concentration, in µg/L	Maximum detected concentration, in µg/L	Herbicide-application rate in Illinois ² , in 1,000 pounds	
	<u>2001-02</u>	<u>2001-02</u>	<u>2001-02</u>	<u>1991</u>	<u>2001</u>
Any parent herbicide	4.3	0.07	0.22	na	na
Any herbicide or TP	34.2	.16	7.24	na	na
Acetochlor	0	na	na	0	8,059
Acetochlor ESA	9.4	.16	4.18	na	na
Acetochlor OA	5.5	.16	.25	na	na
Alachlor	0	na	na	9,400	0
Alachlor ESA	28.2	.12	2.15	na	na
Alachlor OA	6.0	.09	.41	na	na
Atrazine	3.4	.06	.22	10,615	14,143
Deethylatrazine ³	4.3	.08	.21	na	na
Deisopropylatrazine ⁴	0	na	na	na	na
Cyanazine	0	na	na	4,267	0
Cyanazine amide ⁵	0	na	na	na	na
Dimethenamid	0	na	na	0	2,270
Dimethenamid ESA	2.6	.05	.16	na	na
Dimethenamid OA	0	na	na	na	na
Glyphosate	0	na	na	381	7,157
Metolachlor	.9	.16	.16	9,277	993
Metolachlor ESA	26.5	.34	7.24	na	na
Metolachlor OA	14.5	.18	2.95	na	na
Metribuzin	0	na	na	395	0
Propachlor	0	na	na	0	0
Propachlor ESA ⁶	1.0	.10	.10	na	na
Propachlor OA	0	na	na	na	na
Simazine	0	na	na	0	265

¹U.S. Environmental Protection Agency (2003b).

²U.S. Department of Agriculture (2003). Data are not reported for herbicides applied on less than 1 percent of corn and soybean row-crop acreage or herbicides applied on sweet or processed-corn acreage, which generally represents less than 1 percent of total application on row-crop acreage.

³Transformation product of atrazine.

⁴Transformation product of atrazine, cyanazine, and simazine.

⁵Transformation product of cyanazine.

⁶Ninety-nine samples were collected for analysis of propachlor ESA and OA, and all SAA compounds.

detected in Illinois ground water but were not analyzed for in this study include hydroxyatrazine and deethyldeisopropylatrazine (Kelly L. Warner and William S. Morrow, U.S. Geological Survey, written commun., 2003). Frequency of occurrence and concentrations of these compounds in ground water are expected to be low, as indicated by field experiments and (or) sampling history. Hydroxyatrazine has a greater tendency to sorb to soils than atrazine, its primary parent compound, or other atrazine transformation products (Barbash and Resek, 1996). Thus, frequent occurrence of hydroxyatrazine in ground water, particularly at concentrations above those of other atrazine compounds, would be unexpected.

Deethyldeisopropylatrazine is a transformation product of the first-order products deethylatrazine, deisopropylatrazine, and hydroxyatrazine. In a study of herbicides in shallow ground water (depth less than about 50 ft) in central Illinois (Kelly L. Warner and William S. Morrow, U.S. Geological Survey, written commun., 2003), hydroxyatrazine was detected in only 4 percent of 69 samples collected for the study; the maximum concentration was 1.14 µg/L. Deethyldeisopropylatrazine was detected in only 4 percent of 28 samples (1 sample); the maximum concentration was 1.0 µg/L.

The extensive use of alachlor, acetochlor, and metolachlor during the past decade (1991-2001) (fig. 10)

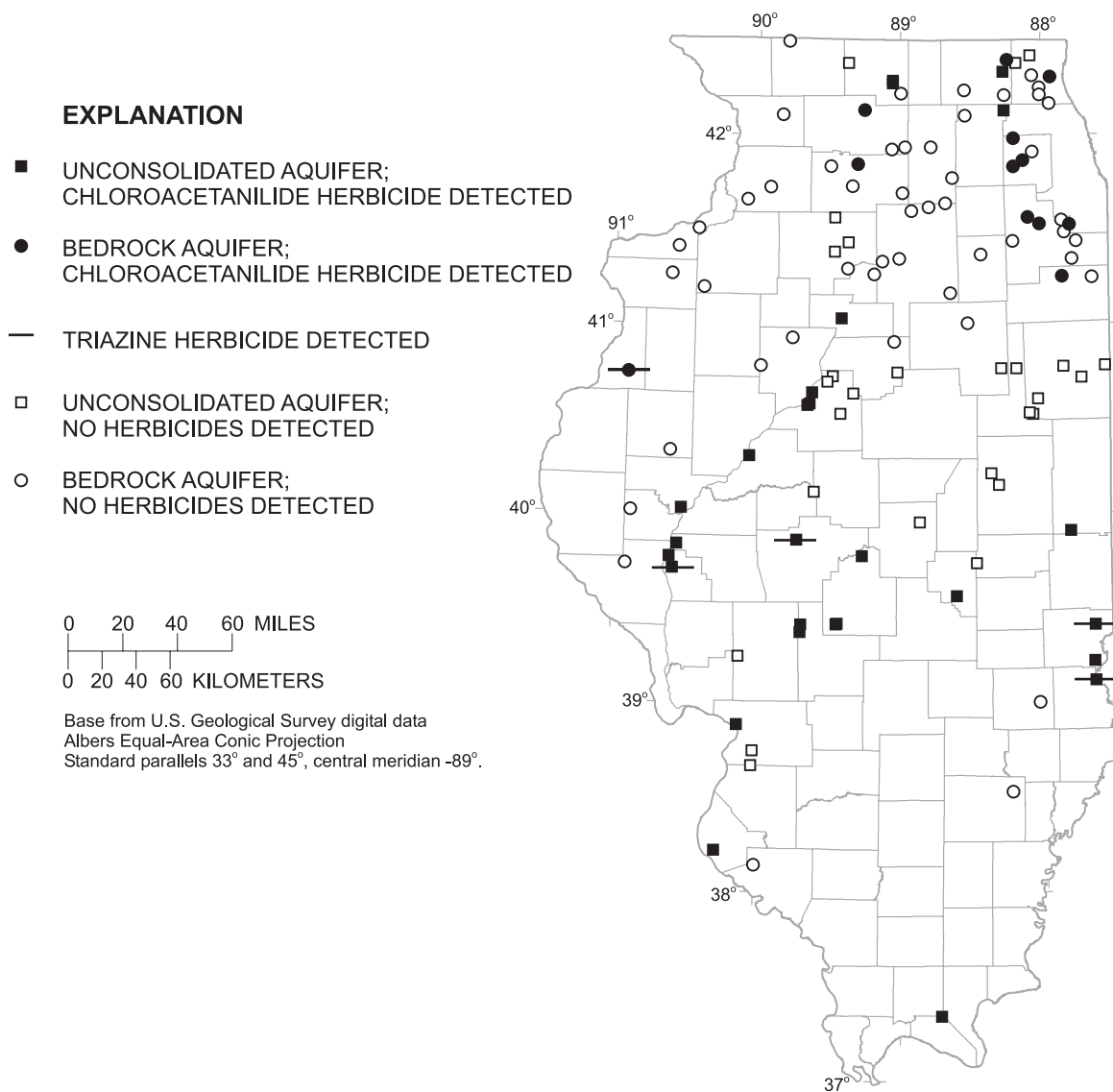


Figure 7. Locations of selected public-supply wells that tap source-water aquifers in Illinois, aquifer type (unconsolidated or bedrock) that the wells tap, and occurrence of herbicides or transformation products, 2001-02.

along with their comparatively low detection rates and concentrations in ground water as parent compounds and comparatively high detection rates and concentrations as transformation products (ESA and OA compounds) (table 1) confirms previous observations that each of these structurally related chloroacetanilide herbicides transforms similarly (Kolpin and others, 1996; Aga and others, 1995). Each of the parent herbicides degrade readily in the soil zone and persist in ground water as mobile transformed compounds. Furthermore, the frequencies of detection and concentrations in this and other studies (Kalkhoff and others, 1998, Kolpin and others, 2000b) for the parent compounds and their transformation products support conclusions that regardless of which chloroacetanilide, ESA compounds are more mobile and persistent than OA compounds (Kalkhoff and others, 1998). The finding that frequencies of detection of metolachlor compounds consistently are greater than those of the alachlor compounds and much greater than those of acetochlor compounds can be attributed, in part,

to the extent to which these compounds have been used in Illinois (fig. 10) and other Midwestern States in recent years. However, the comparatively low occurrence of acetochlor relative to its comparatively heavy use since about 1995 indicates that differences in the physical properties and related rates of transformation of the various chloroacetanilide compounds are contributing factors (Kalkhoff and others, 1998) to the consistent ranking of the detection frequencies of these compounds.

The more even distribution between the detection frequencies of atrazine (detected in 3 percent of samples) and deethylatrazine (detected in 4 percent of samples) than that determined for the chloroacetanilide herbicides and their transformation products (table 1) is related to the comparatively slower transformation rate for atrazine, particularly under hypoxic conditions (Clay and others, 1995; Agertved and others, 1992; McMahon and others, 1992; Klint and others, 1993; Nair and Schnoor, 1992), and is indicative of the relative stability of atrazine and deethylatrazine (Thurman and others, 1992;

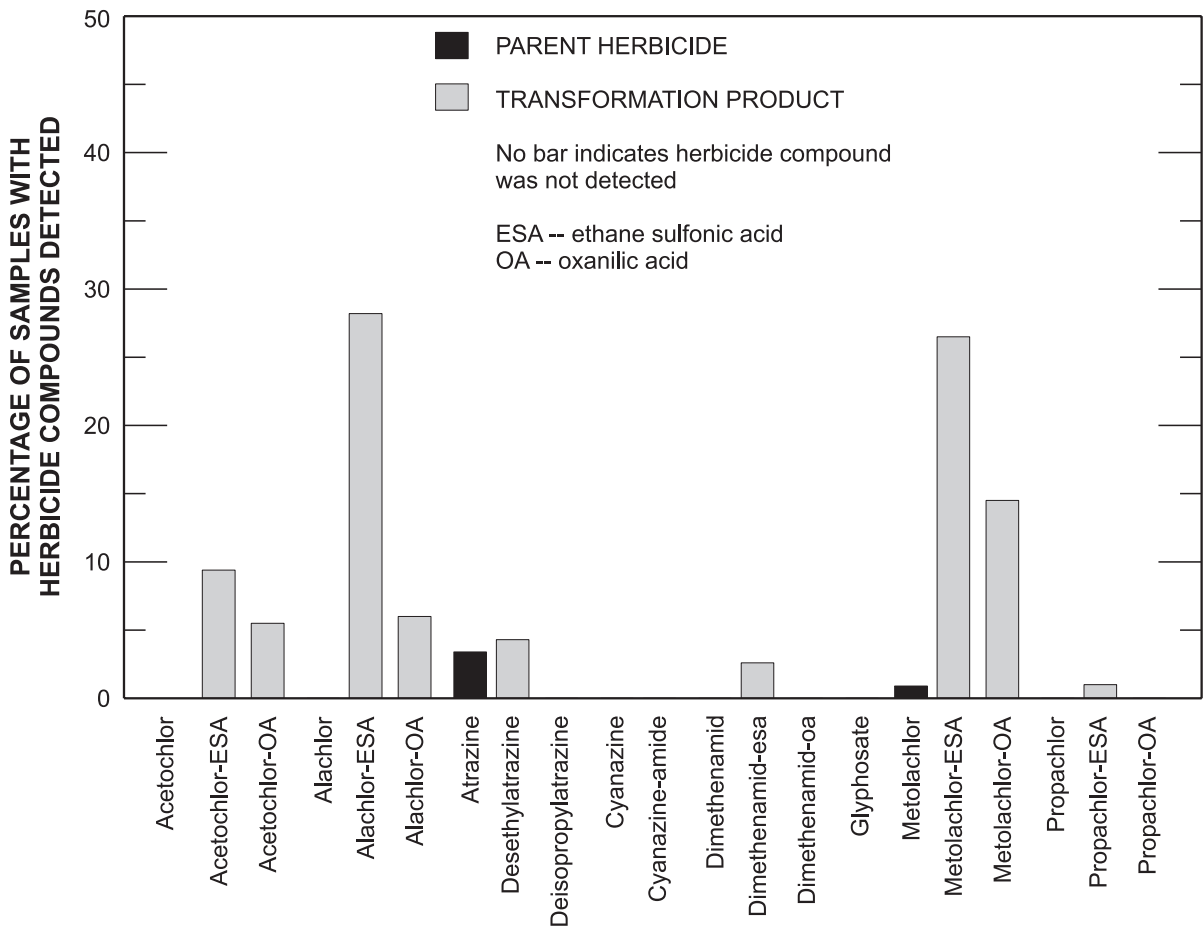


Figure 8. Frequency of detection of herbicides and their transformation products in source-water aquifers in Illinois, 2001-02.

Roy and Krapac, 1994; Jayachandran and others, 1994). The slow transformation of atrazine allows more of it to be transported to ground water than the parent chloroacetanilides.

The concentration ratios of deethylatrazine to atrazine (DAR's) recorded in this study (from 0.95 to 4.2) indicate that the atrazine detected in the ground-water samples likely was derived from slow infiltration through well-oxygenated soil, as typically associated with non-point sources (Adams and Thurman, 1991; Thurman and others, 1991). Such hydrogeologic conditions allow for increased transformation of atrazine to deethylatrazine by soil microorganisms. Rapid infiltration to poorly oxygenated hydrogeologic environments below the soil zone, as typically associated with point sources and (or) preferential flow, limits transformation of atrazine and, thus, results in lower DAR's than those recorded in this study (ratios may range down to 0.1 or less).

Deisopropylatrazine, a transformation product of atrazine, cyanazine, and simazine, was not detected in samples collected for this study. Its nondetection probably relates in part to (1) its instability relative to atrazine and deethylatrazine (Geller, 1980; Adams and Thurman, 1991) and (2) the limited recent and (or) historical use of cyanazine and simazine in Illinois row-crop production (fig. 10).

The extensive use of glyphosate since 1996 (fig. 10), following introduction of Roundup Ready soybeans, along with its nondetection in Illinois' source-water aquifers as either a parent compound or transformation product (AMPA) confirms previous observations (Giesy and others, 2000) that the mobility and persistence of glyphosate are low. Field and laboratory studies indicate that glyphosate sorbs strongly to soils and degrades readily by microbial processes (Extension Toxicology Network, 2003).

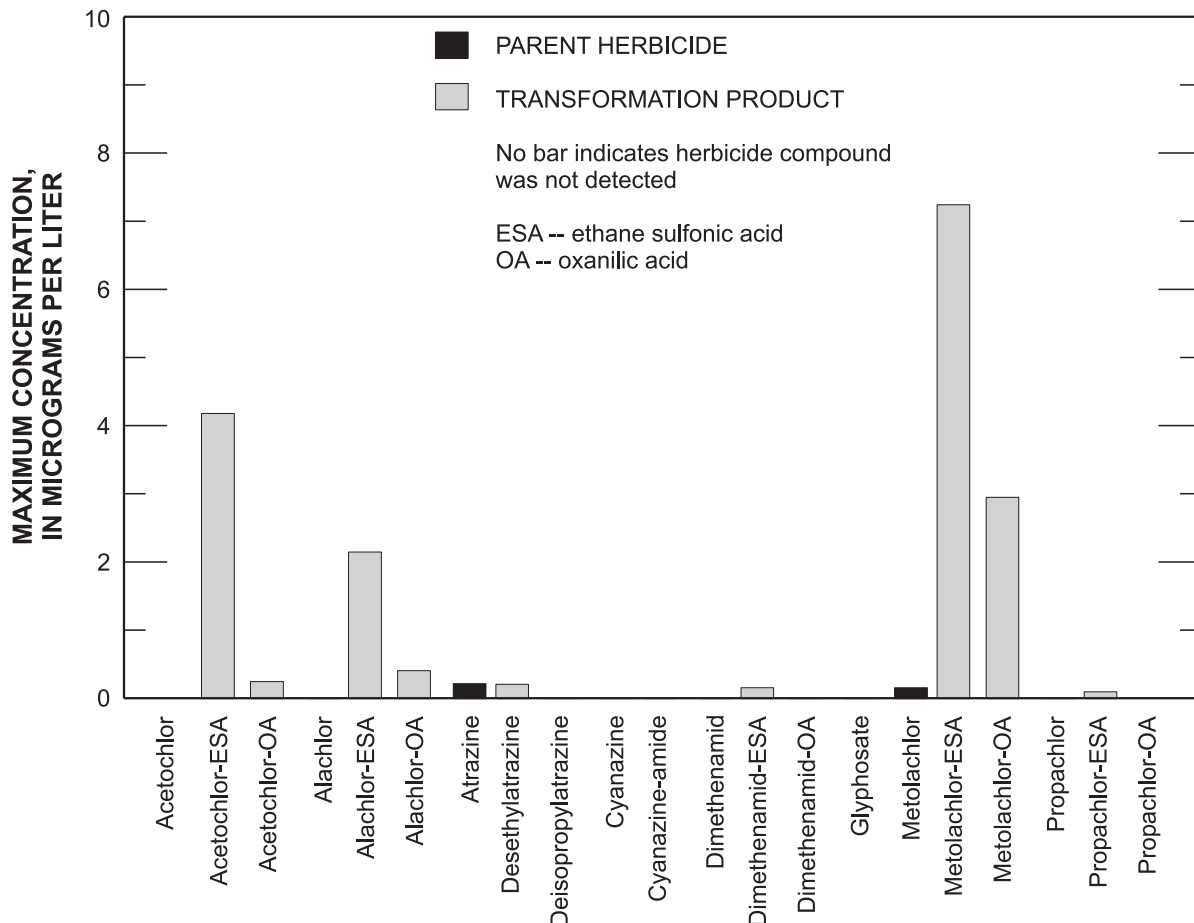


Figure 9. Maximum concentrations of herbicides and their transformation products in source-water aquifers in Illinois, 2001-02.

Comparison to Other Studies

The findings of the present study generally are similar to those of other statewide herbicide studies in

Illinois (Dana W. Kolpin, U.S. Geological Survey, written commun., 2004) and Iowa (Kolpin and others, 1997, 1998b, 2000b; Kalkhoff and others, 1998), particularly for the various relations associated with frequencies

of detection and concentrations between parent herbicides and their transformation products. In the previous statewide studies and the present study, transformation products were detected in ground-water samples more frequently and at higher concentrations than their parent compounds. Typically frequencies of detection and concentrations of almost all of the herbicide compounds analyzed for were lower in the present study than in the other statewide studies. For example, in the previous Illinois study (Dana W. Kolpin, U.S. Geological Survey, written commun., 2004), one or more parent herbicide or transformation products were detected in 56 percent of the ground-water samples collected from 55 wells during fall 2000; the maximum concentration detected was 40 µg/L (metolachlor ESA). In the Iowa study (Kalkhoff and others, 1998), one or more parent herbicide or transformation products were detected in 75 percent of the ground-water samples collected from 88 wells during summer 1996; the maximum concentration detected was 50 µg/L (alachlor ESA).

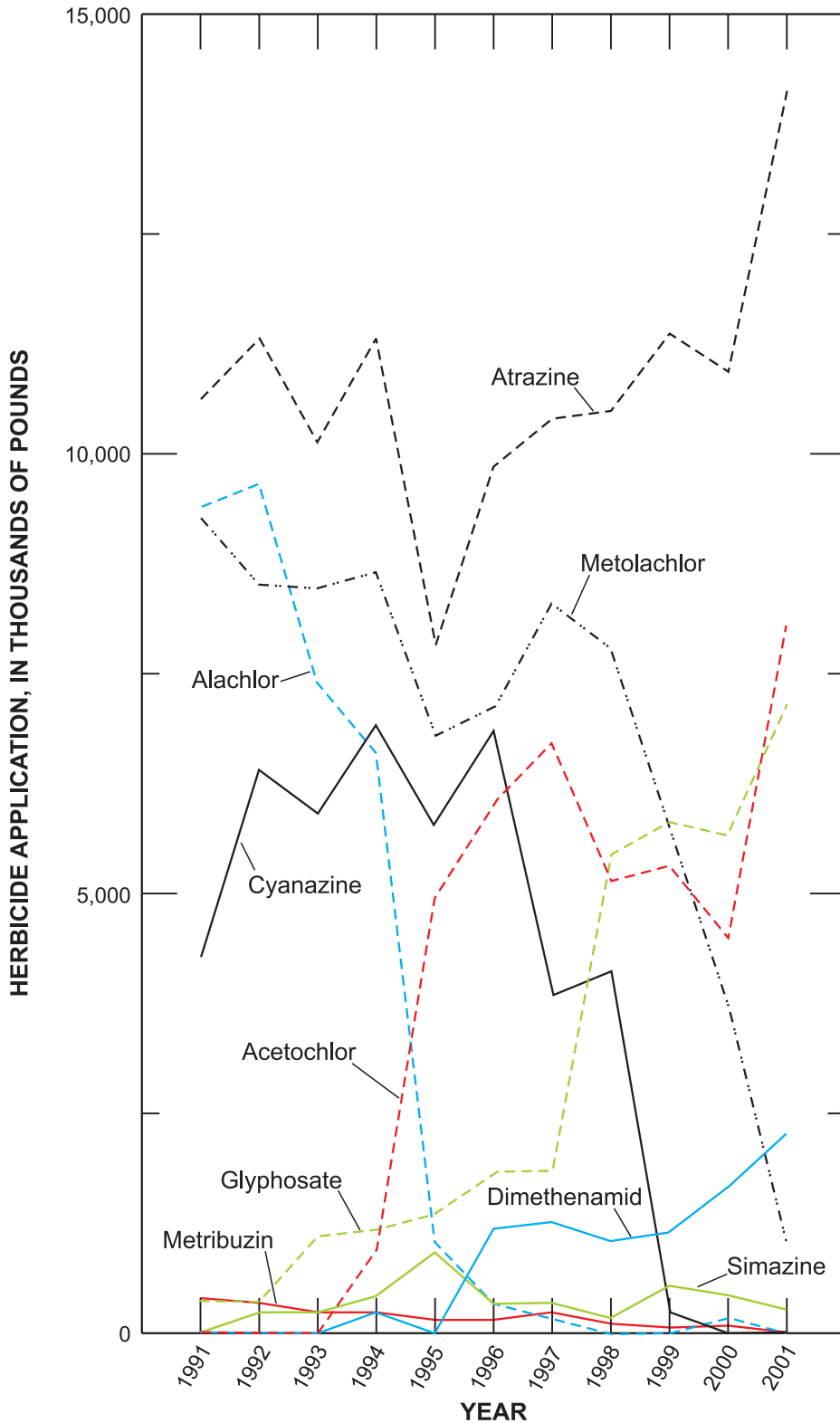


Figure 10. Annual herbicide-application rates in Illinois during 1991-2001 (herbicide-application-rate data are from U.S. Department of Agriculture, 2003; data are not reported for herbicides applied on less than 1 percent of corn and soybean acreage).

Each of the statewide studies described above used the same sample-collection methods, laboratories, analytical methods, and reporting concentrations, and analyzed for essentially the same herbicide compounds. Differences between the results of the present study and those of the previous Illinois study (Dana W. Kolpin, U.S. Geological Survey, written commun., 2004) can be attributed primarily to differences in the ground-water systems under investigation and the types of wells that were sampled. The previous study focused on aquifers expected to be vulnerable to herbicide contamination – that is, on shallow aquifers (unconsolidated and bedrock aquifers less than 50 ft below land surface) in areas where at least 25 percent of the land use was for row-crop production. Wells of various types were sampled, of which only 13 were public-supply wells. Differences between the results of the present study and those of the Iowa study cannot be attributed readily to differences in the ground-water systems under investigation and the types of wells that were sampled. The Iowa samples, like those in the present study, were collected from public-supply wells of various depths that tap Iowa's major types of source-water aquifers (alluvial, glacial drift, bedrock/karst, bedrock/nonkarst, as defined in that study). Temporal sampling bias (Detroy and others, 1988; Risch, 1994; Kolpin and others, 1994) likely accounts for much of the difference in results. In the present study, samples were collected year-round, whereas in the Iowa study, samples were collected during the summer growing season (thus, closer to the time of herbicide application).

The findings of the present study also are similar to those of the Midwestern study that included Illinois (Kolpin and others, 1994, 1995, 1996, 1998a). However, as with the statewide studies, frequencies of detection and concentrations of almost all of the herbicide compounds analyzed for were lower in the present study than in the Midwestern study. In the Midwestern study, one or more parent herbicide or atrazine-transformation products were detected in 28 percent of the ground-water samples collected from about 300 wells during summer 1991; the maximum concentration was 2.3 µg/L (deethylatrazine). Differences between the results of the present study and those of the Midwestern study can be attributed primarily to differences in the ground-water systems under investigation and the types of wells that were sampled. The focus of the Midwestern study was the same as that of the previous Illinois study (aquifers

expected to be vulnerable to herbicide contamination) (Dana W. Kolpin, U.S. Geological Survey, written commun., 2004). As with the present study and the statewide studies, the same collection methods, laboratories, analytical methods, and reporting concentrations were used and essentially the same herbicide compounds were analyzed for (although analysis of transformation products in the Midwestern study was limited primarily to analysis of atrazine compounds).

Comparison of results of the present study with other large-scale studies is difficult because, typically, herbicide transformation products were not analyzed for in samples collected in other studies. In addition, higher analytical reporting limits and different well-selection and sample-collection methods usually were used in other studies. The largest comparable study of public-supply wells is the National Pesticide Survey (NPS) (U.S. Environmental Protection Agency, 1990, 1992). The frequency of detecting one or more herbicide compound was lower in the present study (4 percent, for parent herbicides) than in the NPS study (9 percent, for parent herbicides plus the atrazine transformation product deethylatrazine); concentrations were lower than MCL's or health advisory levels in both studies. Reasons for the greater frequency of detection in the NPS study than the present study are uncertain. Given the typically higher reporting limits and analysis of fewer transformation products in the NPS study, the comparatively higher detection frequencies of the NPS study could be attributed, in part, to differences in the population of wells/aquifers that were sampled and temporal sampling bias (use of herbicides may have been greater in and near the time of the NPS study than that of the present study).

Factors Related to Occurrence of Herbicide Compounds

Awareness of the types of herbicides identified in large-scale studies, such as the present study of Illinois' source-water aquifers, and the factors that may be related to their occurrence can aid in determining the vulnerability of various source-water aquifers to herbicide contamination by certain herbicides and developing more efficient strategies for sample collection. Sampling can be focused on herbicides that likely are to be detected in ground water and on locations and times where potential for contamination is greatest. Focused sampling should

reduce time and costs associated with the collection of samples and with regulatory management of these contaminants. As a result, there may be increased opportunities for addressing other water-quality issues, including further study of the toxicity of various herbicide transformation products and their fate and transport.

Various factors that may be related to the occurrence and detection of herbicides in Illinois' source-water aquifers are examined in the following section. These factors include herbicide use, various hydrogeologic characteristics, well-construction aspects, and land use. Excess nitrate in ground water also is examined as an indicator of herbicide occurrence. Specific herbicide-use factors examined include rates and timing of herbicide applications. Hydrogeologic characteristics examined include depth to the top of the aquifer, thickness of the confining unit, designation as a confined aquifer, and stream proximity. Well-construction aspects examined include well depth and depth to base of the well casing.

Herbicide Use

When only parent compounds are considered, a moderate positive relation ($r = 0.72$) was found between current (2001) herbicide-application rates and current (2001-02) frequency of detection of herbicides in Illinois' source-water aquifers (table 1). Atrazine, the most frequently detected parent herbicide in ground-water samples collected from these aquifers, is consistently the most heavily applied herbicide in Illinois (fig. 10). In 2001, about 14 million pounds of atrazine were applied to the State's corn crops -- almost double the amount of the next most heavily applied herbicides (acetochlor and glyphosate). Metolachlor, the only other parent herbicide that was detected during this study, was the second most heavily applied herbicide during most of 1991-98 (fig. 10).

When herbicide transformation products are considered, there is little to no relation between current herbicide-application rates and current frequency of detection of herbicide compounds in the State's source-water aquifers ($r = -0.20$) (fig. 11A). For example, in 2001,

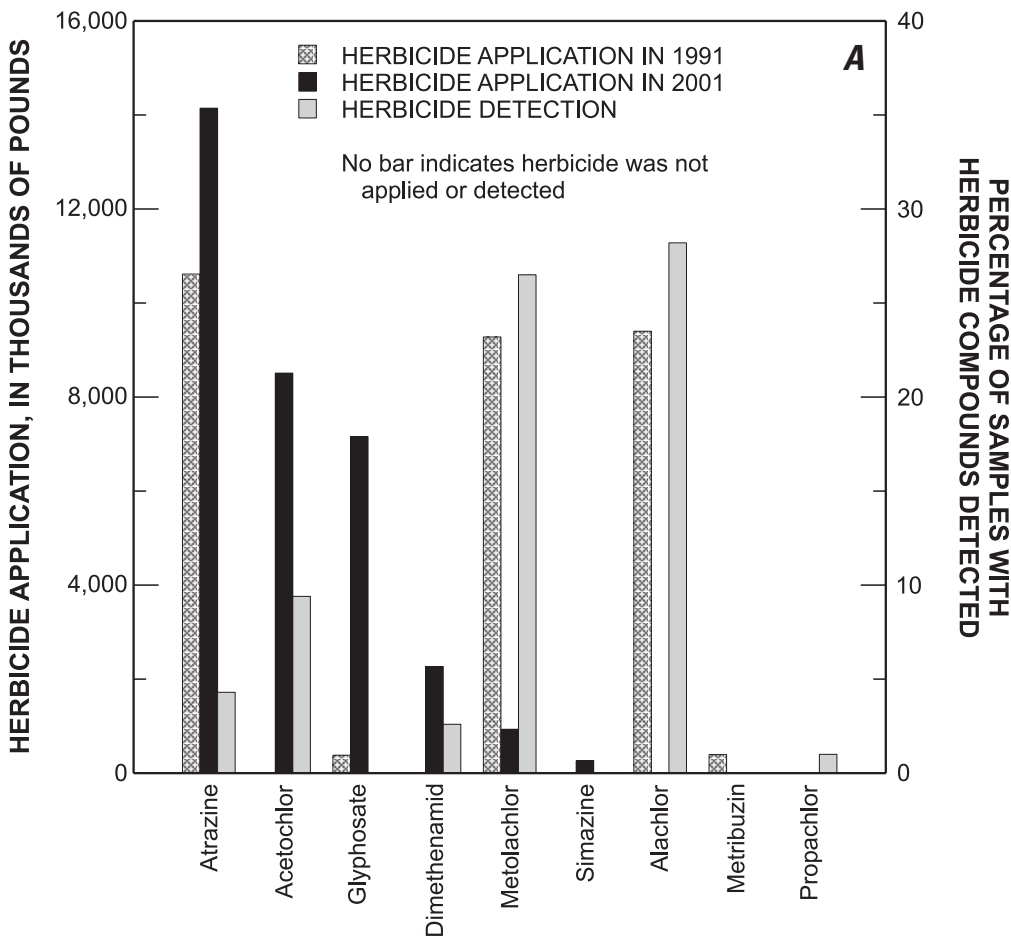


Figure 11. Relation of (A) frequency of detection of herbicides and their transformation products and (B) maximum total concentration of herbicides and their transformation products in source-water aquifers in Illinois (2001-02) to annual herbicide-application rates in Illinois (1991, 2001) (herbicide-application-rate data are from U.S. Department of Agriculture, 2003; data are not reported for herbicides applied on less than 1 percent of corn and soybean acreage).

there was no recorded use of alachlor in the State (U.S. Department of Agriculture, 2003). Yet, alachlor ESA was the most frequently detected herbicide compound (28 percent) in samples collected from these aquifers during approximately the same time period (2001-02). Similarly, there is little to no relation between current herbicide-application rates and current herbicide concentrations in the State’s source-water aquifers (fig. 11B). The time lag between land application of herbicides and herbicide transport to ground water requires that the mobility and persistence of herbicide transformation products and historical herbicide-application rates be considered to better determine the relations between herbicide-application rates and the occurrence and concentrations of herbicides in source-water aquifers. Use of certain herbicides has varied substantially during the past decade (1991-2001) (figs. 10, 11). Other contributing factors related to hydrogeology, herbicide chemistry, and soil biochemistry that can affect the mobility and persistence of many herbicide transformation products also need to be considered when relating application

rates of herbicides to their occurrence and concentrations in ground water. The weak relation between herbicide-application rates and detection frequency, as determined in this study, also may be attributed, in part, to the use of statewide-application-rate data. Annual statewide-application-rate data available from the U.S. Department of Agriculture (2003) were used for the examination, because location-specific data, even at the county scale, were not readily available.

When the timing of herbicide application during the cycle of crop planting to harvesting is considered, it is evident that herbicides and their transformation products are detected most frequently (50 percent of samples) in the State’s source-water aquifers during the spring crop-planting and herbicide-application period (fig. 12). At least 90 percent of the annual application of the detected herbicides currently (2001) in use in Illinois (atrazine, acetochlor, dimethenamid, and metolachlor) is during March through June (most in Aril and May), primarily for pre-emergent control of competing weeds and grasses (Aaron Hager, University of Illinois Extension, oral commun., 2003; Dennis P. McKenna, Illinois Department of Agriculture, written commun., 2003).

Concentrations of herbicide compounds detected in the State’s source-water aquifers also are indicated to be highest during the spring crop-planting and herbicide-application period. The highest total concentration of all wells sampled during an application period was from samples collected in the spring period (26.7 µg/L). Additionally, three of the five highest total concentrations (12.9, 2.7, and 2.1 µg/L

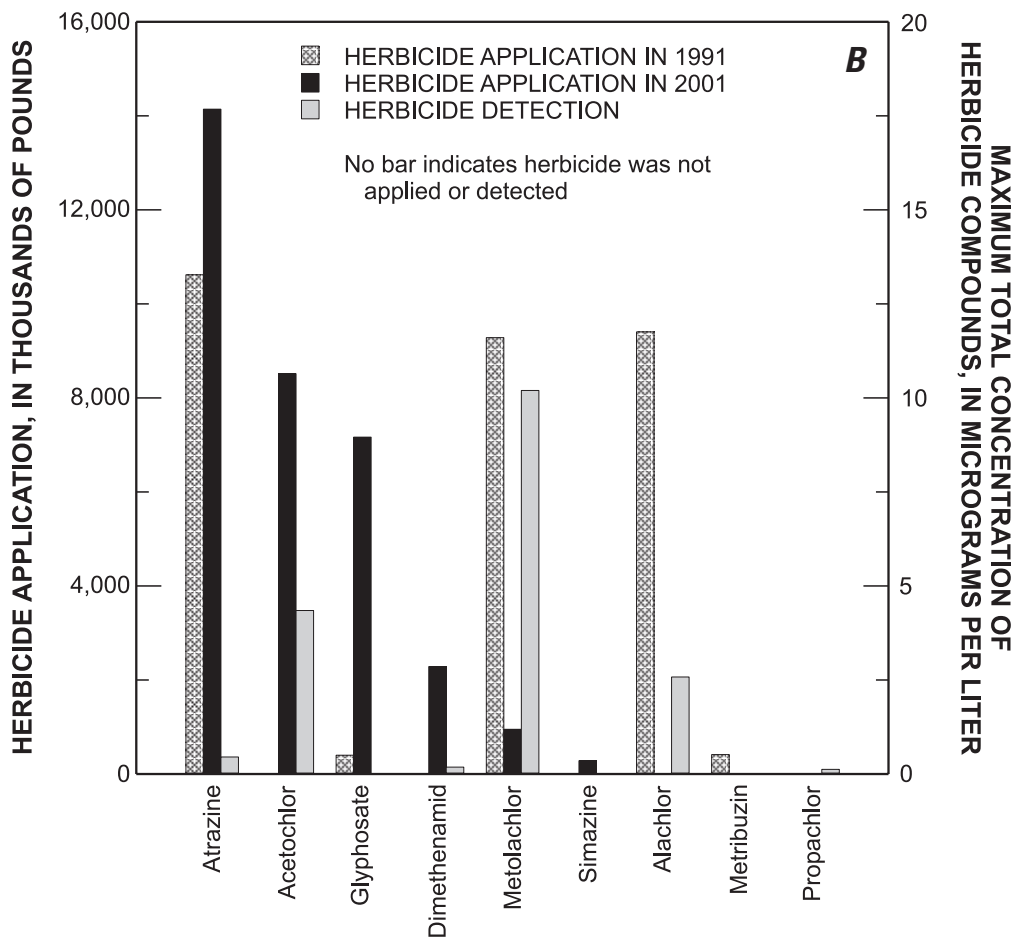


Figure 11. – Continued.

L; 1st, 4th, and 5th highest, respectively) in samples from individual wells and three of the five detections of parent compounds were from samples collected during this period. The comparatively high frequency of detection of herbicide compounds during the fall through winter crop-harvesting (and post-harvesting) period seems to represent the detection of increasing numbers of herbicide compounds with low concentrations as the parent herbicides transform and (or) the transportation of herbicide compounds in ground water to increasing distances from their application source areas. The higher percentage of sample wells open to unconsolidated aquifers in the crop-harvesting period (33 percent) than in the summer crop-growing period (17 percent) also may account for the comparatively high frequency of detection of herbicide compounds in the crop-harvesting period (fig. 12). Eighty-four percent of herbicide-compound detections were in samples from wells open to unconsolidated aquifers in which the ground water typically is recharged more recently than in bedrock aquifers.

Hydrogeology

Ground water typically is younger in unconsolidated aquifers than in bedrock aquifers. The younger age of ground water in unconsolidated aquifers can be

attributed, in part, to the comparatively shallower depths and more rapid recharge rates of most unconsolidated aquifers (Kolpin and others, 2000b). Considering the factors of age and aquifer depth, unconsolidated aquifers are expected to be more vulnerable to contamination by herbicide compounds than bedrock aquifers; shallow bedrock aquifers are expected to be more vulnerable to contamination than deep bedrock aquifers.

Herbicide compounds were detected in more than twice as many samples from unconsolidated source-water aquifers in Illinois (representing 46 percent of sample locations) than from shallow bedrock aquifers (representing 46 percent of sample locations) (figs. 7, 13). No herbicide compounds were detected in samples from deep bedrock aquifers (representing 8 percent of sample locations). As indicated previously, source-water bedrock aquifers in Illinois are considered to be shallow where the depth to the top of the aquifer is less than or equal to 500 ft and are considered to be deep where the depth to the top of the aquifer is greater than 500 ft. Depth to the top of shallow bedrock aquifers with detections of herbicide compounds ranged from 71 to 246 ft, with 85 percent of the detections from aquifers with depths of 150 ft or less.

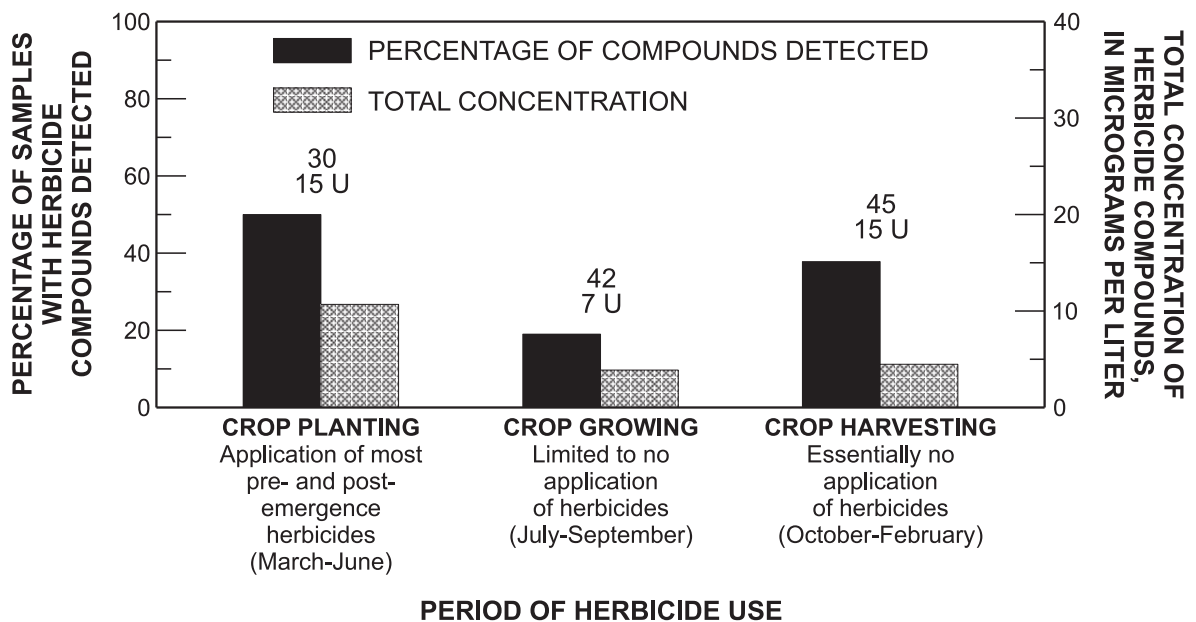


Figure 12. Relation of frequency of detection and total concentration of herbicides and their transformation products in source-water aquifers in Illinois to timing of herbicide application, 2001-02 (total number of wells and number of wells open to unconsolidated aquifers (U) in herbicide-application period are shown above bar).

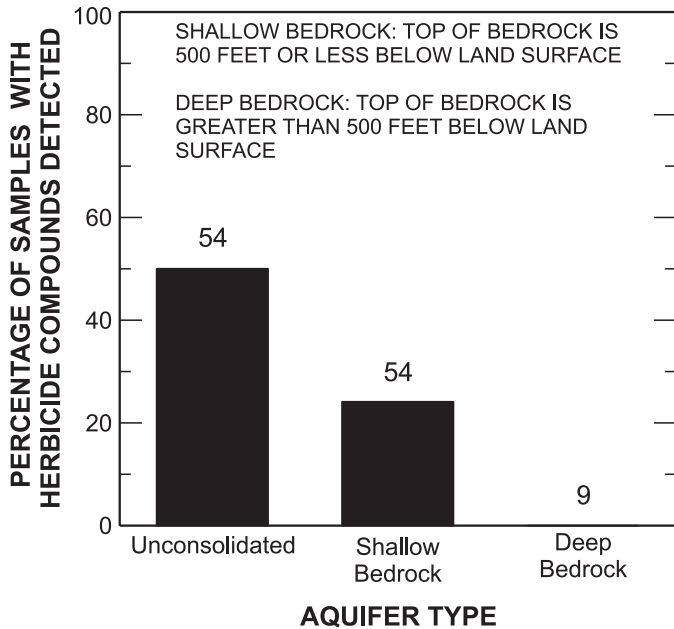


Figure 13. Relation of frequency of detection of herbicides and their transformation products in source-water aquifers in Illinois to aquifer type, 2001-02 (total number of samples in aquifer type is shown above bar).

With travel times for recharge to most confined aquifers (whether bedrock or unconsolidated) used in Illinois for public-water supply expected to be greater than 50 years (assuming only advective water movement through continuous porous media), occurrence of herbicide compounds in these aquifers generally should not be expected. Most synthetic organic herbicides, including the herbicides examined in this study, have been used routinely for less than about 40 years. By standard definition, aquifers are considered confined when the potentiometric surface (water level) in the aquifer is above the top of the aquifer; confined aquifers are bounded above and below by lithologic units of distinctly lower permeability than that of the aquifer (U.S. Geological Survey, 1989). For the present study, water-level data generally were unavailable for direct designation of aquifers as confined or unconfined and, thus, the relation between aquifer confinement and herbicide occurrence in the State’s source-water aquifers could not be evaluated directly. Alternatively, thickness of the confining unit, frequently used as an indirect indicator of aquifer confinement, was evaluated to determine its relation to occurrence of herbicide compounds. For the evaluation, designations of confining-unit thickness were made by IEPA on the basis of geologic information available from

well-construction logs or from other sources (Illinois Environmental Protection Agency, 1995).

There was a strong inverse relation ($r = -0.93$) between confining-unit thickness and frequency of detection of herbicide compounds in Illinois’ source-water aquifers (fig. 14). Herbicide compounds were detected in 88 percent of samples from wells that tap aquifers confined below low-permeability units 10 ft thick or less and in 47 percent or less of samples from wells that tap aquifers confined below low-permeability units greater than 10 ft thick. Aquifer depth (depth to the top of the aquifer) seemed to be a factor where herbicide compounds were detected in samples from aquifers confined by units greater than 10 ft thick. For example, for aquifers confined below units greater than 10 to 20 ft thick, herbicides were not detected where aquifer depths exceeded 163 ft. Unexpectedly, herbicide compounds were detected in 20 percent of samples (4 samples) from wells that tap aquifers presumably confined below units greater than 50 ft thick (to a maximum thickness of 153 ft). One of the wells (00572) (fig. 3) where herbicide compounds were detected tapped an unconsolidated aquifer; three of the wells (20180, 20766, 20328) tapped a shallow bedrock aquifer of fractured carbonate (Silurian). For this study, construction logs of the sampled

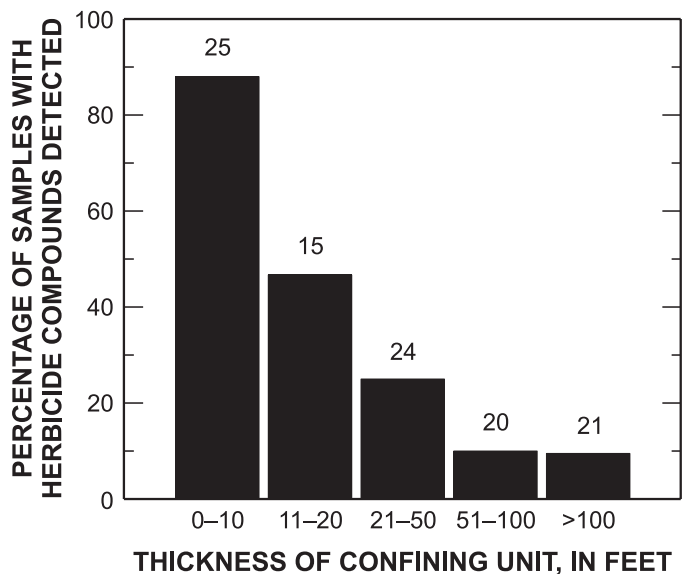


Figure 14. Relation of frequency of detection of herbicides and their transformation products in source-water aquifers in Illinois to thickness of the confining unit, 2001-02 (>, greater than; total number of samples in classification is shown above bar, confining-unit thicknesses were not available for 12 sampled wells).

wells were unavailable for evaluation of the lithology and lateral extent of the confining units. However, the occurrence of herbicide compounds in these samples indicates that the confining units in the vicinity of the sampled wells may not be vertically and (or) horizontally continuous. The occurrence of herbicide compounds in samples from three wells that tapped a fractured-carbonate aquifer indicates the fractures may, in some undetermined way, contribute to preferential movement of water and herbicides through the confining unit that overlies the aquifer.

Wells included in IEPA’s ambient ground-water-quality well network have been designated officially as tapping either confined or unconfined aquifers to evaluate the vulnerability of Illinois’ source-water aquifers to contamination (Illinois Environmental Protection Agency, 1995). The primary approach used for the official designations was a weighted-ranking method that includes five hydrogeologic criteria determined from well-construction logs and other data sources. For example, one criteria is – Does at least one contiguous unit of impermeable geologic materials greater than 10 ft thick overlie the aquifer (excluding the top 10 ft of soil materials)? When sufficient data are unavailable for the weighted-ranking method, the designations are based on alternative hydrogeologic-related vulnerability criteria (Berg and others, 1984), tritium data (Illinois Environmental Protection Agency, 2003c; Mills and others, 2002, p. 9), evidence of human sources of contaminants (such as synthetic organic compounds), and (or) information from detailed hydrogeologic investigations of the aquifer (Wade Boring, Illinois Environmental Protection Agency, oral commun., 2003). Each of these approaches for designating aquifers as confined or unconfined for the evaluation of aquifer vulnerability to contamination is based on the assumption that ground water from confined aquifers generally represents old recharge (about 50 years or older) and ground water in unconfined aquifers generally represents comparatively young recharge (about 50 years or younger). Thus, ground water in confined aquifers generally is considered to be less vulnerable to anthropogenic contamination (contaminants from human sources) than ground water in unconfined aquifers.

Aquifer confinement, as designated by the IEPA, was related strongly to frequency of detection of herbicide compounds in Illinois’ source-water aquifers (fig. 15). Herbicide compounds were detected in samples

from 11 percent of wells that tap aquifers designated as confined (representing 68 percent of wells/aquifers) and 84 percent of wells that tap aquifers designated as unconfined (representing 32 percent of wells/aquifers). Most of the samples (71 percent) obtained from aquifers designated as confined were obtained from bedrock aquifers. All detections of herbicide compounds in samples from confined aquifers were from bedrock aquifers.

Ground-water age and aquifer vulnerability to contamination by herbicide compounds can be related to proximity and hydraulic connection to recharge areas (Kolpin and others, 1998b). Generally, the closer and (or) better the hydraulic connection to a recharge area, the younger the ground water and more vulnerable an aquifer is to herbicide contamination. The length of the recharge flow path, in part, determines the time available for transport, transformation, or sorption of herbicides. This is important particularly if a thick unsaturated zone overlies an aquifer and, thus, extensive aerobic and biotic transformation of herbicides can result. One indication of proximity to a recharge area is the depth from land surface of various hydrogeologic characteristics (top of aquifer, for example) and well-construction aspects (base of well casing, for example). In this study, depth to the top of an aquifer (or aquifer depth) is defined as depth to

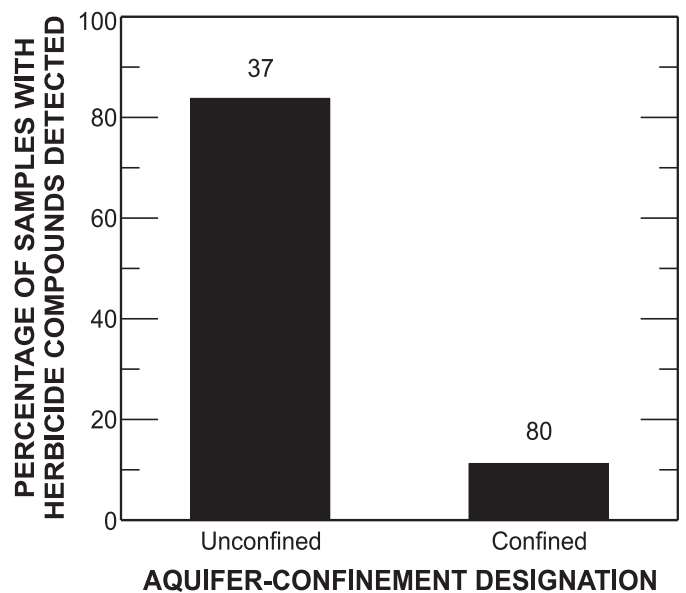


Figure 15. Relation of frequency of detection of herbicides and their transformation products in source-water aquifers in Illinois to designation as a confined aquifer (policy designation of the Illinois Environmental Protection Agency), 2001-02 (total number of samples in designation is shown above bar).

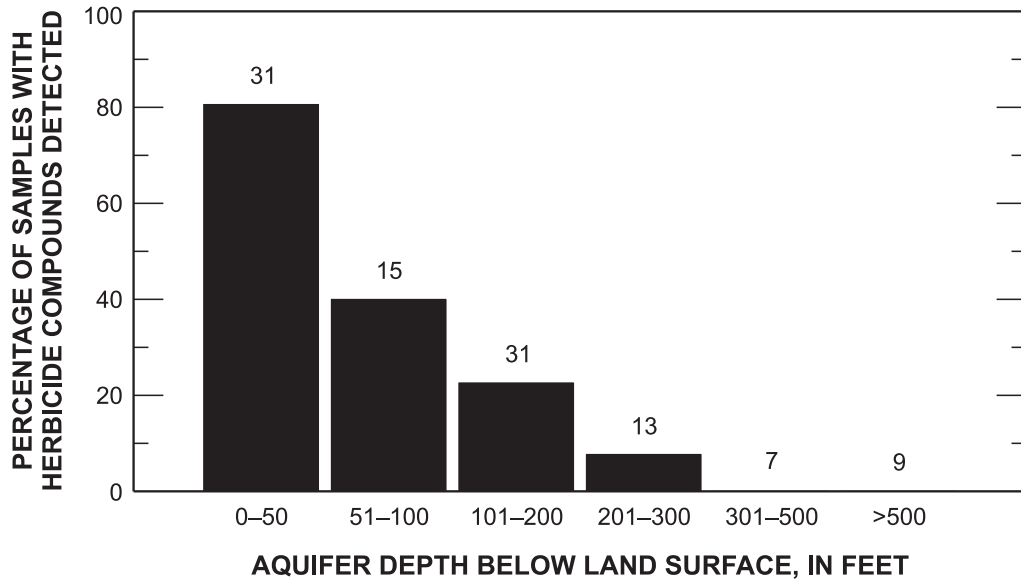


Figure 16. Relation of frequency of detection of herbicides and their transformation products in source-water aquifers in Illinois to aquifer depth, 2001-02 (aquifer depth is the depth from land surface to the top of aquifer material; >, greater than; total number of samples in depth interval is shown above bar; aquifer depths were not available for 11 sampled wells).

the top of the aquifer material, regardless of whether the aquifer material is fully saturated.

There was a strong inverse relation ($r = -0.92$) between aquifer depth and frequency of detection of herbicide compounds in Illinois' source-water aquifers, with a monotonic decline in detections with increasing aquifer depth (fig. 16). The number of samples with detected herbicides from aquifers within 50 ft of land surface was almost twice the number from all other aquifer-depth intervals (25 and 14 samples, respectively). No herbicide compounds were detected in samples from aquifers with depths greater than 300 ft. Of the various depth-related factors examined in the study of Midwestern cornbelt States that included Illinois, aquifer depth was associated most strongly with detection of herbicide compounds (Kolpin and others, 1994).

Proximity of public-supply wells to a stream was related positively to the frequency of detection of herbicide compounds in Illinois' source-water aquifers (fig. 17). Herbicide compounds were detected in 70 percent of samples from the 10 wells within 100 ft of a stream, but in only 31 percent of samples from wells that were further than 100 ft from a stream (fig. 16). Similarly, herbicides were detected in 47 percent of samples from the 34 wells within about 0.25 mi of a stream, but in only 29 percent of samples from wells that were located more remotely (greater than 0.25 mi from a stream). Additionally, herbicides were detected in 78 percent of samples from the nine wells that tap unconsolidated (alluvial) aquifers adjacent to the Illinois and Mississippi Rivers (fig. 3). Two wells (50237, 50238; fig. 3) with

the highest total (12.93, 5.13 $\mu\text{g/L}$, respectively) and individual (7.24, 4.18, 2.95, and 2.15 $\mu\text{g/L}$) concentrations of four herbicide compounds (metolachlor ESA, acetochlor ESA, metolachlor OA, and alachlor ESA, respectively) were immediately adjacent to a stream.

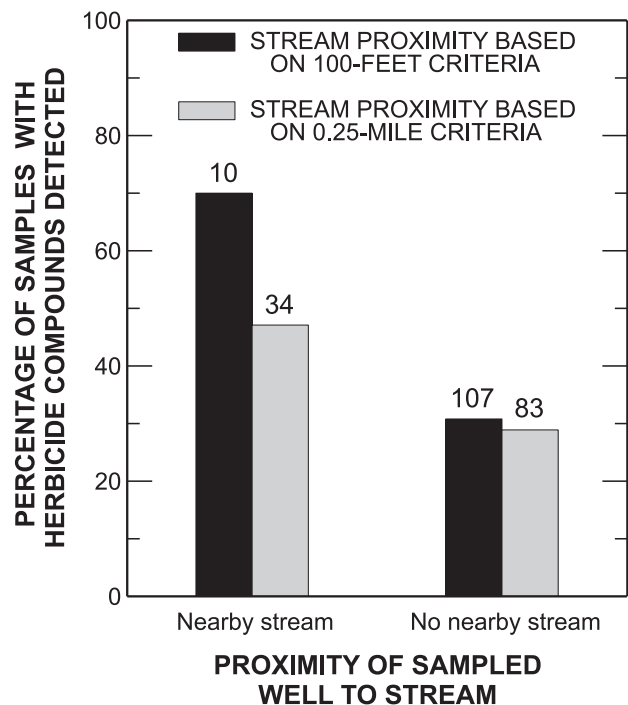


Figure 17. Relation of frequency of detection of herbicides and their transformation products in source-water aquifers in Illinois to proximity of well to a stream, 2001-02 (total number of samples in stream-proximity interval is shown above bar)

Kolpin and others (1994) report similar findings in their study of Midwestern States.

There are various hydrogeologic factors that could contribute to the greater frequency of detection of herbicide compounds and, possibly, higher concentrations in samples from wells near streams. Wells near streams may draw some water from the streams, as hydraulic gradients between the aquifer and stream are reversed during periods of high stream stage and (or) groundwater withdrawal by pumping. Herbicides frequently occur in streams in the Midwestern States and typically their frequencies of occurrence and concentrations substantially exceed those in ground water (Fuhrer and others, 1999). In addition, flow paths, possibly from many areas in an aquifer, tend to converge near discharge locations, such as streams. This comparatively wide source area providing recharge to near-stream wells can increase the likelihood of herbicide contamination of the water provided by the wells. Water in near-stream alluvial aquifers also tends to be younger than water in other aquifers (Kolpin and others, 2000b). The younger the ground water, the closer the source of recharge and potentially contaminating herbicides are likely to be.

Well Construction

As with aquifer depth, there was a strong inverse relation ($r = -0.95$) between well depth (depth from land surface to base of the well) and frequency of detection of herbicide compounds in Illinois' source-water aquifers (fig. 18). However, the decline in detection

frequency associated with increasing well depth was less monotonic (more irregular) than the decline in detection frequency associated with increasing aquifer depth or another construction-related factor (well-casing depth) that was examined. Other studies indicate a weaker relation than this study does between frequency of herbicide detection and well depth (Holden and others, 1992; Kolpin and others, 1994; Dana W. Kolpin, U.S. Geological Survey, written commun., 2004). Herbicide compounds were detected in 100 percent of samples (6 samples) from wells 50 ft deep or less and 79 percent of samples from wells greater than 50 ft deep and less than about 100 ft deep. Detection frequencies in samples from wells between 100 and 500 ft deep were less than half the detection frequency in samples from shallower wells. In addition, herbicide compounds were detected in 7 percent of samples (2 samples) from wells greater than 500 ft deep (to a maximum of 769 ft deep).

The comparatively weaker association between well depth and herbicide detection than that between aquifer depth or well-casing depth and herbicide detection likely pertains to well-construction aspects. Many of the wells included in the study (54 percent) tap bedrock aquifers and, thus, are open to the aquifer from the base of the well casing to the base of the well (lengths of open intervals were up to 1,300 ft). Water may enter these wells from various depths in the aquifer. Generally, screened intervals of wells that tap unconsolidated aquifers more closely approximate total well depths than do open intervals of wells that tap bedrock aquifers.

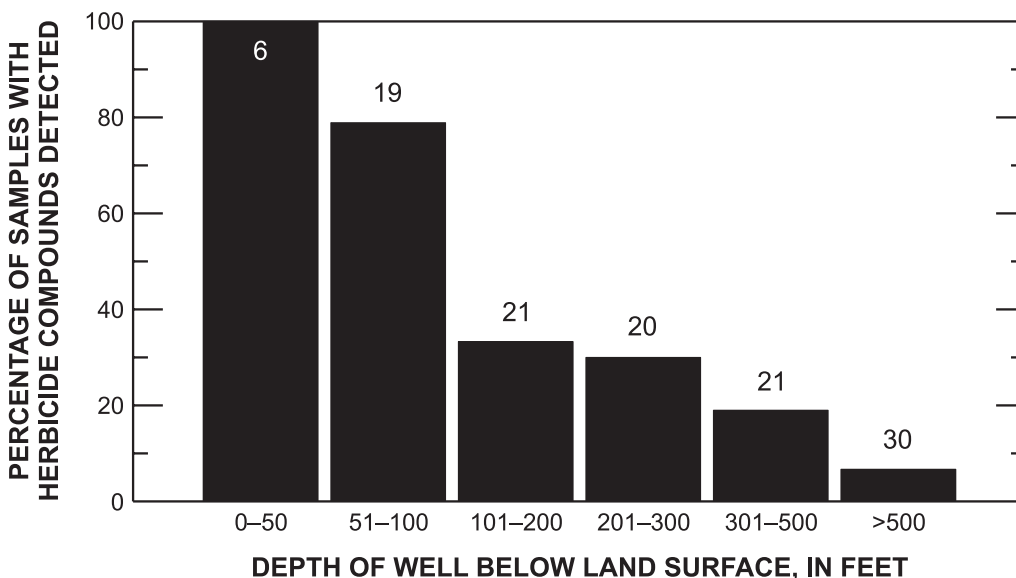


Figure 18. Relation of frequency of detection of herbicides and their transformation products in source-water aquifers in Illinois to well depth, 2001-02 (>, greater than; total number of samples in depth interval is shown in or above bar).

Well-casing depth should provide a more realistic indicator of distance from recharge areas (and, thus, vulnerability to herbicide contamination) than does total well depth. Well-casing depth represents the top of the open interval of a well and, thus, the shallowest depth below land surface at which ground water may enter a well. As with well depth, there was a strong inverse relation ($r = -0.93$) between casing depth and frequency of detection of herbicide compounds in Illinois' source-water aquifers (fig. 19), yet a stronger monotonic relation was indicated than that for well depth. Herbicides were detected in 93 percent of samples from wells with casing depths 50 ft or less and the detections declined steadily with increasing depth. No herbicides were detected in samples from wells with casings depths greater than 300 ft.

There are various explanations other than those given previously for the unexpected detection of herbicide compounds in samples of older ground water from confined aquifers, deep wells, or below thick confining units. Three of the explanations are (1) any given sample water mass is a composite of waters of multiple ages; thus, mixing of only a small quantity of recent recharge containing herbicide compounds with older recharge is necessary to result in detection of trace concentrations, (2) water quality can be affected at recharge locations that are remote from locations of older ground water and the effects can persist over long horizontal flow paths if ground-water velocities are sufficiently rapid and herbicide compounds are sufficiently persistent, and (3) recent recharge may circumvent confining units and (or)

move rapidly to depth in an aquifer by preferential flow through fractures or improperly constructed (grouted), damaged, or unused wells.

Land Use

Land use was evaluated to determine a possible relation to the frequency of detection of herbicide compounds in Illinois' source-water aquifers. Frequencies were compared with percentage of land used for corn or soybean (row-crop) production within radial distances of 1 and 2 mi from sampled wells. Because of the routine use of herbicides in row-crop production, a positive relation between frequency of herbicide detection and percentage of land used for row-crop production is expected. However, there was a strong inverse relation ($r = -0.81$) between frequency of detection of herbicide compounds in ground-water samples collected from the source-water aquifers and percentage of land used in row-crop production (fig. 20). There was little difference in the results for the 1- and 2-mi radial distances.

Interestingly, herbicide transformation products were detected in 71 percent of the samples (5 of 7 samples) from wells with no identified corn or soybean production within a 2-mi radius. One of the samples with detected transformation products was from a well (50383; fig. 3) located adjacent to the Illinois River, indicating that recharge to this well, in part, originates greater than 2 mi from the well and (or) all or part of the recharge is from the river. Four of the five samples with detected transformation products were collected from-

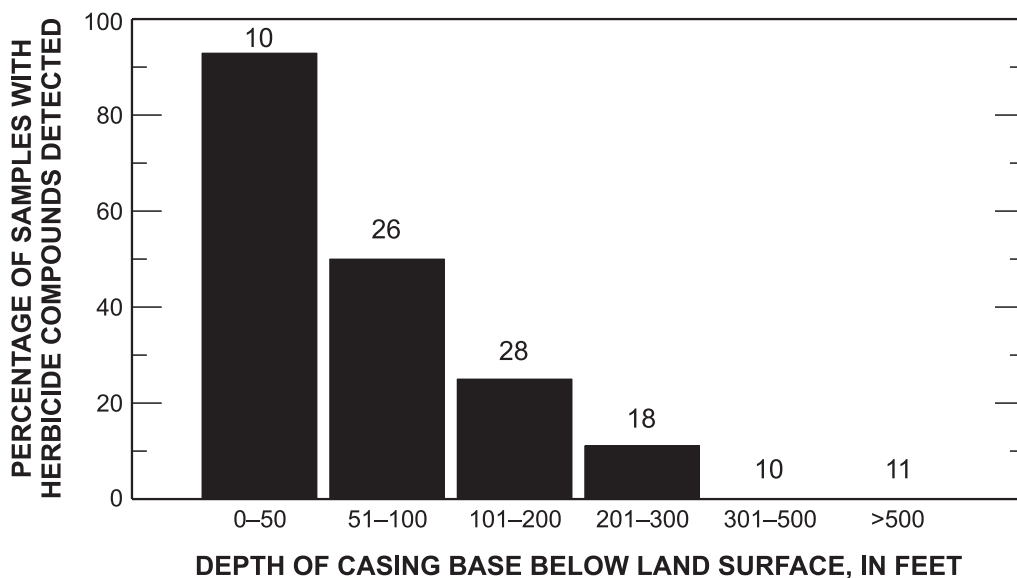


Figure 19. Relation of frequency of detection of herbicides and their transformation products in source-water aquifers in Illinois to depth to base of the well casing, 2001-02 (>, greater than; total number of samples in depth interval is shown above bar).

wells in urbanized areas of Rockford (11629, 11636) and suburban Chicago (20285, 20497). Detections in urban areas have been reported by others (Barbash and others, 1999). Metolachlor, detected as an ESA compound in one sample, sometimes is used in non-agricultural settings (about 1 percent of total national use); however, alachlor, detected as an ESA compound in all four samples, reportedly is not (Barbash and others, 1999). The detections of herbicide compounds in these urban areas may be attributable to previous agricultural activity in the area of the wells, particularly near one well location in suburban Chicago. The detections also indicate the possibility that recharge to the high-capacity public-supply wells that were sampled may originate up to about 10 mi from the wells. Finally, although least likely, atmospheric deposition may account for the occurrence of these herbicide compounds in the urban ground waters (U.S. Geological Survey, 1995; Dana W. Kolpin, U.S. Geological Survey, oral commun., 2003).

Other studies that consider the relation between land use and occurrence of herbicide compounds in ground water report similar findings (Kolpin and others, 1994; Kolpin and others, 1997). Even when land-use patterns are considered in detail (for example, more land-use categories are applied, locations are mapped, and estimated areas contributing recharge to wells are removed from the statistical analysis), the relation between land use and occurrence of herbicide compounds in ground water seems only to be strengthened marginally (Kolpin and others, 1997). These findings pertaining to land use indicate the complexity of identifying factors and

relations associated with the occurrence and concentrations of herbicide compounds in source-water aquifers and other ground waters. Many factors can contribute collectively to the occurrence of herbicides in ground water, including historical trends in land and herbicide use, ground-water age, local flow patterns, geology, soil microbiology, and herbicide chemistry. Furthermore, the detections of herbicide compounds in urban areas point to the necessity of evaluating ground-water-flow systems and mapping areas contributing recharge to wells in detail in development of aquifer-protection strategies by water-resources managers.

Excess Nitrate

Nitrogen fertilizers are used commonly in conjunction with herbicides to increase crop production and frequently nitrate is detected in aerobic ground water where these fertilizers are used (Nolan and others, 1997). Because the occurrence of nitrate in aerobic ground water can indicate the proximity of a source of ground-water recharge, nitrate occurrence, particularly as excess nitrate, also may indicate the co-occurrence of herbicide compounds (Kolpin and others, 1994; Kolpin and others, 2002; Dana W. Kolpin, U.S. Geological Survey, written commun., 2004). In ground water, concentrations of nitrate, as nitrogen, higher than 3.0 mg/L generally are considered to represent excess nitrate; this is considered the division between natural and human sources of nitrate (Madison and Brunett, 1985). Some research indicates concentrations as low as 2.0 mg/L (Mueller

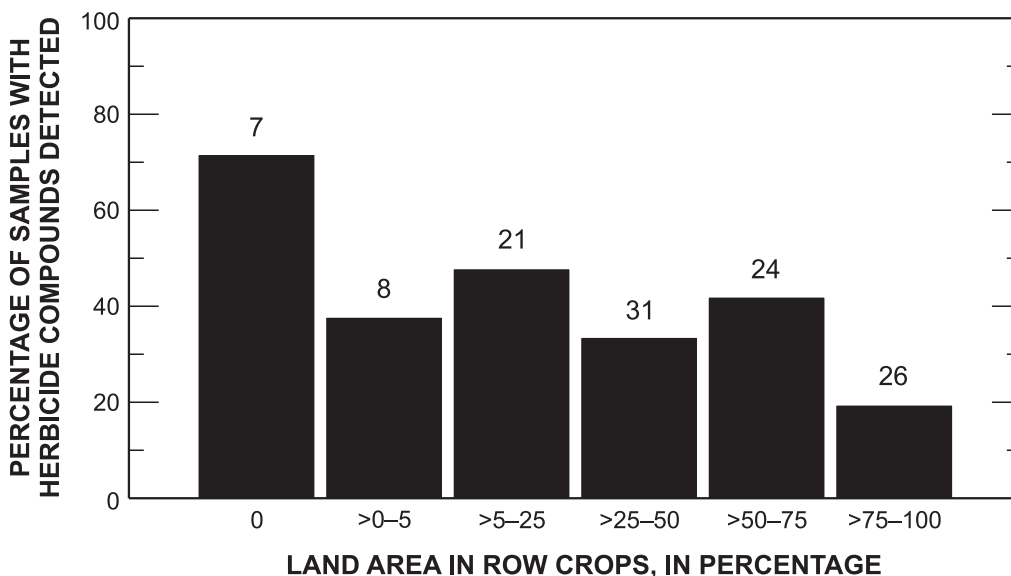


Figure 20. Relation of frequency of detection of herbicides and their transformation products in source-water aquifers in Illinois to percentage of land area used for corn and soybean (row crop) production within a 2-mile radius of the sampled wells, 2001-02 (>, greater than; total number of samples in land-area interval is shown above bar).

and Helsel, 1996) or even 1 mg/L (Nolan and Hitt, 2003) represent excess nitrate.

The occurrence of excess nitrate in Illinois' source-water aquifers generally was indicative of the co-occurrence of herbicide compounds (fig. 21), particularly if nitrate concentrations greater than 1 mg/L are considered representative of excess nitrate. Herbicide compounds were detected in 100 percent of samples (8 of 8) with nitrate concentrations greater than 3.0 mg/L and less than 10 mg/L and in 89 percent of samples (8 of 9) with concentrations greater than 1 mg/L and less than 3.0 mg/L. However, herbicide compounds also were detected in numerous samples with nitrate concentrations less than 1 mg/L, which is below the lowest level considered to represent excess nitrate. Herbicide compounds were detected in 83 percent of samples (5 of 6) with nitrate concentrations greater than 0.2 mg/L and less than 1 mg/L and in 21 percent of samples (19 of 90) with nitrate concentrations less than or equal to 0.2 mg/L. No nitrate concentrations exceeded the MCL of 10 mg/L. The detection of herbicide compounds in samples with nitrate concentrations less than 1 mg/L may be explained, in part, by differences in the amounts of nitrogen fertilizer and herbicide applied near the ground-water-sample sites, and the timing of the application and subsequent transport of these compounds to ground water.

Nitrate (as nitrogen) concentrations in ground-water samples do not seem a reliable indicator of concentrations of herbicide compounds in Illinois' source-water aquifers. A weak to moderate positive relation ($r = 0.52$)

was indicated between nitrate concentrations and total concentrations of herbicide compounds in samples from the State's public-supply wells (fig. 22). The limited strength of this correlation may be attributed, in part, to the relative stability of nitrate concentrations in ground water; concentrations of herbicide compounds generally decrease with time. Water samples collected for this study represent various ages of ground water. Additionally, nitrogen-based fertilizer applications are not restricted to the spring-planting period to the extent of herbicide applications; nitrogen-based fertilizers often are applied during the fall, after crops have been harvested.

Representativeness of Unfiltered Samples

The herbicide analytical results of paired unfiltered and filtered samples were evaluated to determine if the results for unfiltered samples significantly differ from those for filtered samples. Similarity in the results should indicate that the analytical results from unfiltered samples are as representative as those from filtered samples of herbicide concentrations in ground water supplied to the public.

For the purpose of this evaluation, equivalent concentrations were assumed when no herbicide compound(s) (concentrations were less than the reporting limit) was detected in either of the paired samples. Actual differences in concentrations that are less than

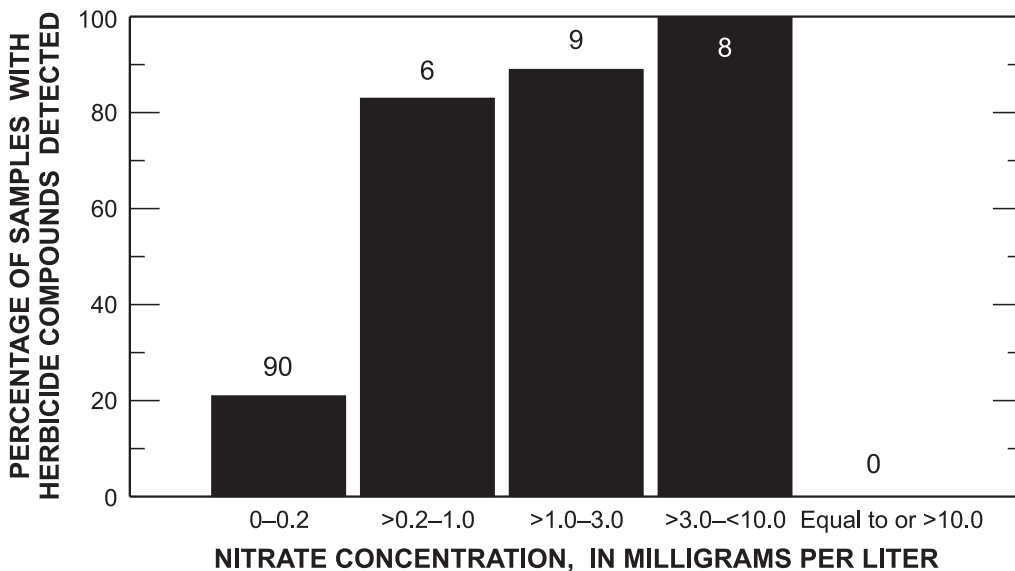


Figure 21. Relation of frequency of detection of herbicides and their transformation products in source-water aquifers in Illinois to concentrations of nitrate (as nitrogen), 2001-02 (>, greater than; <, less than; ≥, greater than or equal to; total number of samples in concentration interval is shown in and above bar).

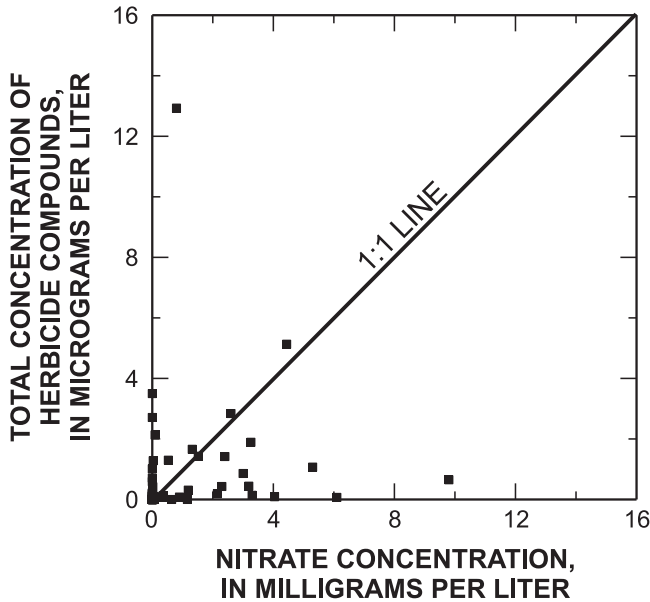


Figure 22. Relation of total concentration of herbicides and their transformation products in source-water aquifers in Illinois to concentration of nitrate (as nitrogen), 2001-02 (herbicide concentrations below the reporting limit of 0.05 microgram per liter are normalized to 0 microgram per liter; nitrate concentrations below the reporting limit of 0.10 milligram per liter are normalized to 0 milligram per liter).

the reporting limits used in this study (0.05 or 0.10 µg/L) can be ignored here because the concentrations would be substantially lower (more than an order of magnitude) than those of applicable Federal (U.S. Environmental Protection Agency, 2003b) or State (Illinois Pollution Control Board, 2003) drinking-water standards. These regulatory standards represent the benchmark for this evaluation. Concentrations that fall below the reporting limits used in this study are well below those of regulatory concern.

No particulates of any size were observed in the 117 water samples collected. However, clay-sized particulates were observed on the filter media of six samples, representing 5 percent of the samples (fig. 6; appendix 1). No difference in analytical results was recorded in 396 of 400 analyte pairs that resulted from analysis of up to 36 herbicide compounds in 13 samples (table 2; fig. 23). Glyphosate, AMPA, and glufosinate were not detected in the nine sample pairs that were analyzed; parent chloroacetanilides were not detected in the eight sample pairs. Triazine compounds were detected in only one of eight sample pairs. For the two detected compounds, the RPD was 0 in one analyte pair (atrazine) and

-10 percent in the other (deethylatrazine, with a -0.02 µg/L difference in concentration between the unfiltered (0.19 µg/L) and filtered (0.21 µg/L) sample). Chloroacetanilide transformation products were detected in only 2 of 11 sample pairs. For the two detected compounds (alachlor ESA and metolachlor ESA) in each sample pair, RPD's ranged from 0 to 18 percent, with no difference in concentration greater than 0.01 µg/L. The measured differences in concentrations were within the expected variability of the analytical methods (Zimmerman and Thurman, 1999; Zimmerman and others, 2000) and, therefore, unlikely to represent consequences of differing sample-collection methods. The statistical evaluation of the paired unfiltered and filtered samples supports this conclusion. There was no significant difference in the analytical results of the paired samples, as indicated by the results of the signed, Student's t, and Wilcoxon signed-ranks tests ($\rho = 0.62, 0.71, \text{ and } 0.88$, respectively).

Although this initial evaluation of herbicide analytical results of unfiltered and filtered samples indicates that there is essentially no difference between resulting concentrations, some unresolved concerns remain regarding the comparative results. Concentrations of herbicide compounds in more than 99 percent of the

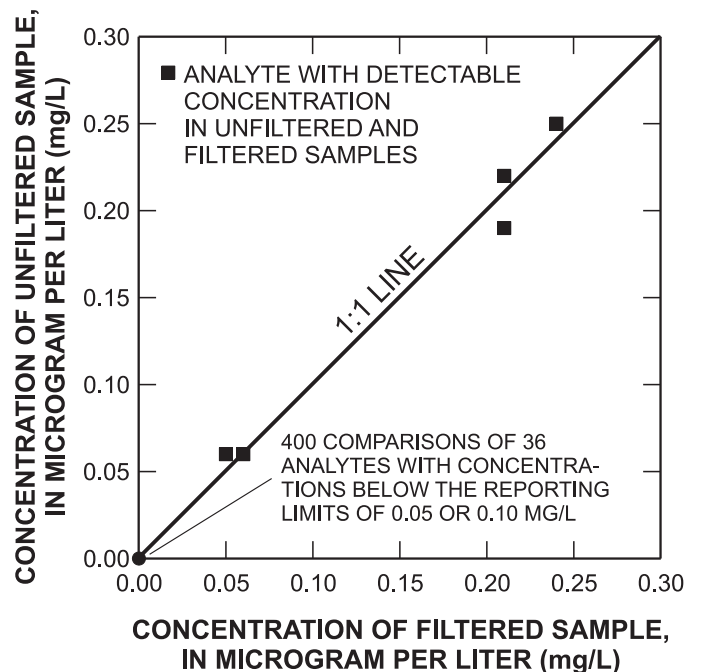


Figure 23. Comparison of herbicide-analytical results for paired unfiltered and filtered samples from selected public-water supply wells that tap source-water aquifers in Illinois, 2001-02.

Table 2. Herbicides and their transformation products detected in paired unfiltered and filtered samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001–September 2002.

[IEPA, Illinois Environmental Protection Agency; µg/L, microgram per liter; ESA, ethanesulfonic acid; OA, oxanilic acid; F, filtered with 0.7-micron baked, glass-fiber filter; U, unfiltered; <, less than; na, not applicable]

Analyzed for but not detected: acetochlor, acetochlor sulfynil acetic acid (SAA), alachlor, alachlor SAA, ametryn, cyanazine, cyanazine amide, deisopropylatrazine, dimethenamid, dimethenamid ESA, dimethenamid OA, flufenacet, flufenacet ESA, flufenacet OA, glufosinate, AMPA, metribuzin, pendimethalin, prometon, prometryn, propachlor, propachlor ESA, propachlor OA, propazine, simazine, and terbutryn. Reporting limit for most herbicide compounds was 0.05 µg/L; reporting limit for glyphosate, amino methyl phosphonic acid (AMPA), and glufosinate was 0.10 µg/L.

IEPA well number	Sample status	Sample date	Atra-zine, dis-solved (µg/L)	Deethyl atra-zine, dis-solved (µg/L)	Glypho-sate dis-solved (µg/L)	Aceto-chlor ESA, dis-solved (µg/L)	Aceto-chlor OA, dis-solved (µg/L)	Ala-chlor ESA, dis-solved (µg/L)	Ala-chlor OA, dis-solved (µg/L)	Metola-chlor ESA, dis-solved (µg/L)	Metola-chlor OA, dis-solved (µg/L)
47518	F	12-04-01	<0.05	<0.05	<0.10	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
do.	U	do.	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
50251	F	12-12-01	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
do.	U	do.	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
50094	F	12-18-01	<.05	.21	<.10	<.05	<.05	.21	<.05	.24	<.05
do.	U	do.	<.05	.19	<.10	<.05	<.05	.22	<.05	.25	<.05
47532	F	01-15-02	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
do.	U	do.	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
11347	F	03-05-02	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
do.	U	do.	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
11363	F	04-09-02	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
do.	U	do.	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
50298	F	04-29-02	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
do.	U	do.	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
00276	F	05-20-02	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
do.	U	do.	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
60089	F	08-14-02	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
do.	U	do.	na	na	na	<.05	<.05	<.05	<.05	<.05	<.05
47586	F	08-28-02	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
do.	U	do.	na	na	na	<.05	<.05	<.05	<.05	<.05	<.05
¹ 52095	F	09-04-02	<.05	<.05	<.10	<.05	.06	.05	<.05	<.05	<.05
do.	U	do.	<.05	<.05	<.10	<.05	.06	.06	<.05	<.05	<.05
60171	F	09-18-02	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
do.	U	do.	na	na	na	<.05	<.05	<.05	<.05	<.05	<.05
² 11456	F	09-24-02	<.05	<.05	<.10	<.05	<.05	<.05	<.05	<.05	<.05
do.	U	do.	na	na	na	<.05	<.05	<.05	<.05	<.05	<.05

¹Tan-to-orange, clay-sized particulates on filter media; well taps an unconsolidated aquifer.²Light tan, clay-sized particulates on filter media; well taps a bedrock aquifer.

analyte pairs were below reporting limits, and of the few compounds that were detected, most of the measured concentrations were low (less than 0.25 µg/L, thus, an order of magnitude or more lower than typical MCL's for herbicides (table 1; appendix 1)). Additionally, comparative analyses were done on only two water samples from wells with observable particulates on the filter media. The evaluation of about 10 more unfiltered/filtered sample pairs (thus, representing about 20 percent of total field samples) could provide more conclusive results regarding the representativeness of unfiltered herbicide samples. Further evaluation of unfiltered/filtered sample pairs would benefit from pairs that represent (1) high herbicide-compound concentrations, as measured during the initial evaluation and (2) samples with visible particulates, including those from wells at which particulates previously were identified, but unfiltered samples were not collected (and, if possible, wells where particulates are identified for the first time during the additional sampling). Before the results of this evaluation are applied to uses other than regulation of herbicides in public-water supplies, the evaluation probably should be repeated using more sensitive laboratory analytical methods with lower reporting limits than those used in this evaluation.

Summary

During 2001-02, the U.S. Geological Survey, in cooperation with the Illinois Environmental Protection Agency, studied the occurrence and factors related to the distribution of herbicides and their transformation products (also referred to as degradates, metabolites, or breakdown products) in source-water aquifers tapped by the State's public-supply wells. Herbicides, used heavily in Illinois to control grass and weeds during production of corn and soybeans (row crops), have been detected in ground water in other studies in Illinois and the Midwestern States.

Ground-water samples were collected from 117 public-supply wells selected using a stratified-random method to ensure distributed representation of the major types of source-water aquifers (sand and gravel; Pennsylvanian to Cambrian bedrock) in the State. Samples were analyzed for 18 herbicides and 18 transformation products, including 3 triazine and 14 chloroacetanilide products. Eleven percent of the herbicide samples were

collected unfiltered to determine if analytical results of unfiltered samples collected from public-supply wells are similar to the results of paired filtered samples and, thus, can be considered equally representative of herbicide concentrations in ground water supplied to the public.

Herbicide compounds (field-applied parent herbicides and their transformation products) were detected in 34 percent of all samples collected; only 4 percent of the samples contained residues of parent herbicides. The six most frequently detected herbicide compounds (from 6 to 28 percent of samples) were transformation products of the chloroacetanilides metolachlor, alachlor, and acetochlor. The frequent occurrence of transformation products and their higher concentration relative to those of most other parent herbicides confirm the importance of obtaining information on transformation products to understand the mobility and fate of herbicides in ground-water systems. No concentrations exceeded current (2003) Federal or State drinking-water standards; however, standards are established for only seven parent herbicides. In addition, the toxicity and aquatic effects of multiple herbicide compounds in water are not considered in the setting of standards.

Factors related to the occurrence of herbicide compounds in the State's source-water aquifers include unconsolidated and unconfined conditions, various hydrogeologic characteristics (top of aquifer, for example) and well-construction aspects (base of well casing, for example) at shallow depths, and proximity to streams. Generally, the closer an aquifer (or well location) is to a recharge area and (or) the stronger the hydraulic connection between an aquifer and a recharge area, the younger the ground water and the more vulnerable the aquifer will be to contamination by herbicide compounds. The weak relation ($r = -0.20$) between current (2001) statewide application rates of herbicides (in pounds) and current (2001-02) occurrence of herbicide compounds in source-water aquifers indicates that additional factors must be considered when relating herbicide-application rates to occurrence. These factors include historical application rates and the mobility and persistence of the various herbicide compounds in ground-water systems. Frequency of detection and concentrations of herbicides compounds in the State's source-water aquifers are indicated to be highest during the spring, when crops are planted and herbicides are primarily applied. Excess nitrate (concentrations

of nitrate, as nitrogen, higher than 3 mg/L) in ground water strongly indicates the co-occurrence of herbicide compounds. However, nitrate concentrations are not a reliable indicator of herbicide-compound concentrations. Concentrations of nitrate and total concentrations of herbicide compounds in samples were weakly to moderately related ($r = 0.52$). The strong inverse relation ($r = -0.81$) between current use of land for corn and soybean production and current occurrence of herbicide compounds in underlying aquifers indicates that various factors, along with current agricultural land use, contribute to herbicide occurrence. These factors include, among others, land-use history, ground-water age, ground-water-flow patterns, geology, soil microbiology, and chemistry and persistence of the herbicide compounds. Detection of agriculture-specific herbicide compounds in 71 percent of samples from urban areas with no current or recent agricultural land use near the sampled wells indicates that recharge to the high-capacity supply wells may originate at considerable distances (up to about 10 mi) from the wells. Essentially no difference was found between the analytical results for herbicides in paired unfiltered and filtered samples, although additional study of this issue is warranted. Further evaluation of unfiltered/filtered sample pairs would benefit from pairs that represent (1) high herbicide-compound concentrations, as measured during the initial evaluation and (2) samples with visible particulates, including those from wells at which particulates previously were identified, but unfiltered samples were not collected.

Awareness of the types of herbicides identified in large-scale studies, such as this study, and the factors that may be related to their occurrence can aid in determining the vulnerability of various source-water aquifers to herbicide contamination and result in more efficient strategies for sample collection. Sampling could be focused on herbicide compounds that likely are to be detected in ground water and on locations where potential for contamination is greatest.

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Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002

Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002.

[IEPA, Illinois Environmental Protection Agency; USGS, U.S. Geological Survey; FT, feet below land surface; US/CM, microsiemens per centimeter; DEG C, degrees Celsius; UG/L, micrograms per liter; ESA, ethanesulfonic acid; OA, oxanilic acid; SAA, sulfynil acetic acid; <, less than; --, not analyzed; geologic unit codes are listings in USGS National Water Information System (NWIS) data base; numbers listed under units in column headings are parameter codes for listings in U.S. Environmental Protection Agency STORET data base]

GEOLOGIC UNIT: 110QRNR, Quaternary; 350SLRN, Silurian; 360ODVC, Ordovician; 340DVSL, Silurian-Devonian; 367OVCB, Cambrian-Ordovician; 365ANCL, Ancell; 333VLMR, Valmeyeran; 320PSLV, Pennsylvanian; 362MQKT, Maquoketa; 355NIGR, Niagaran; 365GLPV, Galena-Platteville; 372IRGL, Ironton-Galesville; 330MSSP, Mississippian; 365STPR, St. Peter

IEPA WELL NUMBER	USGS STATION NUMBER	USGS STATION NAME	GEO- LOGIC UNIT	SAMPLE DATE	DEPTH OF WELL, TOTAL (FT) (72008)	SPE- CIFIC CON- DUCT- ANCE (US/CM) (00095)	PH WATER WHOLE FIELD (STAND- ARD UNITS) (00400)	TEMPER- ATURE WATER (DEG C) (00010)
47583	403143088054701	24N10E-20.8g1	110QRNR	10-09-01	226	690	7.3	12.7
00823	411447087513101	32N12E-20.1f	350SLRN	10-10-01	262	963	7.0	12.0
20458	412603087452601	34N13E-17.5e1	350SLRN	10-10-01	460	1080	7.2	11.5
50060	403432089380901	25N 5W-35.4d1	110QRNR	10-15-01	145	1280	6.8	14.2
60053	383932090012601	3N 8W-31.2a1	110QRNR	10-16-01	102	772	6.8	14.4
11782	415551088575201	40N 2E-23.2f2	360ODVC	10-23-01	723	492	6.9	11.6
31409	404418089011802	26N 2E- 5.7a1	110QRNR	10-23-01	120	709	6.4	12.9
50055	403116089251401	24N 3W-23.8e1	110QRNR	10-30-01	75	613	7.1	12.6
50057	403404089390701	24N 5W- 3.3h1	110QRNR	10-30-01	91	708	7.1	14.3
20250	421433088002701	44N10E-36.2b1	340DVSL	10-31-01	204	918	7.4	11.7
00602	414320089201301	20N10E-15.6e1	367OVCB	11-07-01	1115	607	6.2	11.7
11470	413654088475601	36N 4E- 8.4h1	350SLRN	11-07-01	230	552	6.4	11.8
11678	421256088593801	43N 2E-10.7d2	365ANCL	11-07-01	530	560	6.2	10.9
50308	401754090032001	21N 8W- 6.8e	110QRNR	11-13-01	96	346	7.8	13.9
00366	421840088033001	44N10E-10.6g	350SLRN	11-20-01	250	767	7.3	11.1
02305	422225088102501	45N 9E-15.6a1	110QRNR	11-20-01	123	1010	6.5	11.5
20357	412608088121401	34N 9E- 9.4a1	365ANCL	11-21-01	765	850	7.8	13.0
47561	404625087335301	26N11W- 2.4g1	110QRNR	11-27-01	116	465	7.6	12.7
01118	400111090312502	1N 1W-33.6e	110QRNR	12-04-01	60	655	7.0	13.1
11509	411928089073001	33N 1E-20.1h1	367OVCB	12-04-01	2591	1560	6.4	24.0
47518	410002088313401	29N 6E-10.8e1	367OVCB	12-04-01	1940	2220	6.7	20.6
20152	422231088221101	45N 7E-13.6c1	110QRNR	12-09-01	220	551	6.9	10.9
20141	421222088152701	43N 8E-14.1e1	367OVCB	12-09-01	1300	430	6.9	15.3
11891	422931089473201	29N 6E-22.2b1	367OVCB	12-11-01	355	530	6.4	11.2
20330	413137088011901	35N11E-18.5g	340DVSL	12-11-01	192	962	7.1	12.0
50251	400623089361201	19N 5W-13.2h2	110QRNR	12-12-01	145	465	6.8	13.0
50376	403737089195401	25N 2W-16.2g1	110QRNR	12-12-01	335	556	6.9	12.4
50094	404417090541502	9N 5W-25.1c1	333VLMR	12-18-01	71	664	6.6	12.4
47819	385946088020701	7N11E-31.8a2	320PSLV	12-19-01	269	784	8.2	14.2
50224	394605089155301	15N 2W-12.6g1	110QRNR	01-09-02	70	710	6.4	13.4
52120	394557090361601	15N14W-12.4g1	110QRNR	01-09-02	93	663	6.5	18.2
20285	421803087554801	44N11E-10.3b1	350SLRN	01-14-02	242	1030	7.2	7.2
47532	404532088111201	26N 9E- 4.2f1	110QRNR	01-15-02	78	709	6.5	12.4
47551	404614087512502	26N13W- 5.6h2	110QRNR	01-15-02	132	691	6.8	13.0
00757	372000088431001	14S 4E- 1.5f1	110QRNR	01-22-02	101.5	413	6.7	14.6
20700	415410088034301	39N10E- 2.4h1	362MQKT	01-23-02	350	972	7.2	11.3
31307	410134089244503	30N 3W-26.1b3	110QRNR	01-29-02	50	580	6.5	13.3
31428	405404089022301	28N 2W- 7.5c2	367OVCB	01-29-02	2005	2780	6.9	21.9

Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002—Continued

IEPA WELL NUMBER	USGS STATION NUMBER	USGS STATION NAME	GEO- LOGIC UNIT	SAMPLE DATE	DEPTH OF WELL, TOTAL (FT) (72008)	SPE- CIFIC CON- DUCT- ANCE (US/CM) (00095)	PH WATER WHOLE FIELD (STAND- ARD UNITS) (00400)	TEMPER- ATURE WATER (DEG C) (00010)
11562	415035089175901	21N10E- 1.7g1	367OVCB	02-05-02	769	550	6.3	11.1
11636	421611089031101	44N 2E-19.7b1	110QRNR	02-05-02	237	810	6.3	11.5
11406	415552088465601	40N 4E-21.4f1	367OVCB	02-06-02	1307	473	6.6	12.4
11438	413805088405102	37N 5E-32.1c2	367OVCB	02-06-02	502	608	6.5	11.6
20497	415134088075001	39N10E-17.8a1	350SLRN	02-11-02	200	989	6.6	17.2
47692	395411087485701	17N13W-27.6e1	110QRNR	02-19-02	28	530	6.9	12.7
60127	381238090160001	4S11W- 1.5a1	110QRNR	02-25-02	59	621	6.1	14.9
00251	391251087393801	9N11W-20.6h2	110QRNR	03-04-02	115	684	6.4	14.0
47811	390644087391802	8N11W-29.4h2	110QRNR	03-04-02	32	647	6.3	12.9
11327	411722089221201	15N10E-17.7g1	355NIGR	03-05-02	334	3260	7.2	13.4
11347	412534089215601	17N10E-29.5c1	110QRNR	03-05-02	270	655	6.5	11.8
11904	414305089550901	20N 5E-15.8b1	365GLPV	03-06-02	820	571	6.4	14.0
00795	420559088322101	42N 6E-21.3b2	372IRGL	03-11-02	1195	508	6.6	13.2
01416	394953090331202	16N13W-22.5g2	110QRNR	03-12-02	90	623	6.3	14.3
47725	395640088515501	17N 3E- 9.2e1	110QRNR	03-12-02	132	893	6.1	12.6
45155	392418087392101	11N11W- 8.4a1	110QRNR	03-18-02	68	536	7.1	11.1
11892	413920090044401	19N 4E- 6.3a1	350SLRN	03-19-02	567	498	6.5	12.3
31889	412421090334501	16N 2W- 1.6d1	340DVSL	03-19-02	509	647	6.5	12.9
50101	394212090344901	15N13W-31.2d2	110QRNR	04-01-02	76	680	7.2	13.4
50227	400022090522301	1S 4W- 4.1b1	330MSSP	04-01-02	483	158	8.6	15.4
20207	421943088160501	45N 8E-35.5a1	110QRNR	04-02-02	60	1200	6.4	12.2
45081	400836088185101	20N 8E-33.8a1	110QRNR	04-08-02	338	614	8.1	12.9
47687	401217088220301	20N 7E-12.8c1	110QRNR	04-08-02	282.5	634	7.7	12.5
11363	413328089274501	18N 9E- 9.5c2	110QRNR	04-09-02	404	477	7.6	12.1
71531	383124088135401	1N 9E-17.5g1	320PSLV	04-16-02	215	1650	7.4	15.0
50395	391411090072001	9N 9W- 8.5b2	110QRNR	04-22-02	51	867	6.8	13.3
20297	420947087561801	43N11E-34.5f1	350SLRN	04-23-02	280	940	7.2	11.1
20447	413337088055501	36N10E-33.7e1	350SLRN	04-23-02	303	992	6.9	12.0
50298	401930090361701	4N 2W-15.2b1	330MSSP	04-29-02	380	1200	6.9	13.8
50383	403758089370801	25N 5W-12.5e	110QRNR	04-29-02	78	969	7.1	13.4
11367	412232089275101	16N 9E-16.6g	110QRNR	04-30-02	270	497	7.5	11.9
11495	412030089001901	33N 2E- 9.7b1	367OVCB	04-30-02	1078	1430	7.0	13.3
11600	411529089105701	32N 1W-11.1e1	365ANCL	04-30-02	1800	1580	7.4	19.6
20180	422322088140901	45N 9E- 7.8d1	350SLRN	05-14-02	294	573	6.7	11.6
22040	412143088254901	33N 7E- 4.4c1	367OVCB	05-14-02	1462	648	7.1	15.8
00276	421359088323201	43N 6E- 4.5d1	365STPR	05-20-02	760	500	7.1	12.8
11560 ^a	415027089175501	21N10E- 1.6f1	350SLRN	05-20-02	298	760	6.9	11.8
00572	393324088363301	13N 5E-23.3f	110QRNR	05-21-02	115	742	7.2	12.8
50237	392439089262001	11N 3W- 8.3a2	110QRNR	05-21-02	44	830	6.9	13.4
52062	394338090542001	4S 4W- 7.5a1	330MSSP	06-05-02	429	554	8.5	15.6
20613	415839088113901	40N 9E- 3.5b1	350SLRN	06-11-02	392	716	6.6	11.5
50351 ^b	404511090004001	9N 5E- 7.6d1	367OVCB	06-11-02	1572	3710	8.5	21.9
20442	412854087503501	35N12E-34.6g1	350SLRN	06-17-02	428	936	7.0	12.0

^aMinor light tan, clay-sized particulates on filter media.

^bBlack clay-sized particulates on filter media.

40 Herbicides and Their Transformation Products in Source-Water Aquifers Tapped by Public-Supply Wells in Illinois, 2001-02

Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002—Continued

IEPA WELL NUMBER	USGS STATION NUMBER	USGS STATION NAME	GEO- LOGIC UNIT	SAMPLE DATE	DEPTH OF WELL, TOTAL (FT) (72008)	SPE- CIFIC CON- DUCT- ANCE (US/CM) (00095)	PH WATER WHOLE FIELD (STAND- ARD UNITS) (00400)	TEMPER- ATURE WATER (DEG C) (00010)
47573	403551088021302	25N10E-26.6d2	110QRNR	06-17-02	152	1200	7.3	13.4
11557	414955089291901	21N 9E- 5.5a1	367OVCB	06-18-02	1870	537	6.9	11.4
11629	421656089031301	44N 2E-18.7a2	110QRNR	06-18-02	295	651	6.9	11.4
20029	420727088153901	42N 8E-14.2h1	110QRNR	06-24-02	183	783	6.5	11.4
11570	414122088585401	37N 2E-10.1c1	367OVCB	06-25-02	1053	378	7.3	12.9
11943 ^c	415509089032801	40N 1E-25.2h1	367OVCB	06-25-02	888	534	7.0	11.5
20766	414945088115101	39N 9E-34.5h1	350SLRN	07-01-02	365	1210	6.4	11.2
50003	395106089432801	16N 6W-12.5g	110QRNR	07-02-02	55	703	6.4	13.0
60058	385235090072601	5N 9W-20.4h2	110QRNR	07-02-02	92	815	9.1	15.0
50051	404126089305001	26N 4W-24.5a	110QRNR	07-17-02	260	695	7.3	13.4
11707	420608089501401	24N 6E- 5.6d1	367OVCB	07-29-02	1082	544	6.9	12.8
11514	410931088384401	31N 5E-16.1d1	320PSLV	07-30-02	280	986	7.3	12.9
20328 ^d	413117087481701	35N12E-13.6e1	350SLRN	08-06-02	500	1050	6.4	12.2
20389	413234087513401	35N12E- 9.4h1	350SLRN	08-07-02	420	1400	6.5	12.0
20436	412015087472301	33N12E-24.2g1	350SLRN	08-07-02	300	1000	6.3	18.4
31701	411129090225701	14N 1E-21.1f1	367OVCB	08-13-02	1209	1560	7.5	17.5
31820	411537090363701	15N 2W-27.8c1	34ODVSL	08-13-02	604	1890	7.5	14.4
31930	413003090252401	18N 1E-31.4a1	350SLRN	08-13-02	554	577	7.2	12.5
60089	384417090005201	3N 8W- 5.6d1	110QRNR	08-14-02	106	800	6.4	15.1
11706	420614089500101	24N 6E- 5.5e1	367OVCB	08-19-02	1100	524	7.0	12.2
11778	420739089132901	25N11E-32.6g1	367OVCB	08-19-02	740	607	7.1	11.6
00546	422448088041901	45N10E- 4.4g2	110QRNR	08-27-02	150	668	7.0	12.0
47501	404533088173901	26N 8E- 3.8g1	110QRNR	08-28-02	100	1000	6.9	15.7
47578	403059088041202	24N10E-28.4h2	110QRNR	08-28-02	158	1060	6.8	14.3
47586	404247087434701	26N12W-29.2g2	110QRNR	08-28-02	124	845	6.9	13.2
40013	394343088281801	15N 7E-19.8c1	110QRNR	09-03-02	84	814	6.6	15.0
50238	392438089262101	11N 3W- 9.8c1	110QRNR	09-04-02	47	592	6.7	19.4
52095 ^e	392422089411901	11N 5W-18.4h1	110QRNR	09-04-02	44	645	6.6	18.1
50064	404305089283501	26N 3W-17.5h1	110QRNR	09-09-02	333	385	7.3	12.8
01233	421234088002501	43N10E-13.2b	350SLRN	09-16-02	259	1990	7.4	11.8
60171	380805089594701	5S 8W- 4.7h1	330MSSP	09-18-02	315	560	7.4	17.6
00140	392154089413401	11N 5W-30.6b1	110QRNR	09-23-02	59	724	6.9	13.2
11419	414608088375201	38N 5E-14.4d1	367OVCB	09-24-02	573	546	7.1	11.2
11456 ^f	413528088552101	36N 3E-18.4d1	367OVCB	09-24-02	150	576	7.4	13.5
22073	411436087384801	32N14E-19.1b1	350SLRN	09-24-02	330	830	6.9	12.4
50138	405525089452201	11N 6E-24.1e1	367OVCB	09-24-02	1680	2450	7.2	22.1

^cMinor light brown, clay-sized particulates on filter media.

^dMinor light gray-to-brown, clay-sized particulates on filter media.

^eTan-to-orange, clay-sized particulates on filter media.

^fLight tan, clay-sized particulates on filter media.

Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002—Continued

IEPA WELL NUM- BER	USGS STATION NUMBER	SAMPLE DATE	ACETO- CHLOR, DIS- SOLVED (UG/L) (49260)	ACETO- CHLOR ESA, DIS- SOLVED (UG/L) (61029)	ACETO- CHLOR OA, DIS- SOLVED (UG/L) (61030)	ACETO- CHLOR, SAA, DIS- SOLVED (UG/L) (62847)	ALA- CHLOR, DIS- SOLVED (UG/L) (46342)	ALA- CHLOR ESA, DIS- SOLVED (UG/L) (50009)	ALA- CHLOR OA, DIS- SOLVED (UG/L) (61031)	ALA- CHLOR, SAA, DIS- SOLVED (UG/L) (62848)
47583	403143088054701	10-09-01	<0.05	<0.05	<0.05	--	<0.05	<0.05	<0.05	--
00823	411447087513101	10-10-01	<.05	.21	<.05	--	<.05	<.05	<.05	--
20458	412603087452601	10-10-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
50060	403432089380901	10-15-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
60053	383932090012601	10-16-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
11782	415551088575201	10-23-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
31409	404418089011802	10-23-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
50055	403116089251401	10-30-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
50057	403404089390701	10-30-01	<.05	.45	.18	--	<.05	<.05	<.05	--
20250	421433088002701	10-31-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
00602	414320089201301	11-07-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
11470	413654088475601	11-07-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
11678	421256088593801	11-07-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
50308	401754090032001	11-13-01	<.05	<.05	<.05	--	<.05	.06	<.05	--
00366	421840088033001	11-20-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
02305	422225088102501	11-20-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
20357	412608088121401	11-21-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
47561	404625087335301	11-27-01	<.05	<.05	<.05	--	<.05	<.05	<.05	--
01118	400111090312502	12-04-01	<.05	<.05	<.05	<0.05	<.05	.07	<.05	<0.05
11509	411928089073001	12-04-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47518	410002088313401	12-04-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20152	422231088221101	12-10-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20141	421222088152701	12-10-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11891	422931089473201	12-11-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20330	413137088011901	12-11-01	<.05	<.05	<.05	<.05	<.05	.09	<.05	<.05
50251	400623089361201	12-12-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50376	403737089195401	12-12-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50094	404417090541502	12-18-01	<.05	<.05	<.05	<.05	<.05	.21	<.05	<.05
47819	385946088020701	12-19-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50224	394605089155301	01-09-02	<.05	<.05	<.05	<.05	<.05	.07	<.05	<.05
52120	394557090361601	01-09-02	<.05	.16	.16	<.05	<.05	.34	.09	<.05
20285	421803087554801	01-14-02	<.05	<.05	<.05	<.05	<.05	.05	<.05	<.05
47532	404532088111201	01-15-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47551	404614087512502	01-15-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
00757	372000088431001	01-22-02	<.05	<.05	<.05	<.05	<.05	.11	<.05	<.05
20700	415410088034301	01-23-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
31307	410134089244503	01-29-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
31428	405404089022301	01-29-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11562	415035089175901	02-05-02	<.05	<.05	<.05	<.05	<.05	.38	<.05	<.05
11636	421611089031101	02-05-02	<.05	<.05	<.05	<.05	<.05	.05	<.05	<.05
11406	415552088465601	02-06-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11438	413805088405102	02-06-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20497	415134088075001	02-11-02	<.05	<.05	<.05	<.05	<.05	.06	<.05	<.05
47692	395411087485701	02-19-02	<.05	<.05	<.05	<.05	<.05	.09	<.05	<.05
60127	381238090160001	02-25-02	<.05	.25	.25	<.05	<.05	.19	.08	<.05
00251	391251087393801	03-04-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47811	390644087391802	03-04-02	<.05	.08	<.05	<.05	<.05	.12	<.05	<.05

Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002—Continued

IEPA WELL NUM- BER	USGS STATION NUMBER	SAMPLE DATE	ACETO- CHLOR, DIS- SOLVED (UG/L) (49260)	ACETO- CHLOR ESA, DIS- SOLVED (UG/L) (61029)	ACETO- CHLOR OA, DIS- SOLVED (UG/L) (61030)	ACETO- CHLOR, SAA, DIS- SOLVED (UG/L) (62847)	ALA- CHLOR, DIS- SOLVED (UG/L) (46342)	ALA- CHLOR ESA, DIS- SOLVED (UG/L) (50009)	ALA- CHLOR OA, DIS- SOLVED (UG/L) (61031)	ALA- CHLOR, SAA, DIS- SOLVED (UG/L) (62848)
11327	411722089221201	03-05-02	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
11347	412534089215601	03-05-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11904	414305089550901	03-06-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
00795	420559088322101	03-11-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
01416	394953090331202	03-12-02	<.05	<.05	<.05	<.05	<.05	.08	<.05	<.05
47725	395640088515501	03-12-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
45155	392418087392101	03-18-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11892	413920090044401	03-19-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
31889	412421090334501	03-19-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50101	394212090344901	04-01-02	<.05	<.05	<.05	<.05	<.05	.13	<.05	<.05
50227	400022090522301	04-01-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20207	421943088160501	04-02-02	<.05	<.05	<.05	<.05	<.05	.12	<.05	<.05
45081	400836088185101	04-08-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47687	401217088220301	04-08-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11363	413328089274501	04-09-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
71531	383124088135401	04-16-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50395	391411090072001	04-22-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20297	420947087561801	04-23-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20447	413337088055501	04-23-02	<.05	.05	<.05	<.05	<.05	.52	.06	<.05
50298	401930090361701	04-29-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50383	403758089370801	04-29-02	<.05	.07	.09	<.05	<.05	.41	.06	<.05
11367	412232089275101	04-30-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11495	412030089001901	04-30-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11600	411529089105701	04-30-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20180	422322088140901	05-14-02	<.05	<.05	<.05	<.05	<.05	.18	<.05	<.05
22040	412143088254901	05-14-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
00276	421359088323201	05-20-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11560	415027089175501	05-20-02	<.05	<.05	<.05	<.05	<.05	.39	<.05	<.05
00572	393324088363301	05-21-02	<.05	.11	.20	<.05	<.05	.81	.41	<.05
50237	392439089262001	05-21-02	<.05	.13	<.05	<.05	<.05	2.15	.41	<.05
52062	394338090542001	06-05-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20613	415839088113901	06-11-02	<.05	<.05	<.05	<.05	<.05	.13	<.05	<.05
50351	404511090004001	06-11-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20442	412854087503501	06-17-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47573	403551088021302	06-17-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11557	414955089291901	06-18-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11629	421656089031301	06-18-02	<.05	<.05	<.05	<.05	<.05	.07	<.05	<.05
20029	420727088153901	06-24-02	<.05	<.05	<.05	<.05	<.05	.17	<.05	<.05
11570	414122088585401	06-25-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11943	415509089032801	06-25-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20766	414945088115101	07-01-02	<.05	<.05	<.05	<.05	<.05	.11	<.05	<.05
50003	395106089432801	07-02-02	<.05	.28	.06	<.05	<.05	.11	<.05	<.05
60058	385235090072601	07-02-02	<.05	<.05	<.05	<.05	<.05	.37	.12	<.05
50051	404126089305001	07-17-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11707	420608089501401	07-29-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11514	410931088384401	07-30-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20328	413117087481701	08-06-02	<.05	<.05	<.05	<.05	<.05	.10	<.05	<.05

Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002—Continued

IEPA WELL NUMBER	USGS STATION NUMBER	SAMPLE DATE	FLUFEN- ACET, DIS- SOLVED (UG/L) (62481)	FLUFEN- ACET ESA, DIS- SOLVED (UG/L) (61952)	FLUFEN- ACET OA, DIS- SOLVED (UG/L) (62483)	GLYPHO- SATE, DISSOLVED (UG/L) (62722)	GLUFO- SINATE, DISSOLVED (UG/L) (62721)	AMINO- METHYL PHOS- PHONIC ACID, DISSOLVED (UG/L) (62649)
47583	403143088054701	10-09-01	<0.05	<0.05	<0.05	<0.10	<0.10	<0.10
00823	411447087513101	10-10-01	<.05	<.05	<.05	<.10	<.10	<.10
20458	412603087452601	10-10-01	<.05	<.05	<.05	<.10	<.10	<.10
50060	403432089380901	10-15-01	<.05	<.05	<.05	<.10	<.10	<.10
60053	383932090012601	10-16-01	<.05	<.05	<.05	<.10	<.10	<.10
11782	415551088575201	10-23-01	<.05	<.05	<.05	<.10	<.10	<.10
31409	404418089011802	10-23-01	<.05	<.05	<.05	<.10	<.10	<.10
50055	403116089251401	10-30-01	<.05	<.05	<.05	<.10	<.10	<.10
50057	403404089390701	10-30-01	<.05	<.05	<.05	<.10	<.10	<.10
20250	421433088002701	10-31-01	<.05	<.05	<.05	<.10	<.10	<.10
00602	414320089201301	11-07-01	<.05	<.05	<.05	<.10	<.10	<.10
11470	413654088475601	11-07-01	<.05	<.05	<.05	<.10	<.10	<.10
11678	421256088593801	11-07-01	<.05	<.05	<.05	<.10	<.10	<.10
50308	401754090032001	11-13-01	<.05	<.05	<.05	<.10	<.10	<.10
00366	421840088033001	11-20-01	<.05	<.05	<.05	<.10	<.10	<.10
02305	422225088102501	11-20-01	<.05	<.05	<.05	<.10	<.10	<.10
20357	412608088121401	11-21-01	<.05	<.05	<.05	<.10	<.10	<.10
47561	404625087335301	11-27-01	<.05	<.05	<.05	<.10	<.10	<.10
01118	400111090312502	12-04-01	<.05	<.05	<.05	<.10	<.10	<.10
11509	411928089073001	12-04-01	<.05	<.05	<.05	<.10	<.10	<.10
47518	410002088313401	12-04-01	<.05	<.05	<.05	<.10	<.10	<.10
20152	422231088221101	12-09-01	<.05	<.05	<.05	<.10	<.10	<.10
20141	421222088152701	12-09-01	<.05	<.05	<.05	<.10	<.10	<.10
11891	422931089473201	12-11-01	<.05	<.05	<.05	<.10	<.10	<.10
20330	413137088011901	12-11-01	<.05	<.05	<.05	<.10	<.10	<.10
50251	400623089361201	12-12-01	<.05	<.05	<.05	<.10	<.10	<.10
50376	403737089195401	12-12-01	<.05	<.05	<.05	<.10	<.10	<.10
50094	404417090541502	12-18-01	<.05	<.05	<.05	<.10	<.10	<.10
47819	385946088020701	12-19-01	<.05	<.05	<.05	<.10	<.10	<.10
50224	394605089155301	01-09-02	<.05	<.05	<.05	<.10	<.10	<.10
52120	394557090361601	01-09-02	<.05	<.05	<.05	<.10	<.10	<.10
20285	421803087554801	01-14-02	<.05	<.05	<.05	<.10	<.10	<.10
47532	404532088111201	01-15-02	<.05	<.05	<.05	<.10	<.10	<.10
47551	404614087512502	01-15-02	<.05	<.05	<.05	<.10	<.10	<.10
00757	372000088431001	01-22-02	<.05	<.05	<.05	<.10	<.10	<.10
20700	415410088034301	01-23-02	<.05	<.05	<.05	<.10	<.10	<.10
31307	410134089244503	01-29-02	<.05	<.05	<.05	<.10	<.10	<.10
31428	405404089022301	01-29-02	<.05	<.05	<.05	<.10	<.10	<.10
11562	415035089175901	02-05-02	<.05	<.05	<.05	<.10	<.10	<.10
11636	421611089031101	02-05-02	<.05	<.05	<.05	<.10	<.10	<.10
11406	415552088465601	02-06-02	<.05	<.05	<.05	<.10	<.10	<.10
11438	413805088405102	02-06-02	<.05	<.05	<.05	<.10	<.10	<.10
20497	415134088075001	02-11-02	<.05	<.05	<.05	<.10	<.10	<.10
47692	395411087485701	02-19-02	<.05	<.05	<.05	<.10	<.10	<.10
60127	381238090160001	02-25-02	<.05	<.05	<.05	<.10	<.10	<.10
00251	391251087393801	03-04-02	<.05	<.05	<.05	<.10	<.10	<.10

Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002—Continued

IEPA WELL NUMBER	USGS STATION NUMBER	SAMPLE DATE	FLUFEN- ACET, DIS- SOLVED (UG/L) (62481)	FLUFEN- ACET ESA, DIS- SOLVED (UG/L) (61952)	FLUFEN- ACET OA, DIS- SOLVED (UG/L) (62483)	GLYPHO- SATE, DISSOLVED (UG/L) (62722)	GLUFO- SINATE, DISSOLVED (UG/L) (62721)	AMINO- METHYL PHOS- PHONIC ACID, DISSOLVED (UG/L) (62649)
47811	390644087391802	03-04-02	<0.05	<0.05	<0.05	<0.10	<0.10	<0.10
11327	411722089221201	03-05-02	<.05	<.05	<.05	<.10	<.10	<.10
11347	412534089215601	03-05-02	<.05	<.05	<.05	<.10	<.10	<.10
11904	414305089550901	03-06-02	<.05	<.05	<.05	<.10	<.10	<.10
71531	383124088135401	04-16-02	<.05	<.05	<.05	<.10	<.10	<.10
50395	391411090072001	04-22-02	<.05	<.05	<.05	<.10	<.10	<.10
20297	420947087561801	04-23-02	<.05	<.05	<.05	<.10	<.10	<.10
20447	413337088055501	04-23-02	<.05	<.05	<.05	<.10	<.10	<.10
50298	401930090361701	04-29-02	<.05	<.05	<.05	<.10	<.10	<.10
50383	403758089370801	04-29-02	<.05	<.05	<.05	<.10	<.10	<.10
11367	412232089275101	04-30-02	<.05	<.05	<.05	<.10	<.10	<.10
11495	412030089001901	04-30-02	<.05	<.05	<.05	<.10	<.10	<.10
11600	411529089105701	04-30-02	<.05	<.05	<.05	<.10	<.10	<.10
20180	422322088140901	05-14-02	<.05	<.05	<.05	<.10	<.10	<.10
22040	412143088254901	05-14-02	<.05	<.05	<.05	<.10	<.10	<.10
00276	421359088323201	05-20-02	<.05	<.05	<.05	<.10	<.10	<.10
11560	415027089175501	05-20-02	<.05	<.05	<.05	<.10	<.10	<.10
00572	393324088363301	05-21-02	<.05	<.05	<.05	<.10	<.10	<.10
50237	392439089262001	05-21-02	<.05	<.05	<.05	<.10	<.10	<.10
52062	394338090542001	06-05-02	<.05	<.05	<.05	<.10	<.10	<.10
20613	415839088113901	06-11-02	<.05	<.05	<.05	<.10	<.10	<.10
50351	404511090004001	06-11-02	<.05	<.05	<.05	<.10	<.10	<.10
20442	412854087503501	06-17-02	<.05	<.05	<.05	<.10	<.10	<.10
47573	403551088021302	06-17-02	<.05	<.05	<.05	<.10	<.10	<.10
11557	414955089291901	06-18-02	<.05	<.05	<.05	<.10	<.10	<.10
11629	421656089031301	06-18-02	<.05	<.05	<.05	<.10	<.10	<.10
20029	420727088153901	06-24-02	<.05	<.05	<.05	<.10	<.10	<.10
11570	414122088585401	06-25-02	<.05	<.05	<.05	<.10	<.10	<.10
11943	415509089032801	06-25-02	<.05	<.05	<.05	<.10	<.10	<.10
20766	414945088115101	07-01-02	<.05	<.05	<.05	<.10	<.10	<.10
50003	395106089432801	07-02-02	<.05	<.05	<.05	<.10	<.10	<.10
60058	385235090072601	07-02-02	<.05	<.05	<.05	<.10	<.10	<.10
50051	404126089305001	07-17-02	<.05	<.05	<.05	<.10	<.10	<.10
11707	420608089501401	07-29-02	<.05	<.05	<.05	<.10	<.10	<.10
11514	410931088384401	07-30-02	<.05	<.05	<.05	<.10	<.10	<.10
20328	413117087481701	08-06-02	<.05	<.05	<.05	<.10	<.10	<.10
20389	413234087513401	08-07-02	<.05	<.05	<.05	<.10	<.10	<.10
20436	412015087472301	08-07-02	<.05	<.05	<.05	<.10	<.10	<.10
31701	411129090225701	08-13-02	<.05	<.05	<.05	<.10	<.10	<.10
31820	411537090363701	08-13-02	<.05	<.05	<.05	<.10	<.10	<.10
31930	413003090252401	08-13-02	<.05	<.05	<.05	<.10	<.10	<.10
60089	384417090005201	08-14-02	<.05	<.05	<.05	<.10	<.10	<.10
11706	420614089500101	08-19-02	<.05	<.05	<.05	<.10	<.10	<.10
11778	420739089132901	08-19-02	<.05	<.05	<.05	<.10	<.10	<.10
00546	422448088041901	08-27-02	<.05	<.05	<.05	<.10	<.10	<.10
47501	404533088173901	08-28-02	<.05	<.05	<.05	<.10	<.10	<.10

Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002—Continued

IEPA WELL NUMBER	USGS STATION NUMBER	SAMPLE DATE	FLUFEN- ACET, DIS- SOLVED (UG/L) (62481)	FLUFEN- ACET ESA, DIS- SOLVED (UG/L) (61952)	FLUFEN- ACET OA, DIS- SOLVED (UG/L) (62483)	GLYPHO- SATE, DISSOLVED (UG/L) (62722)	GLUFO- SINATE, DISSOLVED (UG/L) (62721)	AMINO- METHYL PHOS- PHONIC ACID, DISSOLVED (UG/L) (62649)
01233	421234088002501	09-16-02	<0.05	<0.05	<0.05	<0.10	<0.10	<0.10
60171	380805089594701	09-18-02	<.05	<.05	<.05	<.10	<.10	<.10
00140	392154089413401	09-23-02	<.05	<.05	<.05	<.10	<.10	<.10
11419	414608088375201	09-24-02	<.05	<.05	<.05	<.10	<.10	<.10
11456	413528088552101	09-24-02	<.05	<.05	<.05	<.10	<.10	<.10
22073	411436087384801	09-24-02	<.05	<.05	<.05	<.10	<.10	<.10
50138	405525089452201	09-24-02	<.05	<.05	<.05	<.10	<.10	<.10

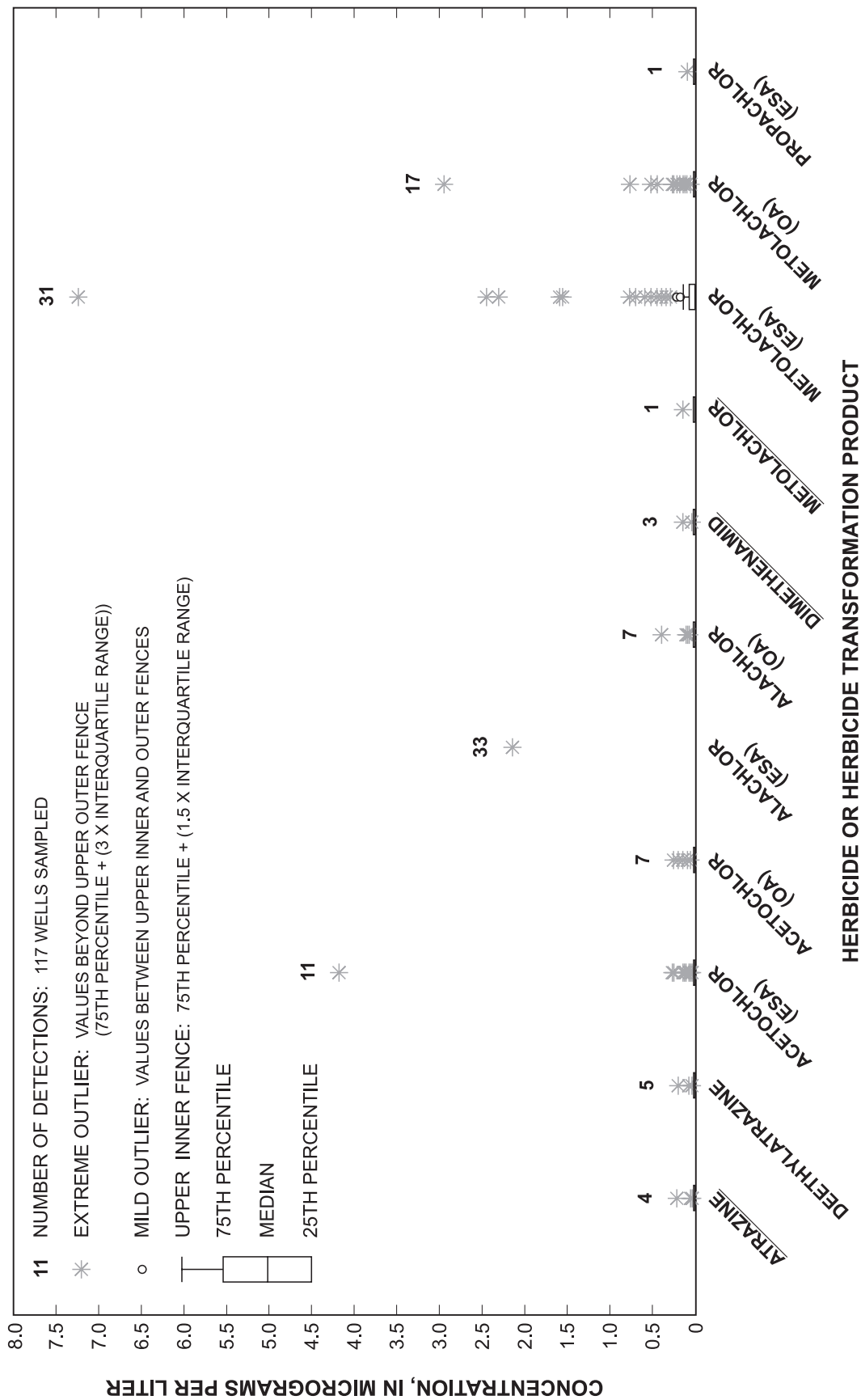
Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002—Continued

IEPA WELL NUMBER	USGS STATION NUMBER	SAMPLE DATE	METOLA- CHLOR, DIS- SOLVED (UG/L) (39415)	METOLA- CHLOR- ESA, DIS- SOLVED (UG/L) (61043)	METOLA- CHLOR OA, DIS- SOLVED (UG/L) (61044)	METRI- BUZIN, DIS- SOLVED (UG/L) (82630)	PENDI- METHA- LIN, DIS- SOLVED (UG/L) (82683)	PRO- METON, DIS- SOLVED (UG/L) (04037)	PRO- METRYN, DIS- SOLVED (UG/L) (04036)
47583	403143088054701	10-09-01	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
00823	411447087513101	10-10-01	<.05	.86	.21	<.05	<.05	<.05	<.05
20458	412603087452601	10-10-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50060	403432089380901	10-15-01	<.05	.09	<.05	<.05	<.05	<.05	<.05
60053	383932090012601	10-16-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11782	415551088575201	10-23-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
31409	404418089011802	10-23-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50055	403116089251401	10-30-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50057	403404089390701	10-30-01	<.05	.57	.23	<.05	<.05	<.05	<.05
20250	421433088002701	10-31-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
00602	414320089201301	11-07-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11470	413654088475601	11-07-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11678	421256088593801	11-07-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50308	401754090032001	11-13-01	<.05	.13	<.05	<.05	<.05	<.05	<.05
00366	421840088033001	11-20-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
02305	422225088102501	11-20-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20357	412608088121401	11-21-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47561	404625087335301	11-27-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
01118	400111090312502	12-04-01	<.05	.17	.07	<.05	<.05	<.05	<.05
11509	411928089073001	12-04-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47518	410002088313401	12-04-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20152	422231088221101	12-09-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20141	421222088152701	12-09-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11891	422931089473201	12-11-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20330	413137088011901	12-11-01	<.05	.12	<.05	<.05	<.05	<.05	<.05
50251	400623089361201	12-12-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50376	403737089195401	12-12-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50094	404417090541502	12-18-01	<.05	.24	<.05	<.05	<.05	<.05	<.05
47819	385946088020701	12-19-01	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50224	394605089155301	01-09-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
52120	394557090361601	01-09-02	<.05	.60	.26	<.05	<.05	<.05	<.05
20285	421803087554801	01-14-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47532	404532088111201	01-15-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47551	404614087512502	01-15-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
00757	372000088431001	01-22-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20700	415410088034301	01-23-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
31307	410134089244503	01-29-02	<.05	.14	<.05	<.05	<.05	<.05	<.05
31428	405404089022301	01-29-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11562	415035089175901	02-05-02	<.05	2.46	<.05	<.05	<.05	<.05	<.05
11636	421611089031101	02-05-02	<.05	.07	<.05	<.05	<.05	<.05	<.05
11406	415552088465601	02-06-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11438	413805088405102	02-06-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20497	415134088075001	02-11-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47692	395411087485701	02-19-02	<.05	.77	<.05	<.05	<.05	<.05	<.05
60127	381238090160001	02-25-02	<.05	.17	.13	<.05	<.05	<.05	<.05
00251	391251087393801	03-04-02	.16	.07	<.05	<.05	<.05	<.05	<.05
47811	390644087391802	03-04-02	<.05	.52	.52	<.05	<.05	<.05	<.05

Appendix 1. Well information, field characteristics of water quality, herbicides, and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001-September 2002—Continued

IEPA WELL NUMBER	USGS STATION NUMBER	SAMPLE DATE	METOLA- CHLOR, DIS- SOLVED (UG/L) (39415)	METOLA- CHLOR- ESA, DIS- SOLVED (UG/L) (61043)	METOLA- CHLOR OA, DIS- SOLVED (UG/L) (61044)	METRI- BUZIN, DIS- SOLVED (UG/L) (82630)	PENDI- METHA- LIN, DIS- SOLVED (UG/L) (82683)	PRO- METON, DIS- SOLVED (UG/L) (04037)	PRO- METRYN, DIS- SOLVED (UG/L) (04036)
11327	411722089221201	03-05-02	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
11347	412534089215601	03-05-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11904	414305089550901	03-06-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
00795	420559088322101	03-11-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
01416	394953090331202	03-12-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47725	395640088515501	03-12-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
45155	392418087392101	03-18-02	<.05	.29	<.05	<.05	<.05	<.05	<.05
11892	413920090044401	03-19-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
31889	412421090334501	03-19-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50101	394212090344901	04-01-02	<.05	.41	.06	<.05	<.05	<.05	<.05
50227	400022090522301	04-01-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20207	421943088160501	04-02-02	<.05	1.56	.45	<.05	<.05	<.05	<.05
45081	400836088185101	04-08-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47687	401217088220301	04-08-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11363	413328089274501	04-09-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
71531	383124088135401	04-16-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50395	391411090072001	04-22-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20297	420947087561801	04-23-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20447	413337088055501	04-23-02	<.05	.21	.06	<.05	<.05	<.05	<.05
50298	401930090361701	04-29-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50383	403758089370801	04-29-02	<.05	.45	.22	<.05	<.05	<.05	<.05
11367	412232089275101	04-30-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11495	412030089001901	04-30-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11600	411529089105701	04-30-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20180	422322088140901	05-14-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
22040	412143088254901	05-14-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
00276	421359088323201	05-20-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11560	415027089175501	05-20-02	<.05	2.32	<.05	<.05	<.05	<.05	<.05
00572	393324088363301	05-21-02	<.05	1.59	.28	<.05	<.05	<.05	<.05
50237	392439089262001	05-21-02	<.05	7.24	2.95	<.05	<.05	<.05	<.05
52062	394338090542001	06-05-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20613	415839088113901	06-11-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50351	404511090004001	06-11-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20442	412854087503501	06-17-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
47573	403551088021302	06-17-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11557	414955089291901	06-18-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11629	421656089031301	06-18-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20029	420727088153901	06-24-02	<.05	.05	<.05	<.05	<.05	<.05	<.05
11570	414122088585401	06-25-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11943	415509089032801	06-25-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20766	414945088115101	07-01-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
50003	395106089432801	07-02-02	<.05	.70	.15	<.05	<.05	<.05	<.05
60058	385235090072601	07-02-02	<.05	.34	.18	<.05	<.05	<.05	<.05
50051	404126089305001	07-17-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11707	420608089501401	07-29-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
11514	410931088384401	07-30-02	<.05	<.05	<.05	<.05	<.05	<.05	<.05
20328	413117087481701	08-06-02	<.05	.20	.12	<.05	<.05	<.05	<.05

Appendix 2. Box-and-whisker plots of concentrations of detected herbicides and herbicide transformation products in samples from selected public-supply wells that tap source-water aquifers in Illinois, October 2001 -September 2002.



District Chief
U.S. Geological Survey
221 N. Broadway Ave.
Urbana, IL 61801



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