Illinois' Statewide Monitoring Well Network for Pesticides in Shallow Groundwater—Network Development and Initial Sampling Results

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EXECUTIVE SUMMARY

A key element of the Illinois Generic Management Plan for Pesticides in Groundwater was the use of a statewide map of aquifer sensitivity to contamination by pesticide leaching. This map included soil properties (hydraulic conductivity, the amount of organic matter within individual soil layers, and drainage class) from a digital soil association map and hydrogeologic properties to a depth of 50 feet. The map displayed six mapped units or levels of aquifer sensitivity, and each map unit was subdivided into two map subunits. Each subunit had a distinct combination of soil and hydrogeologic properties. Prior to the implementation of the Generic Plan, the statewide map was tested by sampling shallow groundwater for pesticides from a dedicated monitoring well network. To test this mapping strategy efficiently, a stratified random sampling plan was adopted that focused on the three most sensitive map units. Project goals were to provide data to test the utility of the aquifer sensitivity map to predict pesticide occurrence and to understand pesticide occurrence in shallow groundwater.

All monitoring wells were located near agricultural production fields (most within 10 feet of corn and soybean fields) where the only known source of pesticides were those pesticides used in normal agricultural production. Most studies of pesticide contamination covering a broad geographic area sample water-supply wells, and this study using monitoring wells was designed to generate data that might provide a unique perspective on the occurrence of pesticides in shallow groundwater.

Prior to the completion of the entire monitoring network, a one-time sampling program of monitoring wells was conducted to assess the distribution of pesticide occurrence across the various units of aquifer sensitivity, and a time-series sampling program was conducted to assess the temporal variability of pesticides in shallow groundwater. For the one-time sampling program, 159 samples were collected from 159 wells from September 1998 through February 2001. For the time-series sampling program, 215 samples were collected from 21 wells from October 1997 through July 2000. These groundwater samples were analyzed for 14 pesticides but no pesticide degradates. In addition, groundwater samples were collected to characterize cations and anions, including nitrate-nitrogen.

Data from these initial sampling programs showed that pesticides were detected in 16 to 18% of the samples. Atrazine was the most commonly detected pesticide, followed by metolachlor, butylate, and bromacil. Only one sample had a concentration of a pesticide (atrazine) that exceeded a federal drinking water standard. Most detections were at concentrations less than 1 µg/L. Pesticide occurrence was generally dependent on sampling time. The strongest temporal relationship was between post-application (June through October) versus other time frames (November through May). Pesticide occurrence during post-application months was three times higher than during other months. Pesticide occurrence was three times more common in samples when the depth to aquifer material was mapped as less than 20 feet than when the depth to aquifer material was mapped as 20 to 50 feet. Thus, pesticide occurrence was found to be dependent on depth to uppermost aquifer material or the hydrogeologic factor of the tested map. Pesticide occurrence was not dependent on the combined soil and hydrogeologic factors of the tested map. Thus, the new map was not a useful predictor of pesticide occurrence.

The median and range of anion and cation concentrations for both sampling programs were similar, except for nitrate-nitrogen concentrations. The median nitrate-nitrogen concentrations

for both programs differed slightly, but were less than 3.0 mg/L, which is well below the 10 mg/L maximum contaminant level for nitrate-nitrogen. The nitrate and sulfate concentrations were not uniform across the six subunits.

Based on the neural network analysis of the one-time sampling data, the time of sample collection and well depth appeared to be the best parameters for predicting pesticide concentration. Depth to uppermost aquifer material and depth to water also were significant. Aquifer sensitivity to contamination and pesticide leaching class values were not able to predict contamination potential independently; however, their presence with other input parameters improved the prediction of contamination by the neural network analysis.

Recommendations

Additional study of the temporal variations of pesticide occurrence is needed to define temporal trends. The wells in this network could be sampled to satisfy this need. Wells from areas where the depth to uppermost aquifer material is less than 20 feet may be the best wells to sample because of the higher pesticide occurrence observed for these wells in the one-time sampling program. Such a study would require consistency in the wells sampled, sampling methods, sampling interval, and analytes.

Pesticide degradates should be included in the list of analytes in all future sampling to provide a more complete picture of pesticides in Illinois groundwater. As other researchers (Kolpin et al. 2000; Morrow, 2003; Mills and McMillan, 2004) have shown, pesticide degradates generally are found more frequently and at higher concentrations than the parent compounds.

Additional research on soils and hydrogeologic properties should be conducted to improve the statewide map of aquifer sensitivity to contamination by pesticide leaching. Installation of additional monitoring wells for this network should be suspended until soil characteristics can be incorporated into the aquifer sensitivity map in a meaningful way. The map tested in this project included three leaching properties (hydraulic conductivity, the amount of organic matter of individual soil layers, and drainage class category) for the soil associations. Median values for these three factors were used to develop the tested map.

In a modeling study, Scheibe and Yabusaki (1998) found that bulk groundwater flow depends on mean hydraulic conductivity values, but contaminant transport is strongly impacted by the existence and connectedness of extreme-valued hydraulic conductivities. Thus, the map may possibly be improved by incorporating these extreme values for soil leaching properties. In addition, neural network analysis could be used to identify soil and other factors that improve our ability to predict pesticide concentration in the project samples and ultimately the statewide map of aquifer sensitivity to contamination by pesticide leaching. The hydrogeologic property, depth to uppermost aquifer material, could be improved by increasing the accuracy of data for those areas where the depth to uppermost aquifer is between 20 and 50 feet.

Once these recommendations have been addressed, samples from the monitoring well network should continue to be collected, analyzed, and interpreted on a regular basis.

CHAPTER 1. INTRODUCTION

Introduction and Project Background

The Pesticide Subcommittee of the Interagency Coordinating Committee on Groundwater completed the *Illinois Generic Management Plan for Pesticides in Groundwater* (Pesticide Subcommittee, 2000), which is also known as the "Generic Plan." A key element of this plan was the use of a map by Keefer (1995a) of aquifer sensitivity to contamination by pesticide leaching (Figure 1.1) to manage pesticide usage by mappable geohydrologic units should groundwater contamination be found. Public comments on an early draft of the Generic Plan included the fact that the map (Keefer, 1995a) had not been tested using groundwater quality data. These comments provided the final impetus to implement a program to collect these groundwater quality data. In 1994, the Illinois Department of Agriculture (IDA) approached the Illinois State Geological Survey (ISGS) and Illinois State Water Survey (ISWS) to design a dedicated monitoring well network that would provide data on the occurrence of pesticides to test this map (Keefer, 1995a).

Work on the installation of the monitoring well network began in February 1995. As designed, the network was to include a total of 225 wells with 75 wells in each of the three most sensitive map units (Excessive, High, and Moderate). During July 2000, the network was expanded at IDA's request to include a fourth map unit (Very Limited) to address the high rate of pesticide occurrence in areas where groundwater is generally obtained using large diameter, hand-dug and bored wells. By June 2001, the network included 191 wells installed in 57 counties across Illinois (Figure 1.2).

Goals of the Project

In this project, we sought to define the regional impacts of pesticide leaching from nonpoint sources resulting from conventional field application on shallow groundwater quality, rather than the impacts of site-specific, point sources (e.g., spills) on shallow groundwater quality. The monitoring well network was designed to address four goals:

1. To test the utility of the map of the aquifer sensitivity to contamination by pesticide leaching in Illinois (Keefer, 1995a) as a predictive tool for the Generic Plan by providing data on the pesticide occurrence in the three most sensitive map units.

2. To provide data on the variability of the pesticide occurrence within these three most sensitive map units.

3. To determine if the occurrence of selected agricultural chemicals varied seasonally and over longer periods of time.

4. To obtain additional geochemical and geological information, when economically feasible, to enhance our understanding of the occurrence of the selected agricultural chemicals.

Development of Maps of Aquifer Sensitivity

In 1990, the IDA contracted with the ISGS to develop a map to predict the sensitivity of shallow aquifers in Illinois to contamination from the agricultural use of pesticides, specifically those

Legend

- Excessive
- High
- Moderate
- Somewhat Limited
- Limited
- Very Limited
- Karst
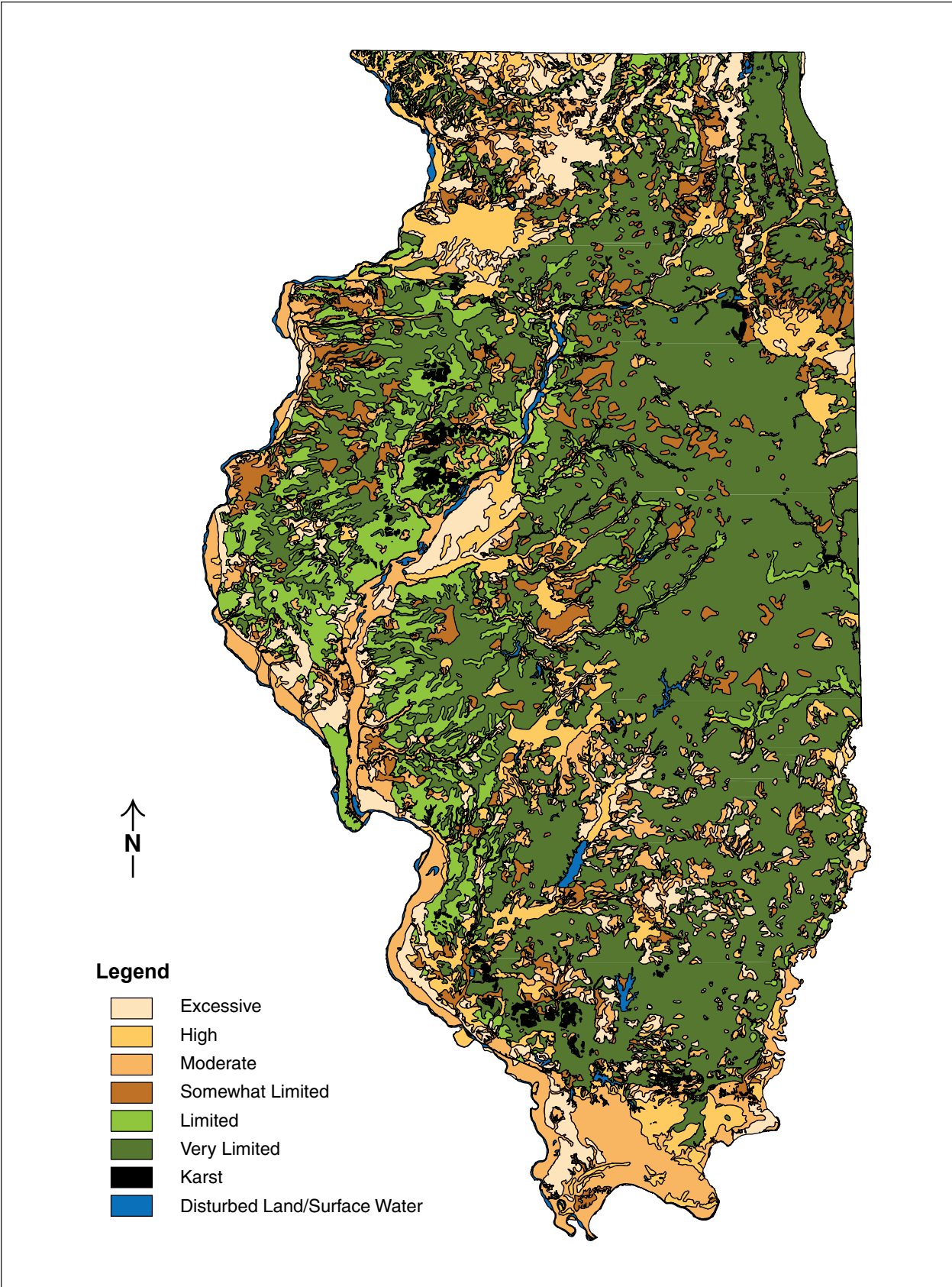- Disturbed Land/Surface Water

Figure 1.1 *Aquifer sensitivity to contamination by pesticide leaching in Illinois (Keefer, 1995a).*
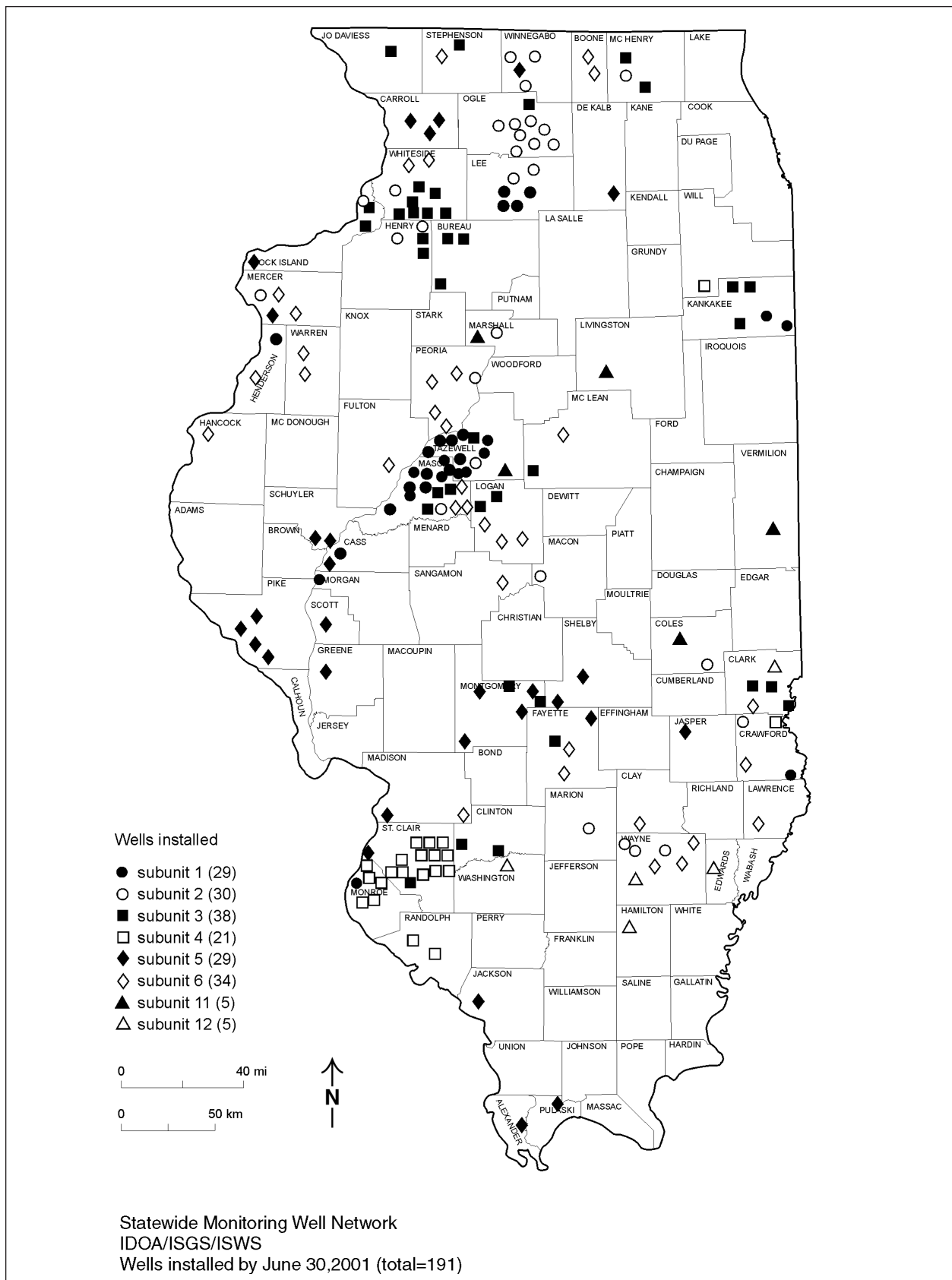
Figure 1.2 *Geographic distribution of the monitoring wells by subunit (defined in Tables 2.1 and 2.2).*

used for the state's major crops, corn and soybeans. This initial study recognized the importance of soil characteristics and the sequence of shallow geologic materials as they affect pesticide fate and transport to shallow aquifers. Because of the lack of suitable soils information, however, a subsequent publication (McKenna and Keefer, 1991) used depth to uppermost aquifer material as the sole criterion for predicting aquifer sensitivity. Schock et al. (1992) confirmed that depth to the uppermost aquifer material can be a useful criterion for evaluating the probability of contamination of rural, private well water by agricultural chemicals (nitrogen and pesticides). That is, if the top of the aquifer material is shallow (<50 feet), wells completed in that aquifer are more vulnerable to contamination by agricultural chemicals than are wells completed in deeper aquifer materials (top of the aquifer material >50 feet).

Keefer (1995a) mapped aquifer materials following stack-unit map criteria (Berg and Kempton, 1988). "Aquifer materials" include sand, sand and gravel, sandstones, and fractured limestone or dolomite with a minimum thickness of 5 feet unless a thinner unit covers at least 1 km². "Aquifer" suggests that these geologic materials are water saturated; however, as discussed by Keefer (1995b), unsaturated geologic units were also included under the premise that pesticide transport through unsaturated geologic materials and saturated geologic materials is similar.

In 1991, the Soil Conservation Service (now the Natural Resources Conservation Service) released a digital soil association map and database for Illinois (U.S. Department of Agriculture, 1991). The detail and accuracy of this soils map were well suited for use in a statewide prediction of the impacts of soils on pesticide leaching. Publications by Schock et al. (1992) and the Soil Conservation Service, together with the growing regulatory pressure to address agrichemical use and related groundwater protection issues, prompted IDA to fund an ISGS revision of the previous map (Keefer, 1995a).

Keefer (1995b) used published studies of pesticide fate in the subsurface and pesticide occurrence in shallow groundwater to develop a method to rank the leaching characteristics of soils. This soil leaching classification was then combined with information on depth to uppermost aquifer material in an effort to better predict aquifer sensitivity to contamination by pesticides. The soil leaching evaluation was based on three factors known to influence fate and transport of pesticides through soils (e.g., Ritter, 2001; Burkart et al., 2001)—(1) hydraulic conductivity, (2) the amount of organic matter of individual soil layers, and (3) drainage class category. Pesticide transport is reduced for soils with more soil organic matter, lower hydraulic conductivity, and slower soil drainage. Soil associations were ranked into six categories based on their median characteristics for these three soil leaching factors (see Table 8 of Keefer, 1995b). Those categories were then combined with three categories of depth to uppermost aquifer material to predict overall aquifer sensitivity to contamination by agricultural use of pesticides (see Table 9 of Keefer, 1995b). This final aquifer sensitivity classification included six categories. This method for defining the six categories was then applied to map information from the Soil Conservation Service (U.S. Department of Agriculture, 1991) and ISGS (Berg and Kempton, 1988) to produce a statewide map of aquifer sensitivity (Figure 1.1). The six aquifer sensitivity categories corresponded to six map units (Excessive, High, Moderate, Somewhat Limited, Limited, and Very Limited).

CHAPTER 2. NETWORK DEVELOPMENT

Overall Network Design

The project goals shaped the design of the monitoring well network. First, the monitoring well network was designed to statistically test the hypothesis that the three most sensitive map units from Keefer (1995a) could be used to predict the occurrence of pesticides in groundwater of shallow aquifers. The three least sensitive map units (Somewhat Limited, Limited, and Very Limited) were initially excluded from this study because Schock et al. (1992) showed that agricultural chemical occurrence was negligible for small-diameter wells completed in areas of these map units. To provide some data on the significance of the pesticide leaching class and depth to uppermost aquifer material, wells in the three most sensitive map units (Excessive, High, and Moderate) were split into two subunits (see Table 2.1). Thus, Excessive was split into subunits 1 and 2. Subunits 1 and 2 have the same depth to uppermost aquifer material, but different pesticide leaching classes. High was split into subunits 3 and 4. Moderate was split into subunits 5 and 6.

Table 2.1 Definition of aquifer sensitivity units and subunits 1 through 6.

Aquifer sensitivity	Subunit	Pesticide leaching class	Depth to uppermost aquifer material (ft)
Excessive	1	Excessive	<20
	2	High and Moderate	<20
High	3	Somewhat Limited and Limited	<20
	4	Excessive	20 to 50
Moderate	5	Very Limited	<20
	6	High and Moderate	20 to 50

A stratified random design with an equal number of wells in each stratum was used to test this hypothesis because it is the most efficient design (Sudman, 1976). The number of wells to be installed in each stratum was determined based on cost considerations and the expected occurrence of pesticides in the different strata. Seventy-five wells were initially going to be installed in each stratum or in the areas mapped as Excessive, High, and Moderate by Keefer (1995a). For design purposes, we assumed that pesticides would be detected in 15% of the groundwater samples from Excessive map areas, in 10% from High map areas, and 3% from Moderate map areas. These assumptions were based on previous monitoring data from Illinois and other midwestern states. Available monitoring data for domestic wells located tens to hundreds of feet from the fields were extrapolated to monitoring wells located at the field perimeter. Monitoring wells were located at the field perimeter where pesticide occurrence was thought to be higher than in water-supply wells.

Prior to the fiscal year 2001 contract period, however, the project was modified to include a limited number of monitoring wells in areas mapped as Very Limited. Water-supply wells in

these Very Limited areas are typically large-diameter, hand-dug or bored wells. Samples from large-diameter, private water wells completed in these Very Limited areas typically have the highest rate of pesticide occurrence (Schock et al., 1992; Goetsch et al., 1992; Wilson et al., 1994; Mehnert et al., 1995; Centers for Disease Control, 1998). To explain the higher contaminant occurrence in large-diameter wells, some have suggested that contaminant sources were all related to near-well point sources; others have demonstrated consistent water quality between private wells and nearby farm fields. Consistent with the approach to create map units 1 through 3, we subdivided map unit 6 (Very Limited) into subunits 11 and 12 (Table 2.2) to maximize the amount of information provided by pesticide occurrence results. For subunits 11 and 12, this subdivision was based on the episode/age of the uppermost glacial materials. Subunit 11 included areas in the Wisconsinan Till Plain, and subunit 12 included areas in the Illinoian Till Plain. We hypothesized that pesticide occurrence would be different in these subunits because of the difference in age and the degree of weathering within the near-surface deposits and the effect of these factors on pesticide fate and transport.

Ten wells were installed in subunits 11 and 12; however, too few samples were collected from these wells to make meaningful conclusions. Thus, no conclusions based on subunit 11 and 12 samples are presented in this report.

Table 2.2 Definition of subunits 11 and 12.

Aquifer sensitivity	Subunit	Pesticide leaching class	Depth to uppermost aquifer material (ft)	Episode (age) of till
Very Limited	11	Moderate to Very Limited	not within 50 feet	Wisconsin
Very Limited	12	Moderate to Very Limited	not within 50 feet	Illinois

Polygon and Site Selection

Before network monitoring wells were constructed, a protocol was developed and followed to ensure that each selected well site met an established, consistent set of criteria regarding hydrogeologic setting and site accessibility:

1. Selected mapped sensitivity areas were subdivided into uniformly sized polygons.
2. A list of polygons was generated for each subunit, and polygons were randomly selected from those lists.
3. Mapped polygons were evaluated using available local, site-specific geologic information.
4. Drilling sites within a polygon were selected based on specific site suitability.
5. Required permission to drill was obtained from governmental officials and/or landowners.

Creation of Uniformly Sized Polygons

As shown in Figure 1.1, the mapped areas—or polygons—represent contiguous, mapped sensitivities ranging in size from less than 1 square mile to hundreds of square miles. To satisfy the requirements of the statistical design, well locations were selected from a set of nearly

uniformly sized polygons. We used section delineations from the U.S. Public Land Survey system (section-township-range) to generate these uniformly sized polygons. A section covers approximately 1 square mile. This size was selected because it was large enough to yield several potential well sites (although only one well was actually completed in any given polygon, multiple sites within a polygon were evaluated against the site selection criteria). The use of sections was also convenient because a digital map of polygons was readily available, and many roads in Illinois are constructed along section lines, facilitating the well site selection process. Using Geographic Information Systems (GIS) software, the aquifer sensitivity map was overlaid with the map of section boundaries to identify individual "uniform" polygons for each aquifer sensitivity subunit. In many cases, a section contained polygons for more than one subunit. In those cases, only polygons having at least 0.5 square mile of a single subunit were included in the set of possible well locations.

Random Polygon Selection

A three-step procedure was used to randomly select the delineated polygons for each subunit. First, a list of unique random numbers, ranging from 1 to the number of polygons within a subunit, was generated using software described by Mehnert (1992). Second, the polygons were numbered sequentially; this sequential number was called the polygon number. In the final step, the polygon numbers were matched to the list of random numbers. This procedure provided a randomly selected, ordered list of polygons.

Office Evaluation of Polygons

Prior to field locating potential well sites, the polygons were evaluated in the office to determine whether a well could be installed. The evaluation included a review of topographic maps to check row crop coverage, to determine available roads and other cultural features such as buildings and pipelines, and to review available well logs of the area to screen the local geology. Office and field verification steps were recorded on a well data sheet.

The first step in the office evaluation involved locating each polygon on a U.S. Geological Survey (USGS) 7.5-minute topographic map. The portion of the section defining the polygon was delineated using individual county versions of the map *Aquifer Sensitivity to Contamination by Pesticide Leaching* (Keefer, 1995a) generated at a scale of 1:250,000, the *Stack-Unit Map of Illinois* (Berg and Kempton, 1988), or both.

Next, to ensure that wells were installed in areas where row crops were grown, an initial estimate was made of the row crop land use in the polygon. We decided that potential well sites should have at least 50% of land within 1 square mile under row crop. For this project, row crops were primarily corn and soybeans, but included wheat, sorghum, other small grains, and pasture/alfalfa if grown in rotation with corn or soybeans. An estimate of the row crop land use was made using information from USGS topographic maps and, for some sites, the map *Land Cover of Illinois* (Luman et al., 1997). If a polygon lacked sufficient row crop coverage, analysis of the site usually was suspended until a site visit could verify crop coverage. Polygons were not dropped until a field visit confirmed that the land surrounding a polygon had less than 50% row crops.

The geology of each polygon having sufficient row crops was evaluated using data from well

records. Evaluations were done independently by staff at both Surveys using their extensive records. Records for wells within and surrounding the section containing the polygon were examined to confirm the presence of the mapped aquifer material at the mapped depth. The polygon was dropped from the list if the data did not confirm the presence of aquifer material within the prescribed depth range.

For each polygon, road access for the drill rig was also assessed in the office. In rare instances, it was obvious from topographic and other maps that no roads existed within or bordering the polygon. In such cases, the polygon was dropped. If a site met all criteria in the office evaluation, the polygon was visited.

Early in the evaluation process, we noticed that the mapped depth to uppermost aquifer material often differed significantly from that observed in individual well logs. These differences were found to be generally consistent with the range in elevation of the local land surface. Because local relief could be considered a source of variability within the *Stack-Unit Map of Illinois* (Berg and Kempton, 1988), we allowed the installation of wells in polygons if the difference between mapped aquifer depth and well log depth was within the local relief. For aquifers mapped as beginning between 20 and 50 feet below land surface, well logs in areas with 10 to 15 feet of local relief would record the uppermost aquifer material as beginning between 20 and 65 feet of land surface. Well logs in areas with 50 to 60 feet of relief would record the uppermost aquifer material as beginning between 20 and 110 feet of the surface. Because of the consistency of these results, we determined that these differences between the map and the well logs could be considered an acceptable part of the strategy used to create this map. The local relief could be seen, in this context, as a component of the total mapping uncertainty that could be accounted for in a reliable way. With this perspective, we determined that this source of difference between the map and the well logs did not present a fatal flaw in the design of the statewide stack-unit map or in its use for the aquifer sensitivity map.

Field Evaluation and Selection of Drilling Sites

The field evaluation of polygons had two purposes: to verify the office evaluation of row crops and site accessibility and to locate exact drilling locations within the polygon. For the purpose of field verification and well siting, the state was divided into northern and southern halves along an east-west line roughly passing through Champaign. The ISWS took responsibility for field verification north of Champaign, and the ISGS took responsibility for field verification south of Champaign.

All wells were located in the right-of-way of a township, county, state, or federal highway, usually on the backslope of a road ditch as far as possible from the road and as close as possible to a farm field. Most wells were located within 10 feet of a farm field. Locations along a township or county right-of-way were preferred over those along a state or federal highway because obtaining permission to install wells was generally easier and less time consuming.

The selection of potential drilling sites was guided by several factors. Sites were located beyond a minimum prescribed distance from potential point sources of contamination (Table 2.3). In rare instances, potential drilling sites within 500 feet of a farmstead or rural residence were retained as long as all other siting criteria were met. In addition, we sought a fairly level section of road right-of-way with sufficient width to accommodate a drill rig. Steep ditches, buried utilities, and

overhead power lines were avoided. To the extent possible, low spots in the landscape, which potentially remain wet for extended periods and could allow standing water around the well head, were avoided. When more than one drilling site was available in a polygon, sites were prioritized based on ease of access. In some cases, the government authority or landowner had a preferred location for a well, which was used as long as all site selection criteria were still honored.

Table 2.3 Minimum setback distances for monitoring wells from various point sources.

Point source description	Minimum distance to well site (ft)
Agricultural chemical facilities and dealerships	1,000
Livestock confinement facilities (>50 hogs or cattle, or equivalent)	500
Farmsteads or rural residences	500
Wastewater treatment facilities	500

In the first year of the study, wells were drilled in all selected polygons having sufficient row crop and suitable drilling sites, regardless of the geologic evaluation completed in the office. In other words, some sites were drilled even if the review of local geologic information indicated that the mapped unit might have been mapped incorrectly. This approach was taken to determine how much emphasis to place on the office geologic evaluation and to help assess the reliability of the mapping at a local scale. It was found that, especially for subunit 6, having logs for nearby wells confirm the accuracy of the mapped unit was essential to minimize the chance of drilling at a location where monitoring wells would not be installed. Therefore, after the first year of the study, the success rate in drilling and finding the mapped unit increased because more polygons were dropped at the office evaluation stage.

Acquiring Permission to Drill

Following the confirmation of the presence of row crops, drilling site accessibility, and potentially suitable geology, permission to install a monitoring well was sought from the proper civil authority and, in some cases, the landowner. In the few instances where the most suitable drilling site was along a state highway or state-maintained road, the appropriate Illinois Department of Transportation district office was contacted, and permits to drill were submitted and acquired. In most cases, initial contact was made with the county highway engineer for the county containing the polygon to determine who had authority over the road right-of-way containing the selected drilling site(s) and the extent of that authority. If the well was in the right-of-way of a county road, permission to drill was obtained from the county engineer. Permission usually was verbal, but, in a few instances (e.g., Peoria and Richland Counties), written permit was required. If the drilling site was located within a township road right-of-way, the township road commissioner was contacted, and permission to drill was usually acquired. When the road commissioner did not grant permission to drill, the polygon was dropped from the list. In some counties, the road commissioner exercised authority over all activities with the right-of-way; in other counties, the road commissioner only had authority over activities directly related to road maintenance, and adjacent landowner approval was required before drilling. If landowner approval could not be obtained, the polygon was dropped from the list.

Clearing Drilling Sites with JULIE

Before drilling, all sites were inspected by JULIE (Joint Utility Locating Information for Excavators; 800-892-0123) for the presence of underground utilities. This inspection sometimes required small adjustments in the position of a borehole, but never resulted in a polygon being dropped from the list.

Drilling at the Site to Determine Actual Geology

As each borehole was drilled, geological samples were examined in the field to determine the presence or absence of aquifer material and the correlation between the samples and the mapped geology. If no aquifer material was found after drilling to a predetermined depth, no well was installed, the borehole was properly abandoned, and the polygon was dropped from the list. Otherwise, a monitoring well was finished in the aquifer material encountered.

A summary of the well siting process and progress is shown in Table 2.4. The goal for the number of wells in each subunit, based on the statistical network design, was 37 or 38 wells such that 75 wells would be completed in each map unit (225 wells for the original network). Subunits 11 and 12 were added later and were not part of the statistical design, although, to allow statistical comparison, a total of 75 wells should be completed in subunits 11 and 12. As of July 2001, 181 monitoring wells were completed in subunits 1 though 6. Another 10 wells were installed in subunits 11 and 12 to bring the total network to 191 wells.

Table 2.4 Summary of well siting by subunit.

Siting process	Subunit							
	1	2	3	4	5	6	11	12
Initial goal of wells per subunit	38	37	53*	22*	38	37	NA**	NA**
Wells installed by July 2001	29	30	38	21	29	34	5	5
Boreholes drilled; no well installed	1	5	2	1	0	13	0	0
Polygons dropped; limited row crop	6	16	22	43	28	45	0	0
Polygons dropped; no drill rig access	3	5	3	1	4	12	0	0
Polygons dropped; mapped geology disagrees with local well records	1	5	2	2	5	29	0	1
Well sites denied access	0	0	2	0	4	2	0	0
Wells destroyed after installation	0	0	0	0	0	1	0	0

* Because only 22 polygons were mapped for Subunit 4, more wells were added in Subunit 3 to reach 75 wells for the unit.

** Not applicable because these subunits were not part of the original network design.

Subunit 6 was the most problematic in terms of matching available geologic information (i.e., site-specific well record information) to the mapped sensitivity. For subunit 6, 29 polygons were dropped because of lack of geologic data to confirm the presence of the mapped aquifer material. Thirteen boreholes drilled into this subunit did not have wells completed in them, which was many more than in any other subunit. In general, geological uncertainty and unpredictability

increased with depth. The poor borehole to well completion ratio for subunit 6 increased the need to check local geology more closely before drilling. Dropping a potential well site because of a poor match between the local well records and the mapped sensitivity was much more cost effective than drilling a borehole and not completing a well. Many polygons were dropped because of a lack of row crops. An additional 34 sites were visited and were awaiting owner approval or were ready to be drilled when the project was halted.

Monitoring Well Construction

Monitoring well design and construction methods generally followed production well design and construction techniques; however, the monitoring wells were built specifically to give access to the groundwater so a "representative" sample of water could be withdrawn and analyzed. Emphasis was placed on constructing a well that would provide easily obtainable groundwater samples that would give reliable water quality data. Therefore, the materials and techniques used for constructing a monitoring well must not materially have altered the quality of the water being sampled. Principal considerations were drilling method, geologic material sampling, casing and screen material and diameter, screen length and "slot" size, depth of screen placement and sand pack, annular seal, well security, and well development.

Drilling Method and Geologic Material Sampling

Hollow Stem Auger Drilling All holes completed in unconsolidated geologic materials were drilled by hollow stem auger, either with the ISWS Mobile B57 rig or with the ISGS Mobile B35 and CME 75 rigs. The ISGS used its Mobile rig in 1996 and the CME 75 rig after 1996. All drilling equipment (e.g., augers, split spoons) were steam-cleaned before beginning each hole. All augers had a 4¼-inch inside diameter for constructing 2-inch diameter monitoring wells. A split-spoon sampler was used to collect "undisturbed" geologic samples. When using the ISWS drill rig, split-spoon sampling began at a depth of 10 feet, and 18-inch split-spoon samples were collected every 2½ feet. The ISGS collected continuous split-spoon samples after drilling 10 feet. This sampling strategy was followed until thick unsaturated sands were encountered, where fewer samples were collected until the saturated zone was reached. The sampled geological materials were examined immediately to determine if the site geology agreed with mapped conditions and if a well would be installed.

Mud Rotary Drilling All holes completed in consolidated bedrock were drilled by mud rotary drilling using the ISWS Mobile B57 rig. All drilling equipment (e.g., drilling bits, rods) was steam-cleaned before beginning each hole. Drilled holes had a minimum diameter of 5 inches, which is suitable for constructing 2-inch diameter monitoring wells with sand pack and annular seal. Because a split-spoon sampler cannot be used in consolidated rock, washed samples or cuttings flushed from the borehole during drilling were used to determine lithology at the borehole. Samples were examined at a minimum of every 5 feet and at discernible changes in formation (e.g., rock color or drilling penetration rate). For this project, wells drilled into bedrock were completed in the uppermost sandstone, limestone, or dolomite, which were easily distinguished from shale and other soft, impermeable geological materials.

Well Construction Materials

All wells were constructed of 2-inch diameter polyvinyl chloride (PVC), which is considered to be a suitable well casing for sampling low concentrations of organic chemicals (Parker and Ranney, 1994). All casing and screen connections were threaded with flush threads and sealed with butyl rubber O-rings to inhibit leakage through casing joints. Screens were generally 5 feet long with 0.010-inch opening slots (10-slot). Where the mapped unit was very thin, a 2½-foot length screen was used. Well screens were sand-packed with 20-40 sand or equivalent sieve retention. For augered holes, the sand pack extended to no more than 1 foot above the well screen. A natural pack was used when the well was completed within a thick sequence of sand or gravel. In such cases, the natural formation was allowed to collapse around the well screen as the augers were withdrawn.

Well Depth for Subunits 1 through 6

This project was originally designed to address the occurrence of pesticides within three aquifer sensitivity classes: Excessive, High, and Moderate at two depths to the uppermost aquifer material—less than 20 feet or between 20 and 50 feet. Prior to drilling a hole at a particular location, the likely well depth was determined based on our knowledge of the depth to the uppermost aquifer material for that location using the statewide map of aquifer sensitivity and available well logs. The decision to determine if the site materials matched the regional geologic description depicted on the statewide map made for interesting drilling rules. Statewide maps are generalized because not all geologic details can be portrayed. In deciding if the observed geologic materials matched the mapped geologic setting, we sought to answer this question: Do these geologic materials, in light of available well logs, match the mapped geologic setting?

If aquifer materials were mapped as within 20 feet of land surface but were not actually encountered within 20 feet, the hole was drilled another 10 feet. If no aquifer materials were encountered within 30 feet, the hole was abandoned. If aquifer materials were encountered in the 20- to 30-foot interval where aquifer materials were predicted to be within 20 feet, a well was built if regional well information suggested these aquifer materials were regionally continuous and were encountered in nearby wells within 20 feet of land surface. These rules were also relaxed for sites with significant, local topographic relief, as discussed in the Office Evaluation of Polygons section.

Similarly, if aquifer materials were predicted to occur between 20 and 50 feet of land surface and were not encountered during drilling to a depth of 50 feet, no more than an additional 10 feet was drilled before abandoning the hole. Again, a well was constructed in the 50- to 60-foot range if regional information suggested the aquifer materials extended to within the 20- to 50-foot predicted range.

If aquifer materials were encountered at depths of less than 20 feet when mapped predictions suggested aquifer materials should occur in the 20- to 50-foot interval, drilling proceeded until it was confirmed that aquifer materials did not occur again within 50 feet (i.e., drilled until other aquifer materials were encountered or until 50 feet depth). If no other suitable aquifer materials were found, the well was completed in the shallower aquifer materials, again provided that regional information suggested that regionally the aquifer materials occurs within 20- to 50-foot range.

Where aquifer materials were encountered within 20 feet, but regional data indicated that the aquifer materials were generally found in the 20- to 50-foot range, data from this well were classified to be from the 20- to 50-feet depth for the purpose of statistical analysis. Similarly, where aquifer materials exceeded the 20-foot depth but regional data indicated that aquifer materials were found within 20 feet, data from these wells were classified to be from within 20-foot depth for the purpose of statistical analysis.

To summarize, we chose to look at the regional geologic setting over the site specific setting because we were attempting to test a statewide map, one that depicted regional geology.

Finally, where aquifer materials were encountered within 20 feet of land surface but the hole remained dry, drilling proceeded until the water table was reached as long as the geologic materials did not change. If the mapped aquifer materials were dry and non-aquifer materials were penetrated, the hole was abandoned.

The drilling rules just discussed affected the well depths, generally allowing the wells to be deeper than the assigned depth to uppermost aquifer. The deepest wells were installed in subunit 6, and the shallowest wells were installed in subunit 3 (Table 2.5 and median values, Figure 2.1). Wells exceeding 75 feet deep were installed in all subunits except subunits 11 and 12. The box plot (Figure 2.1) was drawn using SYSTAT Version 9 (1998) and shows the distribution of well depth. The bottom of the box shows the 25th percentile. The center of the box shows the 50th percentile or the median. The top of the box shows the 75th percentile. The difference between the 75th percentile and 25th percentile, which is termed the Hspread or interquartile range, is used to define other elements of the box plot.
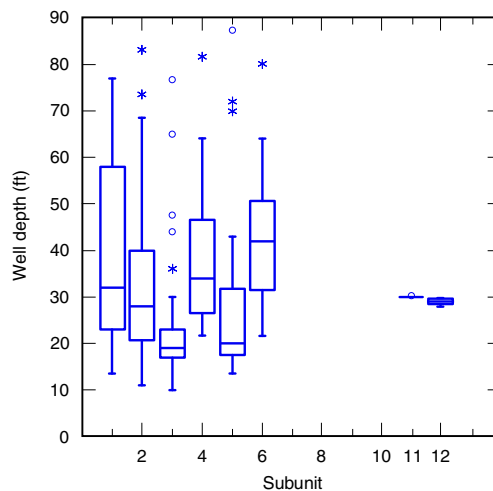

Figure 2.1 *Well depth by subunit for all wells installed through July 2001. *, 1.5 times the H spread (interquartile range); 0, points more than three times the H spread.*

Table 2.5 Well depth by subunit (includes all wells installed by July 2001).

Aquifer sensitivity	Subunit	Depth to uppermost aquifer material (ft)	Well depth (ft)		
			Minimum	Maximum	Median
Excessive	1	<20	13.5	77.0	32.0
	2	<20	11.0	83.0	28.0
High	3	<20	10.0	76.7	19.0
	4	20 to 50	21.6	81.5	34.0
Moderate	5	<20	13.5	87.3	20.0
	6	20 to 50	21.7	80.0	41.9
Very Limited	11	not within 50	30.0	30.2	30.0
	12	not within 50	28.0	29.6	29.0

The "whiskers"—the thin vertical bar extensions—show the range of observed values that fall within 1.5 Hspreads of the box, that is, approximately the 95th percentile (top) and the 5th percentile (bottom). Additional data outside these ranges are shown with asterisks (points between 1.5*Hspread and 3*Hspread) and circles (points > 3*Hspread). All but three wells were completed at depths exceeding 15 feet, so, with the use of 5-foot-long screens, wells were screened at minimum depths of 10 to 15 feet. All wells were completed in the uppermost saturated aquifer materials, except wells built in rotary-drilled boreholes.

Well Depth for Subunits 11 and 12

During July 2000, IDA requested that monitoring wells be placed in areas mapped as having no aquifer materials within 50 feet of land surface in order to examine groundwater quality in hydrogeologic environments where large-diameter bored or hand-dug wells typically are used and to compare pesticide occurrence in large-diameter wells. These monitoring wells were constructed in a manner similar to that for large-diameter wells but without actually increasing the diameter of the monitoring wells. Instead, a longer sand pack was used to ensure collected samples would be similar to those collected from a large-diameter well. All monitoring wells constructed in subunits 11 and 12 were drilled by hollow-stem auger and were completed at a depth of 30 feet. All wells were constructed with 2-inch diameter PVC and were screened at approximate depths of 30 to 25 feet (0.010-inch slot). Each well was packed with 20-40 sand from 30 to 10 feet below the ground surface.

When bedrock was encountered before a depth of 30 feet, an attempt was made to drill to 30 feet. Typical bedrock in the subunit 11 and 12 settings was soft shale, and augering into the upper weathered portions was occasionally possible. Three subunit 11 and 12 wells were installed in bedrock. No well in these subunits was completed at a depth shallower than 28 feet (Table 2.5).

Annular Seal

It was critical that the screened portion of each monitoring well access groundwater from a specific depth interval. Vertical movement or leakage of water down along the well casing can

greatly influence sample quality and must be prevented. Monitoring wells were usually sealed with neat cement grout, dry bentonite (chips, granulated, pelleted, and powdered), or bentonite slurry. Well seals usually occured at two places within the annulus created by the drilling operation. One area was within the saturated zone just above the screened interval to isolate that interval for sampling. The other area was at or near the ground surface to inhibit downward leakage of surface water.

For this project, a bentonite annular seal consisting of either granular bentonite or bentonite chips was placed immediately above the depth of aquifer material collapse within the borehole. The seal had a minimum thickness of 3 feet. Where the top of aquifer material collapsed within 1 foot of the top of the well screen, additional clean sand was placed above the collapsed materials to bring the sand pack at least 2 feet above the top of the screen. The rest of the annulus was backfilled using drill cuttings to within 4 feet of land surface. At this depth, another annular seal consisting of 1 foot of bentonite chips was placed. Additional backfill was placed in the borehole to a depth of approximately 1.5 feet, leaving room for the well cover and surface concrete.

Construction of Monitoring Wells in Bedrock

Whenever possible, holes drilled into bedrock penetrated at least 20 feet into the aquifer formation and were deeper if available information suggested static water levels were deeper. Even though rock holes will stay open without a well screen, bedrock monitoring wells for this project were constructed with 5-foot screens (0.010-inch slot openings). After the casing and screen were placed in the hole, the hole was backflushed by pumping clean water down the casing, out the screen, and up the annulus. Backflushing cleaned drilling mud from the hole before sand pack and annular seals were placed and greatly aided well development. After backflushing, the sand pack was placed from the bottom of the hole to the top of the aquifer, followed by 5 feet of granular bentonite or bentonite chips, followed by drill cuttings to within 10 to 15 feet of land surface. Bentonite was again added to the hole up to 3 feet depth, followed by concrete and the well protector.

Well Security

For most monitoring well installations, precautions were exercised to protect the surface portions of the well from intentional or unintentional damage. Monitoring well installations, especially those placed on highway right-of-ways, seemed particularly vulnerable to impacts from mowers. All wells were constructed flush with the land surface. In this way, the wells were less subject to damage from mowers and farm equipment and did not impede typical planting, cultivation, and harvesting practices along adjacent road right-of-ways. Vandalism of the wells was also a concern. Wells finished at grade are less visible and, thus, less likely to be vandalized. Wells finished at grade were sealed against the entrance of surface water. Detailed well location descriptions were also kept, allowing the well to be found during all seasons, especially during summer when weeds were high and during winter snow cover.

Two levels of protection against water entry were used. A watertight well cover, constructed of 8-inch outside diameter aluminum manhole spot welded to a 12-inch-long sheet metal skirt, was used to divert rainfall and snowmelt off the top of the well. The cast aluminum top was secured with two ¼-inch cap screws and was made watertight with an 8-inch diameter butyl rubber O-ring. The skirt formed the access hole around the top of the well and was placed in a concrete

pad. The concrete pad afforded additional support and security for the cover. The pad was built to be deep enough that frost heave would not dislodge the cover. A watertight, locking well cap was also placed on the top of the 2-inch PVC casing to further prevent entry of water into the well. The locking cap also deterred unauthorized well entry. Steel rebar (usually 30 inches long by ¼ inch diameter) was placed through the concrete in most boreholes to minimize frost heave of the concrete.

Well Development

Well development was necessary to remove finer geologic materials near the borehole and other foreign fluids introduced by the drilling process and to leave behind a "natural" pack of coarser-grained materials. After development, the water produced should be less turbid, and the well should produce water more efficiently. Each well was developed prior to sampling.

Most wells were developed with pressurized air, followed, whenever practical, by pumping with a small-diameter centrifugal pump or bladder pump. If the water column was less than one third to one fourth the total depth, compressed air often did not raise the column of water to the surface. Alternative pumping methods using small-diameter pumps were then employed. Development continued until the water appeared to be free of sediment or until additional development did not improve water clarity.

Documentation of Well Location

Map coordinates were determined for each well by transferring well site locations from paper topographic maps to digitized topographic maps maintained on a GIS server at the ISWS. These digitized topographic maps were accessed through ArcView software. With the proper topographic map on-screen, the cursor was moved to the location marked on the paper topographic map. The X- and Y-coordinates of the cursor were displayed on-screen as the cursor was moved. Once the cursor was properly oriented to point to the well location, the Illinois State Plane coordinates were copied to a spreadsheet containing well identification numbers and coordinates. Well coordinates determined in this way are accurate to approximately 100 to 200 feet, which is sufficient for statewide mapping purposes. An ArcView shapefile containing the X,Y coordinates for each well in State Plane and latitude/longitude coordinates was provided to the IDA.

In 1996, most hand-held GPS units were accurate only to ±300 feet; thus, detailed written descriptions of well locations were considered to be more useful than GPS unit information to field crews trying to find a well. Distances and directions from nearest road intersections and structures as well as telephone and power lines, fence lines, edge of pavement, bridge abutments, etc. were recorded for each well and reported on a well data sheet provided to the IDA.

Recordkeeping

The following information was recorded on the well log and/or the well construction record:

> well identification number
>
> well location
>
> date and time drilling started

staff present during construction

general weather conditions

notes on split-spoon analyses

names of staff drilling and logging samples

depth at which aquifer materials were first encountered

total depth of drilled hole

total depth of well

casing length and screened interval

depth of collapse of aquifer materials within borehole

depth of placement and thickness of annular seals and sand packs

development procedures followed, including lengths of time of air injection and water pumping

relative clarity of water when development terminated

any unusual or extenuating circumstances encountered during drilling or well construction

CHAPTER 3. WELL SAMPLING

Sampling Procedures

The ISGS and ISWS were responsible for developing sampling protocols, collecting samples from the monitoring wells, and transporting samples to the IDA analytical laboratory in Springfield. Protocols were used to ensure that high-quality samples were consistently collected. These protocols principally addressed the process and materials used to collect samples from the monitoring wells and to transport the samples to the analytical laboratory.

Pumping Equipment and Well Purging

Groundwater samples were collected using a peristaltic pump when the water levels in the monitoring wells were at depths less than approximately 27 feet, which is the lifting capacity of a peristaltic pump. Samples were collected by bladder pump if the water levels were deeper.

The peristaltic pump was fitted with ¼-inch low density polyethylene (LDPE) and silicon tubing. The LDPE tubing was dedicated to each well and was left in the well after sampling was completed. The LDPE tubing was cut to reach from the middle of the well screen to the top of the monitoring well. Approximately 2 feet of silicone tubing was needed for pump operations and making connections. The silicon tubing was not changed after sampling but was rinsed with deionized distilled water after each well was sampled.

The bladder pump was constructed of stainless steel and had a Viton bladder. The pump was rinsed with deionized distilled water after each use. The LDPE discharge tubing was used with this pump. For the one-time sampling program, the tubing was not dedicated to a single well, but was used once and returned to the lab where it was washed and rinsed. For the time-series sampling program, tubing was dedicated to a single well, but not stored in the well. After each use, the tubing was returned to the lab, washed, and rinsed. The inside of the LDPE tubing was rinsed with tap water and flushed with filtered, compressed air (building source). The outside of the tubing was washed with tap water and Alconox and then rinsed with tap water. The inside and outside of the tubing were then rinsed with deionized distilled water and flushed with filtered, compressed air. After air-drying, the tubing was stored and transported in clean garbage bags.

Each well was purged prior to sample collection. During well purging, the water was pumped into a flow-through cell equipped with electrodes to measure pH, specific conductance, temperature, redox potential, and dissolved oxygen. These water-quality parameters were monitored at 3-minute intervals. Well purging was complete when all of the water-quality parameters stabilized (when a water-quality parameter changed less than 5% over a 3-minute interval). The stabilized water-quality parameter values and sampling date were recorded and entered into the project database.

For wells that did not produce much water (i.e., the well could be pumped dry or nearly so), two strategies were adopted to ensure collection of representative samples. One strategy was to collect a sample without measuring field parameters after the water level in the well recovered from purging. Another strategy was to collect a sample after very limited purging and then to measure field parameters.

Quality Assurance and Quality Control Samples

For each sampling event, approximately 15% of the samples were collected and analyzed for quality assurance and quality control (QA/QC) purposes. These QA/QC samples were duplicates (10%) and field blanks (5%). Duplicate samples were collected simultaneously with the regular samples. Field blanks of deionized distilled water were handled identically and under the same conditions as regular samples. The IDA supplied the deionized distilled water used for blanks. The QA/QC samples were randomly assigned to the sampled wells by IDA using software described by Mehnert (1992).

Sample Volume and Preservatives

For the pesticide samples to be analyzed using U.S. Environmental Protection Agency (USEPA, 2000) method 525.2, 1,000-mL clear glass bottles with Teflon-lined caps were used. For the cation and anion samples, a single 250-mL polyethylene bottle was used. No preservatives were used. The samples were not filtered in the field.

Sample Storage and Transport

All samples were stored on ice at approximately 4°C immediately after collection and returned to the IDA analytical laboratory within 48 hours. The IDA supplied insulated boxes for sample transportation.

Identification of Sample Bottles

All sample bottles were labeled in a waterproof fashion. The labels listed the project name, randomized sample number, and analytical method.

Use, Calibration, and Maintenance of Sampling Equipment

All purging parameter electrodes were calibrated at the beginning of each sampling trip. The flow-through cell and tubing used for sampling were drained after each well was sampled. Manufacturer's instructions were followed for storage and maintenance of the electrodes and meters. Maintenance of the electrodes and meters was completed at least every 6 months.

Sampling Steps

These procedures were followed when sampling each well:

1. Open well cover and locking cap.

2. Measure depth to water and record in field book.

3. From depth-to-water measurement, determine appropriate pump to use and assemble. For a well that has not been previously sampled by peristaltic pump, insert new LDPE tubing into well until end of tubing reaches the well bottom and cut tubing. If bladder pump is to be used, attach discharge tubing to pump, lower pump to bottom of well, and then pull tubing up approximately 2 to 3 feet so pump intake is opposite the midpoint of the screen.

4. Connect discharge tubing to flow-through cell, activate cell electrodes, and commence pumping.

5. Monitor purging parameters until stabilized and record stabilized values in a field book.

6. When the well is properly purged, disconnect discharge tubing from flow-through cell and collect samples in appropriate bottles.

7. When the sample bottles are full, return bottles to coolers for storage and cover with ice.

8. Break down equipment, lock well cap, screw down well cover, and move to next well site.

9. Complete chain-of-custody form for collected samples.

Sampling Programs and Schedule

Groundwater samples were collected under two sampling programs. One sampling program involved collecting samples from a set of wells and was called the one-time sampling program. Samples from the one-time sampling program provided data primarily on the occurrence of pesticides across the 6 subunits. The second sampling program involved repeated sampling from the same wells and was called the time-series sampling program. Samples from the time-series wells primarily provided data on the temporal variation of pesticide occurrence.

One-Time Sampling Program

The original plan for the one-time sampling program called for collecting samples from a total of 208 wells from September 1998 through February 2001. Because of changes in the plan over time, samples were collected from 166 different wells. Four of these samples were not analyzed because of instrument problems, and 3 samples were collected from wells in subunits 11 (1 sample) and 12 (2 samples) were not considered, leaving 159 samples from wells in subunits 1 through 6 available for data analysis. These samples were collected and delivered to the IDA laboratory for analysis. Samples were collected according to the following schedule: 10 samples per month from September 1998 through August 1999, 4 per month from September 1999 through June 2000, 0 in July and August 2000, and 8 per month from September 2000 through February 2001.

So that interim analytical results could be examined across all map units and temporal bias could be avoided, an equal number of wells were sampled across the map units every 3 months. Also, to avoid potential seasonal impacts on water quality variations, monthly sampling trips were scheduled to collect samples from different regions of the state during this 3-month period (e.g., not all sampling trips within a 3-month period were in northern Illinois).

Time-Series Sampling Program

From October 1997 through February 2001, a total of 232 samples were to be collected as part of the time-series sampling program. From October 1997 through July 2000, 6 wells were sampled on a monthly basis, and 4 wells were sampled monthly from August 2000 to February 2001. Fourteen samples could not be collected because the samplers could not find some wells during early sampling trips, because the ground was covered with snow or the wells were dry. A total

of 218 samples were collected from 21 wells and delivered to the IDA laboratory for analysis. Because 1 sample was not analyzed by the laboratory and 2 samples failed surrogate and internal standards tests, data from 215 samples only were available for data analysis.

From October 1997 through June 1999, 3 wells from subunit 1 (1-5-361, 1-7-278, 1-14-251) and 3 wells from subunit 6 (6-45-921, 6-76-1027, 6-89-1091) were sampled monthly. From July 1999 through July 2000, the wells in the time-series program were expanded to 18 wells, including wells from all subunits. These wells were sampled quarterly (6 per month) and included 3 subunit 1 wells (1-4-267, 1-7-278, 1-14-251), 5 subunit 2 wells (2-20-670, 2-21-653, 2-26-746, 2-32-659, 2-52-1792), 4 subunit 3 wells (3-27-1560, 3-44-2013, 3-49-2838, 3-50-3731), 2 subunit 4 wells (4-8-5, 4-20-7), 2 subunit 5 wells (5-4-1583, 5-26-1411), and 2 subunit 6 wells (6-45-921, 6-89-1091). From August 2000 through June 2001, the number of wells samples was reduced from 6 to 4 wells per month to reduce the load on the IDA laboratory. The revised list of wells included 2 subunit 1 wells (1-4-267, 1-14-251), 2 subunit 2 wells (2-21-653, 2-32-659), 3 subunit 3 wells (3-27-1560, 3-49-2838), 2 subunit 4 wells (4-8-5, 4-20-7), 1 subunit 5 well (5-4-1583), and 2 subunit 6 wells (6-45-921, 6-89-1091).

The wells sampled for the time-series program were not randomly selected. Originally, wells from subunits 1 and 6 were chosen. Only wells near Springfield (Logan, Mason, Sangamon, and Tazewell Counties), the location of the IDA laboratory, were selected to allow samples to be collected and delivered to the laboratory in a single day. During July 1999, the time-series sampling program was modified to include wells from all subunits. Three factors were considered for selecting these wells—a pesticide detection in the one-time sampling program, a convenient location, and a previous sample in the time-series sampling program.

CHAPTER 4. CHEMICAL METHODS

Analytes and Field Parameters

Chemical analyses were conducted in the field, at the IDA laboratory in Springfield, and at the ISGS Isotope Geochemistry Laboratory. In the field, the temperature, pH, specific conductivity, dissolved oxygen, and redox potential of the groundwater were determined prior to sampling as discussed in Chapter 3.

The IDA Pesticide Laboratory in Springfield, under the direction of Dr. Walter F. Black, determined the concentrations of the organic and inorganic analytes listed in Table 4.1. The five herbicides atrazine, cyanazine, simazine, alachlor, and metolachlor were included because in the mid-1990s the USEPA considered having the states develop compound-specific pesticide management plans for these herbicides. Other herbicides that could be determined using the same chemical method are also included. The ISGS, ISWS, and IDA discussed including herbicide degradates as in previous studies in Illinois (Goetsch et al., 1992; Schock et al., 1992; Groschen et al., 2000) and in other midwestern states (Kross et al., 1990; Kolpin et al., 1995; Barbash et al., 2001), but IDA declined to include pesticide degradates in the list of analytes.

Table 4.1 Method detection limits (MDLs) for the organic analytes.

Analyte	Organic MDLs (µg/L) and their effective dates	
	10/22/97 through 10/08/99	11/10/99 through 02/09/01
Alachlor	0.13	0.152
Acetochlor	0.12	0.151
Atrazine	0.027	0.038
Bromacil	0.14	0.13
Butylate	0.041	0.052
Chlorpropham	0.18	0.188
Cyanazine	0.079	0.081
EPTC	0.014	0.052
Ethoprop	0.024	0.032
Metolachlor	0.21	0.222
Metribuzin	0.020	0.025
Prometon	0.044	0.047
Simazine	0.030	0.038
Vernolate	0.041	0.051

Common anions and cations were included as analytes to provide some basic geochemical data for the groundwater samples. Hamilton and Helsel (1995) suggested that studies of groundwater quality conducted in agricultural areas should include inorganic constituents that may be found in fertilizers. For example, potash fertilizers are a source of potassium and chloride, and lime fertilizers are a source of calcium and magnesium (Böhlke, 2002).

A limited number of samples (6 wells and a nearby surface water body) were collected and analyzed for tritium. These samples were analyzed by the ISGS Isotope Geochemistry Section.

Chemical Methods

Method for Organics

The organic analytes were determined using a modification of USEPA method 525.2 (Munch, 1995). Some modifications were adopted from Krigbaum (1997). Method 525.2 is a general purpose method for determining organic compounds in water and is applicable to a wide range of organic compounds that are efficiently partitioned from the water to an extraction matrix and sufficiently volatile and thermally stable for gas chromatography (Munch, 1995).

Munch (1995) summarized method 525.2 as follows:

> Organic compound analytes, internal standards, and surrogates are extracted from a water sample by passing 1 L of sample water through a disk containing a solid matrix with a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The organic compounds are eluted from the LSE disk with small quantities of ethyl acetate followed by methylene chloride, and this extract is concentrated further by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high resolution fused silica capillary column of a gas chromatography/mass spectrometry (GC/MS) system. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in the database. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as the internal standard. Surrogate analytes, the concentrations [of which] are known in every sample, are measured with the same internal standard calibration procedure.

IDA prepared the organic samples as follows:

1. Nine 1-L samples of distilled deionized water were prepared. One sample served as the control.

2. Five milliliters of methanol were added to each sample, and each sample was shaken.

3. To each of 8 samples was added 0.1 mL of 101196 WKGA (a laboratory-prepared solution). All 8 samples were augmented with 50 µL of 100996 WKGB (another laboratory-prepared solution). All were shaken well. Note that 101196 WKGA designated the first analytical standard solution made on 10/11/96, and 100996 WKGB designated the second analytical standard solution made on 10/09/96.

4. To each sample, 100 g of NaCl and 50 mL of phosphate buffer (as described in method 525.2) were added. The samples were shaken until the salt was dissolved.

5. The samples were extracted using the Zymark autotrace with a 47-mm C_{18} solid-phase extraction disk.

To determine the concentrations, the following steps were taken:

1. Three grams of sodium sulfate were added to the extracts and vortexed.

2. The samples were transferred to 15-mL centrifuge tubes, and approximately 5 mL of ethyl

acetate were added to the original samples tubes and vortexed. The remainder of the rinse was transferred to the 15-mL centrifuge tube.

3. The samples were concentrated to 1.5 mL using an N-EVAP (nitrogen blowdown apparatus for concentrating samples), brought to 5 mL with ethyl acetate, and concentrated a second time to 1.5 mL.

4. The samples were augmented with 50 μL of 100996 WKGA and brought to a final volume of 5 mL.

5. The samples (2 μL each) were injected into a Hewlett-Packard 6890 Series II gas chromatograph with a nitrogen-phosphorus detector. ChemStation software was used to analyze and interpret gas chromatographic peaks.

The method detection limit was determined by running and analyzing a series of augmented samples according to a USEPA method to determine the lowest concentration of the pesticide that could be consistently and reliably measured on a given instrument. The augmented samples contained the pesticide being tested at a known concentration and went through the entire extraction process in the same way as standard samples. The method detection limit for the pesticides (Table 4.1) was determined based on the standard deviation of 8 pesticide-augmented samples and the Student's t value for a 99% confidence interval and 7 degrees of freedom.

Method for Anion and Cation Determination

The anionic analytes were determined using an ion chromatograph (Dionex model DX-120) with a Dionex AS14A column and an ASRS Ultra suppressor. Prior to November 1999, cation concentrations were determined using a Shimadzu HPLC with SIL-6B autosampler, LC-6A pump, and Alltech 320 conductivity detector with 335 suppressor module. HP ChemStation software was used to determine concentrations from the Shimadzu HPLC. Since November 1999, the cationic analytes have been determined using an ion chromatograph (Dionex model DX-120) with a Dionex CS12A column and a CSRS Ultra suppressor. Anion and cation concentrations were determined using PeakNet software.

The minimum reporting limits (Table 4.2) were determined based on instrument detection limits, which were defined by a signal-to-noise ratio of 3:1 for a given standard.

Method for Tritium Analyses

For tritium analyses, water samples were collected in 1-L high-density polyethylene (HDPE) bottles. Tritium was determined with 200 mL of water using the enrichment technique (Ostlund and Dorsey, 1977). The tritium enriched samples were purified by vacuum distillation, mixed with a scintillation cocktail, and counted in a low-level scintillation counter (Packard 2000 CA/ LL). The tritium results were reported in tritium units (TU), which is defined as one tritium atom per 10^{18} hydrogen atoms.

Extremely low tritium concentrations were reported as less than some minimum reporting value (e.g., <0.5 TU). This minimum reporting value was set at 2.5 times the laboratory average standard deviation for low concentration samples. The standard deviation was computed from tritium activities counted over fifteen 100-minute intervals.

Table 4.2 Minimum reporting limits (MRLs) for the inorganic analytes.

Analyte	Inorganic MRLs (mg/L)			
	Minimum	Median	Maximum	Final
Bromide	0.28	1.3	3.2	3.0
Calcium	0.43	1.9	2.6	2.5
Chloride	0.20	1.4	3.1	3.0
Fluoride	0.15	0.76	1.6	1.5
Magnesium	0.43	1.9	2.5	2.5
Nitrate-nitrogen	0.090	0.23	2.24	0.68
Nitrite-nitrogen	0.12	0.72	0.94	0.91
Phosphate	0.17	0.93	4.7	1.47
Potassium	0.40	2.4	2.6	2.5
Sulfate	0.21	1.9	4.7	4.5

Reporting Limits for the Analytes

The method detection limits for the organic analytes are listed in Table 4.1. The method detection limits for the organic analytes changed after the IDA switched their extraction technique. The inorganic minimum reporting limits are listed in Table 4.2. The minimum reporting limits for the inorganic analytes changed because different laboratory equipment was used.

CHAPTER 5. INITIAL SAMPLING RESULTS AND DISCUSSION

The project results are presented and discussed in the following order—wells sampled, pesticides from the one-time sampling program, pesticides from the time-series sampling program, neural network analysis of the pesticide data from the one-time sampling, anions and cations from the one-time sampling program, and anions and cations from the time-series sampling program.

One well from subunit 11 and 2 wells from subunit 12 were sampled as part of the one-time sampling program. For samples from these 3 wells, no pesticides were detected, and nitrate-nitrogen was less than the method detection limit. The following discussion focuses on samples from wells completed in subunits 1 through 6.

Wells Sampled

One-Time Sampling Program

The 159 wells sampled in this program ranged in depth from 10.3 to 87.3 feet; mean depth was 32.7 feet, and median depth was 25.0 feet. The well depth for each subunit was quite variable (Figure 5.1). These box plots, drawn using SYSTAT Version 9 (1998), show the distribution of well depth. Wells from subunits 3 and 5 have lower medians and less variability than the other four subunits. The depth to water in the well at sampling ranged from 0 (water flowing from the well) to 64.9 feet; mean was 15.2 feet; and median was 10.2 feet. The depth to water for each subunit (Figure 5.2) has a lower median and similar distribution to well depth (Figure 5.1). The depth to water was collected from 156 of the 159 sampled wells.
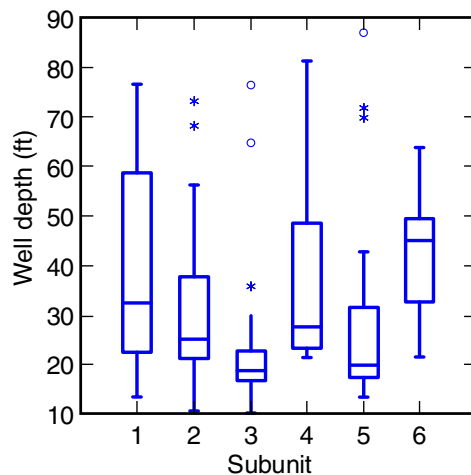

Figure 5.1 *Well depth for wells from the one-time sampling program.*

Time-Series Sampling Program

Time-series samples were collected from 21 wells. The depth of these wells ranged from 13.5 to 80.0 feet; mean was 31.8 feet, and median was 23.5 feet. Well depth is quite variable (Figure 5.3).

Some subunits have a very narrow range of well depth. The well depth in this sampling program is much less variable than the depth of wells in the one-time sampling program (Figure 5.1), most likely due to the lower number of wells sampled (21 vs. 159 wells). The depth to water was available for 205 of these samples. The depth to water ranged from 2.0 to 66.5 feet; mean is 20.5 feet, and median is 15.9 feet. The variability in the depth to water by subunit is shown in Figure 5.4. Many differences in the depth to water can be observed between the time-series wells and the one-time wells. The depth to water from both sampling programs have a similar range, but the mean and median depth to water for the time-series samples are approximately 5 feet deeper than the depth to water for the one-time samples. For the time-series samples, the depth to water for subunits 1, 2, and 4) has less variability than the one-time samples, and subunit 6 has greater variability.
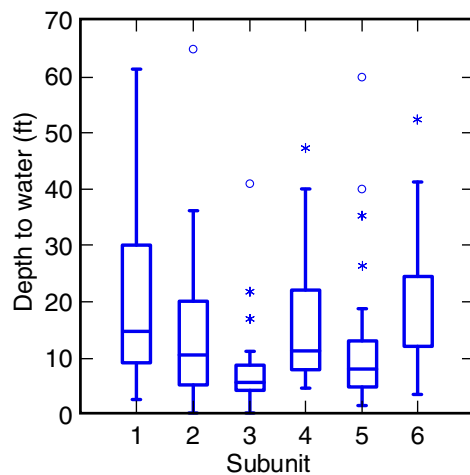

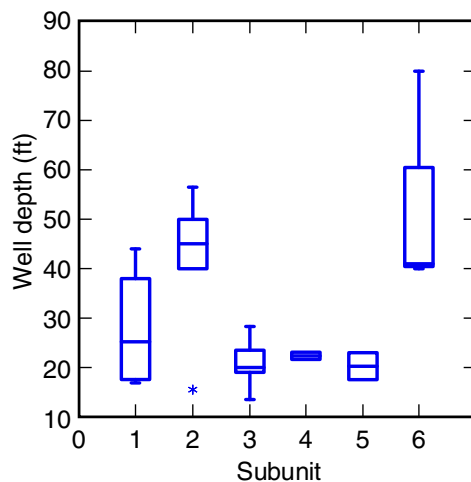**Figure 5.2** *Depth to water on sampling date for wells from the one-time sampling program.*

Figure 5.3 *Well depth for wells from the time-series sampling program.*
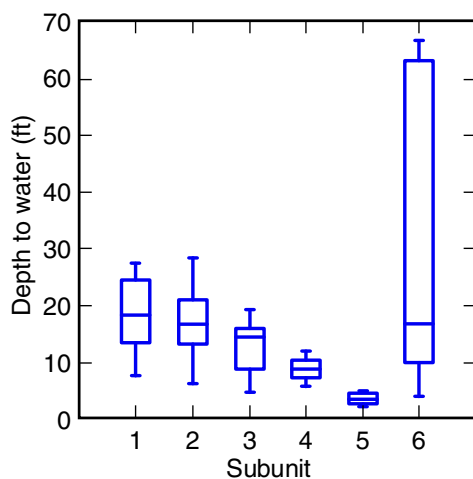
Figure 5.4 *Depth to water on the sampling date in the time-series samples by subunit.*

One-Time Sampling Program—Pesticides

The following discussion focuses on the pesticides detected and the distribution of these pesticides across the six subunits and over time. Pesticide detection is defined as a pesticide concentration exceeding its method detection limit on the date analyzed. The method detection limits for the organic analytes varied slightly during the course of the project (Table 4.1).

Pesticides Detected

Alachlor, chlorpropham, ethoprop, EPTC (S-ethyl dipropylthiocarbamate), prometon, and vernolate were not detected in any sample. The following pesticides were detected in one or more samples: acetochlor, atrazine, bromacil, butylate, cyanazine, metolachlor, metribuzin, and simazine. Atrazine was the most commonly detected pesticide and was detected in 23 of the 159 samples (Table 5.1). Mean concentration was 0.63 µg/L, and median concentration was 0.11 µg/L. Bromacil and metolachlor were the second most commonly detected pesticides (3 of 159 samples). Bromacil concentrations ranged from 1.05 to 2.49 µg/L. Metolachlor concentrations ranged from 0.57 to 3.30 µg/L. As shown in Table 5.1, most pesticides were detected at low concentrations (1 µg/L). Only atrazine was detected at or above its federal drinking water standard. Atrazine exceeded its maximum contaminant level (MCL) in a single sample.

These results are similar to the results of other studies conducted in the Midwest. For example, atrazine, cyanazine, and metolachlor were detected in groundwater samples collected by the USGS in its study of the lower Illinois River basin (Groschen et al., 2000), but no pesticide was detected above its federal drinking water standard. In addition, acetochlor, bromacil, butylate, simazine, and metribuzin were not detected above the common detection limit of 0.05 µg/L in the USGS samples. The USGS also detected acetochlor, atrazine, bromacil, butylate, imazaquin, MCPA ((4-chloro-2-methyl)phenoxy acetic acid), metolachlor, oryzalin, prometon, terbacil, and triclopyr when it sampled monitoring wells and domestic wells in the upper Illinois River basin (Morrow, 2003). Again, none of these pesticides was detected above the federal drinking water standard. Kolpin et al. (1995) also reported that no pesticides were detected above its federal drinking water standard in a sample of 303 midwestern wells. From its National Water

Quality Assessment studies, the USGS (Kolpin et al., 1998) reported that atrazine, simazine, and metolachlor were the three most frequently detected pesticides, and only atrazine was detected at a concentration exceeding an MCL. Because the wells we sampled were assumed to be located much closer to agricultural production fields than the water-supply wells sampled by others, we expected our results to show higher concentrations.

Table 5.1 Pesticides detected in the one-time sampling program.

Analyte	Detects	Maximum concentration (µg/L)	Date and subunit of maximum concentration		Federal drinking water standard[*] (µg/L)
			Date	Subunit	
Acetochlor	1	0.032	Apr 1999	5	0
Atrazine	23	7.54[**]	Oct 1998	4	MCL = 3.0
Bromacil	3	2.49	Mar 2000	5	HA = 90
Butylate	2	0.44	Mar 2000	1	HA = 400
Cyanazine	1	0.43	Jun 2000	5	HA = 1.0
Metolachlor	3	3.3	Sep 1998	3	HA = 100
Metribuzin	1	0.13	Jun 2000	5	HA = 200
Simazine	1	0.054	Jan 1999	6	MCL = 4.0

*USEPA (2000) lists the maximum contaminant level (MCL) and lifetime health advisory (HA) for these compounds.
**Atrazine exceeded the MCL in one sample.

Atrazine was detected in samples from all subunits. All other pesticides were detected in three or fewer subunits (Table 5.2). Six different pesticides were detected in subunit 5, and three or fewer were detected in the other subunits. The samples with maximum pesticide concentrations were most commonly collected from subunit 5 wells (Table 5.1), which suggested that this subunit may be susceptible to contamination at higher concentrations and by a wider variety of pesticides. No temporal correlation was evident for the samples that had maximum concentrations (Table 5.1) or with the maximum number of pesticide occurrences (Table 5.2).

Table 5.2 Pesticides detected in the one-time sampling program by subunit.

Subunit	Maximum pesticides detected in a single sample (no.)	Sampling date that maximum number of pesticides were detected	Pesticides detected
1	2	Mar 2000	atrazine, bromacil, butylate
2	1	Jun 1999	atrazine
3	2	Aug 1999	atrazine, bromacil, metolachlor
4	2	Oct 1998	atrazine, metolachlor
5	3	Jun 2000	acetochlor, atrazine, bromacil, butylate, cyanazine, metribuzin
6	2	Jan 1999	atrazine, simazine

For the one-time sampling program, pesticides were detected in 28 of the 159 (18%) samples. These pesticide occurrences varied by map subunit (Table 5.3). A primary project goal was to determine if map subunits could be used to predict the occurrence of pesticides in shallow groundwater. Contingency table analysis (CTA) allowed the association between two categorical variables (Helsel and Hirsch, 1993) to be measured. Using subunit number and pesticide occurrence as an example, CTA allowed us to determine whether the column (e.g., pesticide occurrence) and row classifications (e.g., subunit) were independent. The null hypothesis was that two variables were independent; the alternate hypothesis was that the variables were dependent or related. Two statistics were involved in hypothesis testing, the significance (α-level) and the p-value. The null hypothesis was rejected when the p-value was less than the α-level. The null hypothesis was never "accepted" or proven to be true; instead, the null hypothesis was assumed to be true until proven otherwise (Helsel and Hirsch, 1993). The α-level was defined as the probability of incorrectly rejecting the null hypothesis and was determined by the analyst. Helsel and Hirsch (1993) noted that "statistical tradition uses a default of 5% for α." The p-value was the probability of obtaining the computed test statistic, or one even less likely, when the null hypothesis was true. The p-value also concisely expressed the evidence against the null hypothesis that was contained in the data. The smaller the p-value, the stronger the evidence for rejecting the null hypothesis (Helsel and Hirsch, 1993).

Table 5.3 Distribution of pesticide occurrences by subunit for the one-time sampling program.

Map unit	Subunit	Occurrences (no.)	Sample (no.)	Occurrence (%)	Occurrence (%)
Excessive	1	5	28	18	20
	2	6	27	22	
High	3	7	34	21	15
	4	1	18	6	
Moderate	5	7	29	24	17
	6	2	23	9	
	Total	28	159	18	18

Based on CTA, the percent occurrence reported in Table 5.3 was not dependent on the six subunits at an α-level of 5% ($p = 0.46$); that is, the six mapping subunits could be used to predict the occurrence of pesticides in the one-time samples. In addition, the percent occurrence was not dependent on the three map units, as reported in Table 5.3 ($p = 0.75$).

When designing the monitoring well network, a major factor in determining the number of wells per map unit was the percent occurrence expected for each map unit. During the network design, we assumed a 15% occurrence for the Excessive map unit, 10% occurrence for the High map unit, and 3% occurrence for the Moderate map unit. As shown in Table 5.3, the actual percent occurrence was higher and more consistent between map units than the percent occurrence used to design this network.

The differences in pesticide occurrence between subunits 3 and 4 ($p = 0.16$) and between subunits 5 and 6 ($p = 0.15$) were noticeable, but were not statistically significant per CTA. However, if additional samples were collected and the percent occurrence remained constant, then these differences would be statistically significant ($p = 0.05$). A total of 95 wells or 43 additional wells from subunits 5 and 6 and a total of 130 wells from subunits 3 and 4 would need to be sampled.

The high number of different pesticides detected (Table 5.2) and the relatively higher pesticide occurrence in subunit 5 (Table 5.3) might be because subunit 5 included more wells in lowland settings and/or because well depth for subunit 5 wells was relatively shallow (Figure 5.1). To evaluate the effect of geographic setting on pesticide occurrence, the well locations were plotted with respect to the 100-year floodplain. The hypothesis was that surface runoff would transport pesticides downgradient; thus, a greater variety of pesticides might be present in lowland settings than in other settings. The GIS coverages of the 100-year floodplains for each county were obtained from the ISWS and joined into a statewide coverage. No wells were installed within the 100-year floodplain, but 4 wells (2-35-1085, 3-55-1947, 3-64-2902, 5-7-3799) were within 100 feet, and 6 wells (1-11-512, 1-24-65, 1-33-269, 2-49-1211, 3-19-1484, 6-104-1522) were within 500 feet of this floodplain. No pesticides were detected in samples from these wells; thus, proximity to the 100-year floodplain does not appear to explain the occurrence of pesticides observed in subunit 5 wells.

Because pesticides are applied to the land surface, it seems logical that they would be detected more frequently in shallower wells such as those in subunits 3 and 5 (Figure 2.1 and Table 2.5). Conversely, low pesticide occurrence might be expected for subunit 6 wells because these were the deepest wells in the study (median, 42 feet). To test whether several independent samples were from the same population, we used the Kruskal-Wallis test, a nonparametric test equivalent to one-way ANOVA (SYSTAT, 1998). This test assumed that the underlying variable (e.g., well depth) had a continuous distribution and required an ordinal level of measurement. For the Kruskal-Wallis test, the general null (H_0) and alternate (H_1) hypotheses (Helsel and Hirsch, 1993) were defined such that for H_0 all groups had identical distributions and for H_1 at least one group differs in its distribution.

Based on the Kruskal-Wallis test, the distribution of well depth for wells with and without a pesticide occurrence were similar for all wells ($p = 0.99$) and for the wells in each subunit ($p > 0.08$). Thus, well depth did not explain differences in pesticide occurrence in subunit 5 or other wells. The pesticide occurrence data for the subunit 5 wells may indicate that more than one mechanism controls the transport of pesticides in the subsurface.

The data in Table 5.3 can be reorganized based on depth to uppermost aquifer material (Table 5.4). Subunits 1, 2, 3, and 5 are map subunits with the depth to uppermost aquifer materials of less than 20 feet; subunits 4 and 6 are map subunits with the depth to uppermost aquifer materials of 20 to 50 feet. The percent occurrence is more than three times higher for samples from areas with a depth to uppermost aquifer material of less than 20 feet than in samples from areas with a depth to uppermost aquifer material of 20 to 50 feet. This difference in pesticide occurrence is statistically significant (p = 0.05) using CTA. Schock et al. (1992) showed that pesticide occurrence in drilled wells was more likely in areas where the depth to uppermost aquifer material was ≤ 50 feet than in areas where the depth to uppermost aquifer material was >50 feet. The occurrence data in Table 5.4 extend the utility of the mapping concept to shallower depths.

Table 5.4 Distribution of pesticide occurrences by depth to uppermost aquifer material for the one-time sampling program.

Depth to uppermost aquifer material (ft)	Subunits	Occurrence (no.)	Sample (no.)	Occurrence (%)
<20	1, 2, 3, 5	25	118	21
20 to 50	4, 6	3	41	7
Total		28	159	18

Ray and Schock (1996) described the problems in comparing different studies of pesticide occurrence in groundwater. One example that these authors described was the difference in definitions used by each project. Schock et al. (1992) defined "occurrence" as the presence of one or more pesticides above some minimum concentration or nitrate-nitrogen above 10 mg/L. To compare our results with those of Schock et al. (1992), we adopted their definition and observed that the number of occurrences for all subunits increased from 18% to 33% (Tables 5.5 and 5.6). This increase in occurrence was fairly consistent across the subunits. Based on CTA, the percent occurrence reported in Table 5.5 was dependent on the six subunits ($p = 0.05$); that is, the six mapping subunits can be used to predict the occurrence in the one-time samples. Similarly, the percent occurrence reported in Table 5.6 was dependent on the two levels of depth to uppermost aquifer material $(p < 0.005)$.

The problems involved in comparing different studies, described by Ray and Schock (1996), are illustrated in Tables 5.3 and 5.5. The occurrences reported in Tables 5.5 and 5.6 could have been much higher because nitrate data were not available (i.e., the lab did not report nitrate concentrations) for 16 of 106 samples that did not have an occurrence of a pesticide. Had nitrate data been available for all samples, the occurrence reported in Tables 5.5 and 5.6 would likely have been higher.

Table 5.5 Distribution of occurrences as defined by Schock et al. (1992) (pesticide occurrence or nitrate-nitrogen >10 mg/L) by subunit for the one-time sampling program.

Map unit	Subunit	Occurrences (no.)	Samples (no.)	Occurrence (%)	Occurrence (%)
Excessive	1	12	28	43	40
Excessive	2	10	27	37	40
High	3	14	34	41	31
High	4	2	18	11	31
Moderate	5	11	29	38	27
Moderate	6	3	23	13	27
	Total	52	159	33	33

Table 5.6 Distribution of occurrences as defined by Schock et al. (1992) (pesticide occurrence or nitrate-nitrogen >10 mg/L) by depth to uppermost aquifer material for the one-time sampling program.

Depth to uppermost aquifer material (ft)	Occurrences (no.)	Samples (no.)	Occurrence (%)	Occurrence* (%)
< 20	47	118	40	30
20 to 50	5	41	12	8
Total	52	159	33	23

*From Schock et al. (1992).

Temporal Distribution of Samples and Pesticide Occurrences

Pesticides are not applied uniformly throughout the year, which suggested that pesticide occurrence in shallow wells would not be uniform over time either. Samples were collected according to the following schedule: 10 samples per month from September 1998 through August 1999, 4 samples per month from September 1999 through June 2000, and 8 samples per month from August 2000 through June 2001. The number of samples for July and August were lower than the number of samples for other months (Table 5.7). The occurrence of pesticides also was not evenly distributed over time for samples from the one-time sampling program. The temporal distribution of pesticide occurrence was analyzed on a calendar basis and a serial basis. To statistically evaluate the existence of a temporal trend in pesticide occurrence, the samples were grouped on a calendar basis as follows:

time frame 1: February, March, and April;

time frame 2: May, June, and July;

time frame 3: August, September, October; and

time frame 4: November, December, and January.

Pesticide occurrence was higher in time frames 2 and 3, and the lowest pesticide occurrence was observed in time frame 4. Pesticide occurrence was shown to be dependent on these four time frames by CTA ($p = 0.025$). This temporal dependence of samples from all subunits is even stronger ($p < 0.001$) if the samples are grouped into post-application (June through October) and other periods (November through May); occurrence is 31% vs. 10%, respectively.

Pesticide occurrence also was shown by CTA to be dependent on these four time frames for samples from subunits 1, 2, 3, and 5 ($p = 0.02$), but not for samples collected from subunits 4 and 6 ($p > 0.50$). As discussed previously, subunits 1, 2, 3, and 5 include areas where the depth to the uppermost aquifer material is less than 20 feet, whereas subunits 4 and 6 include areas where the depth to the uppermost aquifer material is 20 to 50 feet. It seems reasonable that pesticide occurrence would have greater temporal variability in areas where the top of aquifer materials are shallower.

Table 5.7 Temporal distribution of pesticide occurrences from the one-time sampling program.

Month	Occurrences (no.)	Samples (no.)	Occurrence (%)
January	1	16	6
February	1	16	6
March	2	14	14
April	3	14	21
May	2	14	14
June	6	14	43
July	2	10	20
August	2	6	33
September	5	14	36
October	3	14	21
November	1	14	7
December	0	13	0
Total	28	159	18

This temporal variation in pesticide occurrence *may* be explained by the immediate flushing of spring-applied pesticides by post-application precipitation. Transport via macropores through the vadose zone (zone of aeration) and saturated zone may explain this rapid contaminant transport. An alternate hypothesis involves pulsed transport, where surface-applied chemicals move deeper into the subsurface during periods of higher infiltration, when evapotranspiration is lowest (generally late fall through early spring). Transport over longer distances, down to the depths of the project's well screens, may require many periods of higher infiltration.

Data for pesticide occurrence, atrazine concentration, and nitrate-nitrogen were also analyzed to detect trends over the duration of the one-time sampling program (September 1998 through February 2001). We used a nonparametric technique, the Mann-Kendall test, which is suitable for binary and censored data (Gilbert, 1987). Software for the Mann-Kendall test, described by Libiseller and Grimvall (2002), was used. Assuming $\alpha < 0.05$, the Mann-Kendall test indicated that a monotonic or linear trend was not present in the pesticide occurrence data ($p = 0.32$), atrazine concentration ($p = 0.71$), or nitrate-nitrogen concentration ($p = 0.68$) for the one-time sampling program.

Time-Series Sampling Program—Pesticides

Pesticides Detected

Acetochlor, alachlor, chlorpropham, cyanazine, ethoprop, EPTC (S-ethyl dipropylthiocarbamate), metribuzin, prometon, simazine, and vernolate were not detected in any time-series sample. Atrazine, bromacil, butylate, and metolachlor were detected in one or more samples. Atrazine was the most commonly detected pesticide and was detected in 26 of the 215 samples (Table 5.8).

The mean and median concentrations of atrazine in these samples were 0.20 µg/L and 0.15 µg/L, respectively. Metolachlor was the second most commonly detected pesticide and was detected in 7 of 215 samples. Most pesticides were detected at low concentrations (≤1 µg/L), and no pesticide was detected at or above its federal drinking water standard.

Pesticide occurrence was found in 34 of the 215 (16%) samples. The percent occurrence was slightly lower in the time-series program than in the one-time sampling program. In addition, fewer pesticides were detected, most at lower maximum concentrations, in the time-series program than in the one-time program. These data may be explained by reviewing where the samples were collected. Although these samples were collected predominantly from wells in subunits 1 and 6, the one-time sampling program samples were collected nearly evenly across the subunits. For the time-series program, very few samples were collected from subunit 5 wells in which six different pesticides were detected in the one-time sampling program.

Atrazine was detected in samples from five of the six subunits, but other pesticides were detected in only one or two subunits (Table 5.9). The number of pesticides detected in each subunit was lower for the time-series samples than for the one-time samples (Table 5.2), except for subunit 4. The maximum number of pesticides detected in a single sample was generally lower in the time-series samples than in the one-time samples (Table 5.2).

Table 5.8 Pesticide occurrence in the time-series sampling program.

| Analyte | Detects (no.) | Maximum concentration (µg/L) | Date and subunit of maximum concentration | | Federal drinking water standard[*] (µg/L) |
			Date	Subunit	
Atrazine	26	0.67	Aug 1999	4	MCL = 3.0
Bromacil	1	1.2	Aug 1999	4	HA = 90
Butylate	1	0.22	Jun 1999	1	HA = 400
Metolachlor	7	4.4	Jul 1999	3	HA = 100

*USEPA (2000) lists the maximum contaminant level (MCL) and lifetime health advisory (HA) for these compounds.

Table 5.9 Pesticide occurrence in the time-series sampling program by subunit.

Subunit	Wells sampled (no.)	Samples (no.)	Occurrences (no.)	Maximum pesticides detected in a single sample (no.)	Pesticides detected
1	4	71	3	1	atrazine, butylate
2	5	22	8	1	atrazine
3	5	24	13	1	atrazine, metolachlor
4	2	14	6	2	atrazine, bromacil, butylate, metolachlor
5	2	10	0	0	none
6	3	74	4	1	atrazine

Temporal Distribution of Samples and Pesticide Occurrences

Six samples were collected monthly from October 1997 through July 2000, and 4 samples were collected monthly from August 2000 through February 2001. The number of samples collected during each calender month varied from 14 in August to 21 in February (Table 5.10). Pesticide occurrence also was not evenly distributed over time for samples from the time-series sampling program. To statistically evaluate the existence of a temporal trend in pesticide occurrence, we used the same calendar grouping as for the one-time sampling program:

time frame 1: February, March, and April;

time frame 2: May, June, and July;

time frame 3: August, September, and October;

time frame 4: November, December, and January.

Table 5.10 Temporal distribution of pesticide occurrences from the time-series sampling program.

Month	Occurrences (no.)	Samples (no.)	Occurrence (%)
January	2	16	13
February	1	21	5
March	2	18	11
April	2	18	11
May	1	17	6
June	7	18	39
July	3	18	17
August	2	14	14
September	5	16	31
October	4	19	21
November	2	20	10
December	3	20	15
Total	34	215	16

Using CTA, pesticide occurrence was not shown to be dependent on time for all samples using these four time frames ($p = 0.16$) or by the twelve calender months ($p = 0.19$). However, when the samples were grouped by post-application (June through October) and other (November through May) time frames, then pesticide occurrence was time dependent ($p < 0.01$); pesticide occurrence was higher during the post-application period (25%) than otherwise (10%).

The time-series sampling program was designed to collect samples from an equal number of wells from each subunit during each quarter (i.e., 3-month intervals). To assess possible trends in pesticide occurrence over the duration of the project, pesticide occurrence by sample quarter was evaluated. Samples were collected over 14 quarters from October 1997 through February 2001. The pesticide occurrence for all samples collected during each quarter varied considerably (Figure 5.5). Pesticide occurrence was noticeably higher after the seventh quarter (July 1999),

which reflected the change in wells sampled at this time. This change prevented us from making conclusions about possible trends in pesticide occurrence, which was one of the project goals.

We also evaluated long-term trends in atrazine concentrations for the 26 samples exceeding the method detection limit (Figure 5.6). A linear regression model was fit to the atrazine concentrations and the log of atrazine concentrations as a function of sampling date, but these models did not show statistically significant differences.
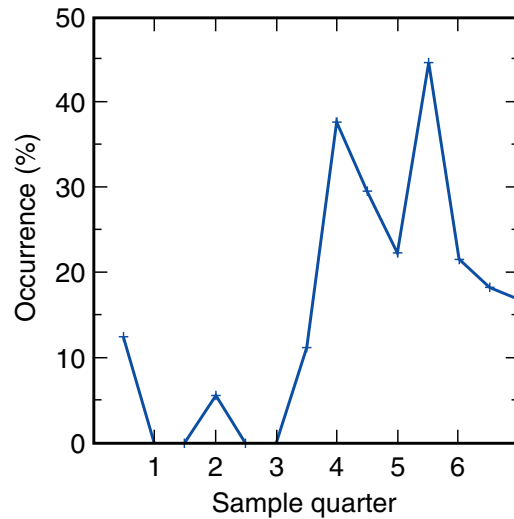

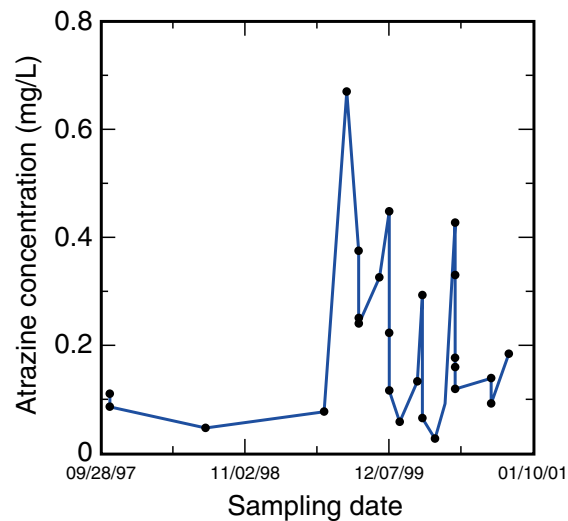**Figure 5.5** *Pesticide occurrence in the time-series sampling program by sampling quarter.*

Figure 5.6 *Atrazine concentration for samples from the time-series sampling program.*

Sampling Frequency and Pesticide Occurrences by Well

In the time-series sampling program, samples were collected from the same 21 wells on a monthly or quarterly basis (Table 5.11). The number of samples collected from each well varied from 3 to 27. Pesticide occurrence also varied by well. Nine wells had no pesticide occurrence. Four wells had a single pesticide occurrence, while 8 wells had two or more pesticide occurrences. Two-thirds of the wells with a pesticide occurrence (8 of 12) had more than one. In 5 of these 12 wells, pesticides were detected in at least 67% of all time-series samples. To summarize, the time-series data indicate that pesticide occurrence seemed to be constant over time. Wells with a pesticide occurrence were likely to have additional pesticide occurrences if resampled, and wells with no pesticide occurrence were not likely to have a pesticide occurrence if resampled.

Table 5.11 Pesticide occurrence and tritium concentrations by well in the time-series sampling program.

Subunit	Well	Occurrences (no.)	Samples (no.)	Occurrence (%)	^{3}H (TU*)
1	1-4-267	2	6	33	
	1-5-361	0	15	0	6.91
	1-7-278	0	24	0	8.18
	1-14-251	1	26	4	6.26
2	2-20-670	0	3	0	
	2-21-653	5	6	83	
	2-26-746	1	4	25	
	2-32-659	2	6	33	
	2-52-1792	0	3	0	
3	3-19-1484	0	1	0	
	3-27-1560	4	6	67	
	3-44-2013	3	3	100	
	3-49-2838	6	7	86	
	3-50-3731	0	7	0	
4	4-8-5	1	7	14	
	4-20-7	5	7	71	
5	5-4-1583	0	7	0	
	5-26-1411	0	3	0	
6	6-45-921	3	26	12	13.2
	6-76-1027	0	21	0	<0.50
	6-89-1091	1	27	4	<0.50

*TU, tritium unit, defined as 1 tritium atom in 10^{18} hydrogen atoms.

The concentration of atrazine over time in the time-series wells generally appeared to be random (Figure 5.7). A more definite temporal pattern is apparent in some wells, such as the subunit 4
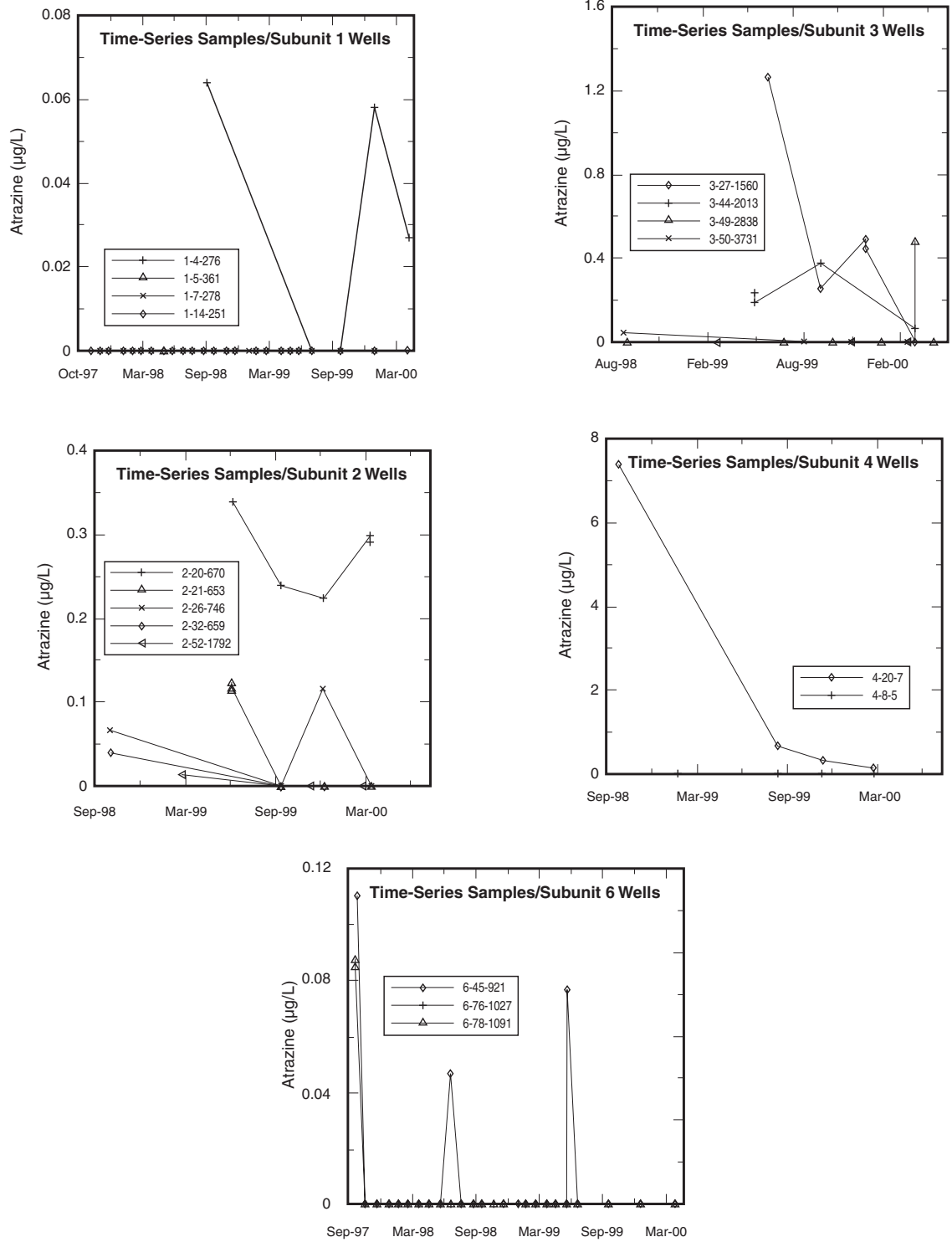
Figure 5.7 Atrazine concentration in the time-series wells. Samples with concentrations less than the method detection limit were plotted as 0.

well 4-20-7. For well 4-20-7, the concentration appears to decline exponentially over time from its peak concentration of 7.5 µg/L.

Tritium Concentrations

Tritium is a hydrogen isotope that geoscientists use to estimate the age of groundwater. Its concentration is reported in TU, which is defined as 1 tritium atom in 10^{18} hydrogen atoms. Tritium undergoes radioactive decay and has a half-life of 12.3 years (Freeze and Cherry, 1979). In Illinois, shallow groundwater often has tritium concentrations similar to those of surface water. Samples for tritium analysis were collected from 6 wells (3 from Mason Co. and 1 well each from Logan, Sangamon, and Tazewell Counties) and Quiver Creek in Mason County on July 15, 1998. The tritium concentration for the Quiver Creek sample was 9.5 TU, which is similar to three samples from subunit 1 and one sample from subunit 6 (see Table 5.11). These samples are considered "modern" water. Two subunit 6 wells (6-76-1027 and 6-89-1091) had very low tritium concentrations, which indicates that the water predates the 1960s.

On the day that tritium samples were collected (7/15/98), only one well had a pesticide occurrence. Atrazine was detected at 0.047 µg/L in 6-45-921, a well with modern water. Over the course of the time-series sampling program (see Table 5.11), pesticides were detected in two of the four wells with modern water and in one of two wells with water that predates the 1960s. In a survey of 303 midwestern wells (Kolpin et al., 1995), pesticides were detected in groundwater of both ages but were detected more frequently in modern than in non-modern groundwater. The data from our study show that pesticides also were detected in modern and non-modern groundwater, which is consistent with the findings of Kolpin et al. (1995).

Neural Network Analysis of One-Time Samples

Multivariate statistical methods have been used by analysts to identify factors that control an experiment or process and have been used to define factors controlling the occurrence of pesticides in wells (e.g., Schock et al., 1992). However, an underlying assumption in multivariate statistical analysis is that a model (linear, quadratic, logarithmic, or exponential) for pesticide occurrence data must be known a priori. Uncertainty in the results of multivariate statistical analysis can be substantial (Schock et al., 1992), reducing the analyst's ability to draw conclusions. As an alternative, artificial neural networks were used to analyze the pesticide concentration in the one-time samples. Neural networks have been used to study rainfall-runoff modeling (Hsu et al., 1995; Shamseldin, 1997), drainage design (Shukla et al., 1996; Kao, 1996; Yang et al., 1996), water quality monitoring (Maier and Dandy, 1996), chemical kinetics (Habiballah et al., 1996), unsaturated flow (Schaap and Bouten, 1996; Schaap et al., 1998), and hazardous waste site assessment (Basheer et al., 1996). Sarle (1994) described some differences between multivariate analysis and neural networks, noting that neural networks do not require a model a priori. Neural networks are multi-input and multi-output nonlinear models and can simulate the complex interaction among the input and output parameters. Ideally, neural networks can be used to develop a model to link the various input parameters to pesticide occurrence in the monitoring wells, preserving the complex interaction among these parameters. Ultimately, a tested model may be used as a screening tool for public health or regulatory decision making.

Systematic studies of the occurrence of pesticides in rural domestic wells have been completed

within the past 15 years by various states (Kross et al., 1990; Schock et al., 1992), USEPA (USEPA, 1990, 1992), USGS (Kolpin et al., 1993, 1994, 1996; Burkart and Kolpin, 1993), and pesticide registrants (Holden and Graham, 1990; Holden et al., 1992). Summaries of such studies can be found in reviews by Ray and Schock (1996) and Ray and Klindworth (2000). From these studies, factors found to influence the occurrence of pesticides in domestic wells included well depth, depth to aquifer material, distance to cropland, topographic setting around the well, method detection limit of the analytical method, potential point sources near the well (surface water bodies, agrichemical mixing and loading facilities), and past incidences of spills or backsiphoning at the wellhead. Physical and morphological characteristics of the subsoil media, such as fractures in till and soil macropores, also affect pesticide migration (Barbash and Resek, 1997). In addition, the soil hydraulic conductivity, pH, clay content, and organic carbon content of the soil may influence the leaching of pesticides to groundwater (Ritter, 2001). However, a detailed characterization including such features for the 159 wells of the one-time sampling program was not completed; rather, some of this information was included as a lumped mapping parameter, pesticide leaching class.

Neural Network Methods

Many different types of artificial neural networks exist, each with a particular range of application (Hecht-Nielsen, 1991; Haykin, 1994). Because feed-forward neural networks are more easily combined with the bootstrap method and are more efficient to calibrate (Schaap and Leij, 1998), combined feed-forward, backpropagation, neural network-bootstrap analysis was conducted with an adapted 'trainlm' training function using the neural network toolbox (Version 12.1) of MATLAB (Version 6). Here, 'trainlm' is a network training function that updates weight and bias values according to the Levenberg-Marquardt optimization technique (Hagan et al., 1996).

The proposed feed-forward, backpropagation, neural network consists of an input layer, two hidden layers, and an output layer. The number of nodes of the input layer corresponds to the number of input variables of the model. The hidden layers are the processing layers and are considered the neurons in the neural network. A single node is used for the output layer. A hyperbolic tangent sigmoid transfer function (tansig) for the hidden layer and a linear transfer function (purelin) for the output layer were used in the analysis. Figure 5.8 shows a feed-forward neural network with multiple input layers, two hidden layers, and multiple output layers.

Samples from 159 wells from the one-time sampling program collected between September 1998 through February 2001 were used for neural network analysis. Data from 100 wells were used for training the network. Training is a procedure that extracts the required information from the input data and updates and modifies the connection weight values. Well-trained weight values are then applied for the remaining wells (test set) to predict pesticide concentration in the wells. The performance of the neural network is evaluated by comparing the predicted values with the measured values. The performance of a well-designed neural network suffers from poorly trained weights. Ray and Klindworth (2000) reported that the random initial weights for a given architecture appeared to have some impact on prediction accuracy. Very little research has been conducted in finding good initial weights (Principe et al., 1999). To handle uncertainties for selection of initial weights, we used the bootstrap method as described by Efron and Tibshirani (1993).
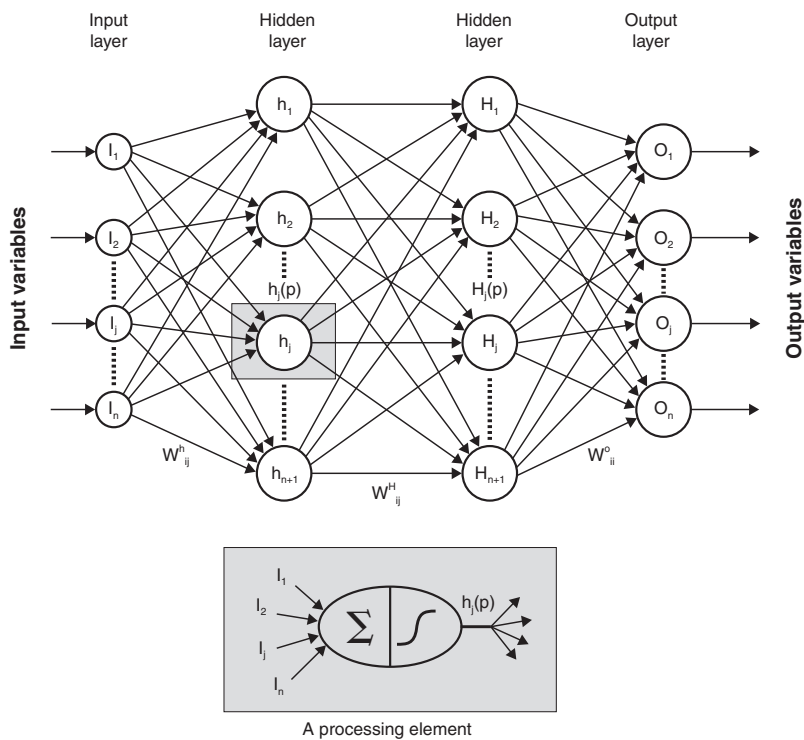
Figure 5.8 *A four-layer feed-forward neural network architecture with n neurons in the input and output layers and n+1 neurons in the two hidden layers. A processing element (bottom) depicts what happens at a given node in a hidden layer*

The bootstrap method is a nonparametric technique used to calculate the probability distribution of any statistic as predicted by the neural network. In the present case, the statistic would be pesticide concentration. The shape of the probability density function was not assumed a priori. However, it was assumed that the data involved were a good representation of the original population and that the data being analyzed were only one particular realization of that population. Thus, calibration with another realization of the data would be expected to give slightly different results. Within bootstrapping, different realizations are simulated by repeated random resampling of the original data set (size N) to yield B bootstrap data sets, also of size N. Each bootstrap data set contains somewhat different data, which results in B neural network models, and all these models may differ slightly. Based on results of previous studies (Efron and Tibshirani, 1993; Schaap and Leij, 1998; Montgomery and Runger, 1999) and the initial performance of our model, we observed that B equal to 100 was adequate.

Input Variables for Neural Network Models

The input values for neural network models can be numerical (e.g., depth of well) or categorical (e.g., ranked contamination potential). A generic procedure to utilize a set of categorical input parameters for predictive purposes has been outlined by Ray and Klindworth (2000). For example, a numeric value of 1 through 4 was assigned for each of the four pesticide leaching classes. Altogether, seven input parameters were available for this analysis: depth to aquifer material, pesticide leaching class, aquifer sensitivity to pesticide contamination, time of sample collection, well depth, depth to water from land surface, and the travel distance in the saturated zone (from water table to mid-point of screen).

1. *Depth to Aquifer Material (DTA).* Because pesticide occurrence generally decreased as DTA increased (Figure 5.9), DTA values were assigned as follows: 4 for DTA less than 20 feet, 3 for DTA from 20 to 50 feet, and 2 if no aquifer material was present within 50 feet of the ground surface (Table 1.1). DTA was set at 4 for subunits 1, 2, 3, and 5 and at 3 for subunits 4 and 6. Later, depth to aquifer material was determined based on the actual DTA material, which was determined during well drilling.

2. *Pesticide Leaching Class (PLC).* Information for PLC data were available from Keefer (1995b). Of the six PLC classes used by Keefer (1995b), wells sampled for the one-time program belonged to four PLC (Excessive, High to Moderate, Moderate to Somewhat Limited, and Limited and Very Limited), which were assigned values of 4, 3, 2, and 1, respectively.

3. *Aquifer Sensitivity to Contamination (ASC).* Keefer (1995b) was the source of information for ASC. Aquifer sensitivity values in the subunits were assigned values of 4 (Excessive), 3 (High), 2 (Moderate), and 1 (Very Limited).
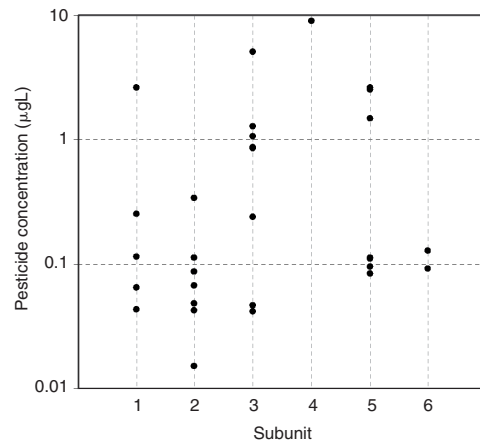

Figure 5.9 *Subunits versus total pesticide concentration during the sampling period. Tables 2.1 and 5.6 present depth to aquifer material values for these subunits.*
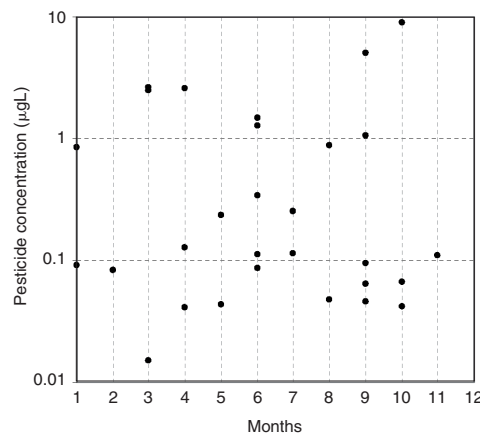

Figure 5.10 *Temporal distribution of total pesticide concentration by month sampled..*

4. *Time of Sample Collection (TSC).* Initially, TSC was season, using ranked index values of 4, 3, 2, and 1 for late spring to early summer, late fall to early winter, late summer to early fall, and late winter to early spring, respectively. Later, TSC was parameterized into 12 categories based upon the month that the sample was collected (Table 5.7, Figure 5.10). A value of 4 was assigned to September, the month that had the highest percentage of contaminated wells, and a value of 0 was assigned to December, the month having the lowest percentage. For January through December, assigned values were January, 0.5; February, 0,25; March, 2.75; April, 2.5; May, 1.0; June, 3.5; July, 1.5; August, 2.0; September, 4.0; October, 3.0; November, 0.75; and December, 0.

5. *Well Depth (WD).* Pesticide concentration generally decreased with WD (Figure 5.11), but no continuous function was found to relate pesticide concentration and WD. The WD was categorized into four zones. The highest value, 4, was assigned to WD of 10 to 30 feet; 3, between 30 to 50 feet; 2, 50 feet to 70 feet; and 1, greater than 70 feet.

6. *Depth to Water (DTW).* The DTW at the time of sampling was available for all wells. Values ranged between 0 (water at land surface) and 64.92 feet. As with the well depth versus pesticide concentration relationship, as the DTW decreased, the risk of pesticide reaching the screen zone increased (Figure 5.12). The input parameters for DTW were 4, 3, 2, and 1 for depth to water of less than 20 feet, 20 feet to 40 feet, 40 feet to 60 feet, and greater than 60 feet, respectively.

7. *Saturated Zone Travel Depth (SZT).* The SZT was calculated from WD, DTW, and screen depth: SZT = WD – DTW – 0.5 screen. It was expected that the thickness of the unsaturated zone would dictate the travel time. The pesticide concentration generally decreased as SZT increased (Figure 5.13). By examining Figure 5.13 and applying the same logic used with the WD criterion, the values 4, 3, 2, and 1 were assigned for SZT having values 10 to 30 feet, 30 to 50 feet, 50 to 70 feet, and greater than 70 feet, respectively. SZT was considered a redundant parameter because it was calculated from WD and DTW.

The sum of all observed pesticide concentrations (total pesticide concentration) in the sampled wells was used initially to scale the output values between 0 and 4, but later, values were scaled from 0 to 10 to improve resolution.
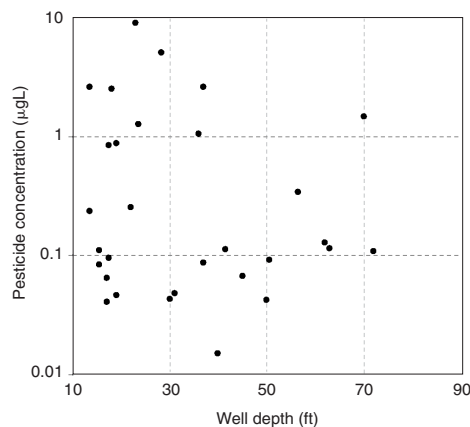

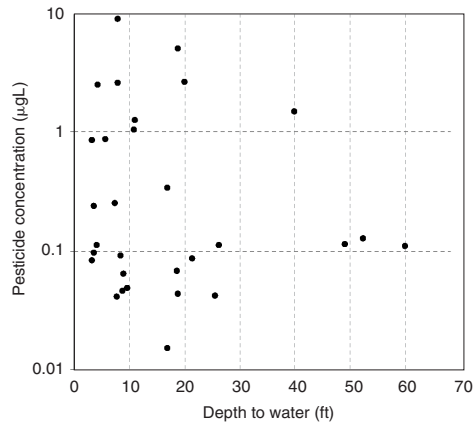**Figure 5.11** *Total pesticide concentration versus well depth.*

Figure 5.12 *Total pesticide concentration as a function of depth to water table.*
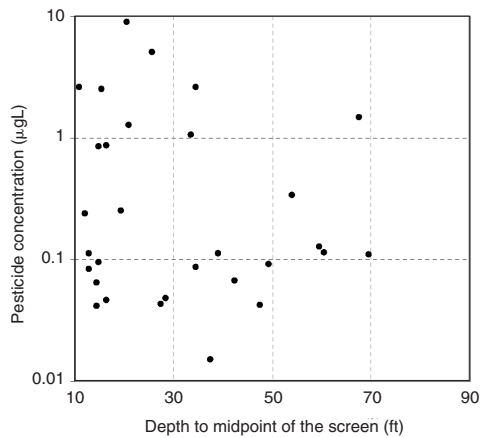

Figure 5.13 *Depth to midpoint of the screen versus total pesticide concentration.*

Neural Network Simulation Strategy

Several combinations of input parameters and three simulation scenarios were considered:

1. *Combination A: input parameters DTA, PLC, ASC, TSC-season, DTW.* The TSC-season was considered for analysis where the input values varied between 1 and 4. WD was eliminated because the DTW was available from sampling events. Because only five bootstrap simulations were performed, this input combination was considered to be an exploratory simulation.

2. *Combination B: input parameters DTA, PLC, ASC, TSC-month, WD, DTW.* TSC-month was considered for analysis where the input values varied between 0 and 4, depending on the month. SZT was not included because it was considered to be a redundant parameter. For this combination, 100 bootstrap simulations were performed. The optimum run was saved for analysis.

3. *Combination C: input parameters DTA, PLC, ASC, TSC-month, DTW, WD, SZT.* All seven parameters were included. One case represented the same set of parameters in combination A

with WD and SZT. WDs were discrete values of 1, 2, 3, or 4 depending on depth categories (DTA, DTW, WD). Only 5 bootstrap runs were conducted on this data. In the second case, SZT was added to combination B.

Performance of the Network

The performance of the neural network was evaluated in the following ways:

1. Using linear regression, the correlation coefficient (R-value) between the network response and the target was computed.

2. Following Schaap and Leij (1998), the bias in predicted values (i.e., the systematic difference between the target and predicted variables) was quantified by the mean error (ME):

   where

   $$ME = \frac{1}{N} \sum_{i=1}^{N} \left(T_i - P_i \right)$$

   T_i and P_i are the target and predicted values for i=1..N, and
   N is the number of total number of data for testing.

3. Following Hagan et al. (1996) and Principe et al. (1999), the mean square error (MSE) was used to measure the performance of training process. MSE is defined as the average sum of squares of errors (difference between actual and predicted values), and mathematically:

The correlation coefficient (R) ranges from –1 to 1. When R = 1, a perfect positive linear

$$MSE = \frac{1}{N} \sum_{i=1}^{N} \left(T_i - P_i \right)^2.$$

correlation exists between measured and predicted values; that is, they covary, which means that they vary by the same amount. When R = –1, a perfect linear negative correlation exists between measured and predicted parameters; that is, they vary in opposite ways (when the input parameter increases, the output decreases). When R = 0, no correlation exists between the measured and predicted values. Intermediate R-values describe partial correlations. The ME is used to assess the bias in the neural network. Negative ME values indicate that predicted values are on average larger than measured values; positive values indicate that the predicted values are smaller than measured values. In the present study, inputs having a higher number should predict a higher pesticide concentration in a well. Low ME values indicate high precision of the neural network response (e.g., the predicted values are very close to the measured values). The ME can be positive or negative if the predicted values are less than or greater than the actual values, respectively. Overall, the neural network responses are more precise if R tends to 1 and ME tends to 0.

The ME was calculated for combinations B and C (only the portion that was extended from B adding SZT). For combination B, sensitivity analyses on the parameters were considered by deleting certain parameters from the input set as shown in Table 5.12.

For combination B, the target goal or the mean square error of the network for the training data was fixed at 10^{-10}. For each scenario listed in Table 5.12, 100 runs were performed. The maximum R-value among these 100 runs, the data set used for that validation, and its corresponding predicted values were recorded for the analysis.

Results and Discussion

Combination A. In this exploratory simulation, the R-value of the calibration set ranged between 0.58 and 0.78. The best performance of the validation set (i.e., test) yielded an R-value of 0.3. Obviously, the model was not trained well, and the prediction was quite low. This result prompted us to use more input parameters and a larger number of bootstrap runs.

Combination B. The performance criteria (R and ME) for each scenario are presented in Table 5.13. For example, R = 0.87 for scenario 1, which implies that the R-value between the neural network responses and measured values is reasonably good. The corresponding negative ME (–0.18) indicates that the predicted values are higher than the measured values. However, it is evident that the smaller the ME, the better is the neural network response. The measured and neural network predicted values of pesticide concentrations were classified into four categories: A for excessive (7.5 to 10), B for high (5 to 7.5), C for limited (2.5 to 5), and D for very limited or no (>0 to 2.5) pesticide concentration, respectively.

Table 5.12 Sensitivity analysis: 12 scenarios for combination B.

Scenario	Parameters* included in each scenario					
	TSC	WD	DTW	DTA	ASC	PLC
1	✓	✓	✓	✓	✓	✓
2	☒	✓	✓	✓	✓	✓
3	✓	☒	✓	✓	✓	✓
4	✓	✓	☒	✓	✓	✓
5	✓	✓	✓	☒	✓	✓
6	✓	✓	✓	✓	☒	✓
7	✓	✓	✓	✓	✓	☒
8	☒	☒	✓	✓	✓	✓
9	✓	✓	☒	☒	✓	✓
10	☒	☒	☒	☒	✓	✓
11	✓	✓	✓	✓	☒	☒
12	✓	✓	✓	☒	☒	☒

* ✓, parameter included; ☒, parameter excluded.

Table 5.13 Measured and predicted number of wells with potential for contamination at various levels for combination B.

Scenario	Calibration Performance	Validation										
		Wells with pesticides in four categories (no.)										
	Performance	Performance		Measured				Predicted at optimum R			
	R	R	ME	A	B	C	D	A	B	C	D
1	1.00	0.87	−0.18	0	0	0	36	1	0	1	34
2	0.70	0.37	−0.32	0	0	0	35	2	1	4	28
3	0.88	0.63	0.19	0	0	3	32	2	2	2	29
4	1.00	0.68	0.22	0	0	2	31	1	0	1	31
5	1.00	0.51	−0.62	0	0	0	40	1	3	2	34
6	1.00	0.53	−0.64	0	0	1	31	2	0	4	26
7	1.00	0.71	−0.34	0	0	0	35	1	0	5	29
8	0.37	0.28	−0.18	0	0	0	40	1	3	8	28
9	1.00	0.79	−0.25	0	0	0	39	2	1	0	36
10	0.25	0.35	−0.13	0	0	0	34	13	0	5	16
11	0.99	0.56	−0.21	0	0	0	40	1	1	2	36
12	0.84	0.45	−0.27	0	0	1	38	3	1	1	34

By examining the ME and R-values of calibration and validation sets and the measured and predicted pesticide concentration level in wells (Table 5.13), it can be inferred that the neural network responses for scenario 1 (all six input parameters considered) are better than other scenarios. In scenario 4, the calibration performance was good (R = 1) and predicted the potential for contamination of the wells satisfactorily (see last 8 columns), but the validation R-value was intermediate (R = 0.68). The predicted and measured values for scenario 9 were also found to agree closely. Based on performance R-values for scenarios 2 through 7, TSC (lowest R when TSC is excluded) is considered the most sensitive input parameter, followed by DTA, ASC, WD, DTW, and PLC. The poor response of the neural network for scenarios 3, 8, and 10 (WD was eliminated in these scenarios) indicates the sensitivity of the neural network to well depth. The poor response of the network for scenarios 2, 8, and 10 (TSC excluded in these scenarios) indicates the sensitivity of the neural network to the time of sample collection. Moreover, poor neural network responses for scenarios 5 and 9 indicate that the DTA criterion was also an important input variable in this assessment. The neural network responses for scenarios 11 and 12 indicate that exclusion of ASC and PLC affects the prediction, but, as shown in scenario 10, ASC and PLC cannot exclusively predict the pesticide concentration. As stated above, a negative ME indicates that the neural network response is undervalued.

4. *Combination C.* For the seven-parameter model that was an extension of combination A, the R-value of the calibration set was nearly 93%. In the calibration set, the normalized concentrations above 0.2 matched well against the actual values for wells, but for lower concentrations, the match between actual and predicted values was worse. However, the calibration set performed poorly (R-value about 0.3), which led us to use a larger number

(100) of bootstrap runs, as discussed earlier. For the model where SZT was added to combination B, sensitivity analyses on the parameters were considered by deleting certain parameters from the input set as shown in Table 5.14. The neural network responses of 11 scenarios are presented in Table 5.15.

Table 5.14 Sensitivity analysis: 11 scenarios for combination C.

Scenario	Parameters* included in each scenario						
	TSC	WD	SZT	DTW	DTA	ASC	PLC
1	✓	✓	✓	✓	✓	✓	✓
2	☒	✓	✓	✓	✓	✓	✓
3	✓	☒	✓	✓	✓	✓	✓
4	✓	✓	☒	✓	✓	✓	✓
5	✓	✓	✓	☒	✓	✓	✓
6	✓	✓	✓	✓	☒	✓	✓
7	✓	✓	✓	✓	✓	☒	✓
8	✓	✓	✓	✓	✓	✓	☒
9	☒	☒	✓	✓	✓	✓	✓
10	✓	✓	☒	☒	✓	✓	✓
11	✓	✓	✓	✓	✓	☒	☒

* ✓, parameter included; ☒, parameter excluded.

Based on the performance R-values for scenarios 2 through 8, TSC (lowest R when TSC is excluded) is considered to be the most sensitive input parameter, followed by DTW, ASC, PLC, WD, SZT, and DTA. Examining the R-values, ME, and measured and neural network responses of each scenario (last 8 columns), TSC and WD are considered to be the most sensitive based on scenarios 2, 9, and 11. The neural network responses are reasonably satisfactory except for scenarios 2, 9, and 11. Because SZT is a redundant parameter for WD and DTW, its presence in the analysis supplements the absence of either WD or DTW where these were excluded.

Results from combinations B and C reveal that TSC is the most sensitive input parameter. However, the order for the sensitivity of other input parameters varied from combinations B and C. The difference in the performance of R for the six- and the seven-input parameter networks (scenario 1 in Tables 5.13 and 5.15) does not indicate that neural network prediction is worse for the seven-input parameter model than for the six-input parameter model for scenario 1. The ME value tends to 0 in the seven-input parameter model and is -0.18 for the six-input parameter model. As already stated, the neural network response is more precise if R is close to 1 and ME tends to 0, which is the ideal case. In reality, these values have deviations from 1 and 0, respectively. Because the test results showed that the categorized (A, B, C, and D groups) neural network responses for the seven-input parameter model were reasonably good and ME = 0, an R = 0.43 is considered to be reasonably good.

Table 5.15 Measured and predicted number of wells with the potential for contamination at various levels for combination C.

	Calibration	Validation									
		Performance		Wells with pesticide contamination (no.)							
	Performance			Measured				Predicted at optimum R			
Scenario	R	R	ME	A	B	C	D	A	B	C	D
1	1.00	0.43	0.00	0	0	0	40	1	0	1	38
2	0.60	0.22	0.25	0	0	2	37	1	1	1	36
3	1.00	0.70	−0.10	0	0	0	34	1	0	3	30
4	1.00	0.75	−0.23	0	0	0	29	1	0	0	28
5	1.00	0.51	0.06	0	0	0	40	1	1	1	37
6	1.00	0.84	−0.18	0	0	0	39	1	1	1	36
7	1.00	0.55	−0.39	0	0	0	37	1	1	1	34
8	1.00	0.68	−0.21	0	0	0	40	1	0	3	36
9	0.55	0.45	−0.18	0	0	0	31	1	2	2	26
10	1.00	0.61	−0.81	0	0	0	38	2	0	2	34
11	0.92	0.42	0.01	0	0	1	36	1	1	1	34

Summary

Based on the one-time sampling data, the time of sample collection and well depth appeared to be the most sensitive parameters in predicting pesticide concentration. Depth to aquifer material and depth to water also were significant in the neural network analysis. Aquifer sensitivity to contamination and pesticide leaching class were not able to predict contamination potential independently. However, their presence in the complete data set was helpful in improving the prediction by the neural network.

One-Time Sampling Program—Anions and Cations

Following the recommendation of Hamilton and Helsel (1995), samples were also collected and analyzed for major anions and cations. The minimum, median, and maximum concentrations for the one-time sampling program are reported in Table 5.16. The number of samples reported here are fewer than the 159 pesticide samples, primarily due to instrument problems at the IDA laboratory. In addition, some ions (bromide, potassium, fluoride, nitrite-nitrogen, and phosphate) had a considerable number of "censored" samples or samples at concentrations below the method reporting limit. Box plots (Figure 5.14) show the distribution of concentrations for some ions within each of the 6 subunits. These plots include a log axis for the concentration data and exclude the samples reported at less than method reporting limit.

The concentrations of calcium, magnesium, potassium, and chloride are generally similar in the different subunits and vary by two orders of magnitude (Figure 5.14). The nitrate-nitrogen and sulfate concentrations (Figure 5.14) varied by subunit. The median concentrations of nitrate-nitrogen and the variability of these concentrations in subunits 4 and 6 are lower than those in the other subunits. The differences in the nitrate-N concentrations (excluding the censored values) across all six subunits are not significant ($p = 0.06$) but are significantly different for subunits 4 and 6 than for subunits 1, 2, 3, and 5 ($p = 0.007$) as determined by the Kruskal-Wallis test. The

difference in the sulfate concentrations across the six subunits also was statistically significant ($p = 0.02$). Conversely, the differences for chloride, calcium, magnesium, and potassium concentrations across the subunits were not statistically significant ($p > 0.28$).

Table 5.16 Major anions and cations for samples from the one-time sampling program.

Ion	Samples (no.)	Samples <MRL* (no.)	Concentration (mg/L)		
			Median	Minimum	Maximum
Bromide	129	128	<1.3	<1.3	4.5
Calcium	138	1	60.5	<1.9	268
Magnesium	138	1	30.0	<1.9	174
Potassium	125	95	<2.4	<2.4	20
Chloride	133	7	11.9	<1.4	241
Fluoride	129	124	<0.76	<0.76	22
Nitrate-N	130	56	1.39	<0.23	45.4
Nitrite-N	131	102	<0.72	<0.72	2.5
Phosphate	128	127	<0.93	<0.93	1.1
Sulfate	133	11	28	<1.9	4,075

* MRL, method reporting limit.

The differences in the nitrate-nitrogen concentrations (Figure 5.14) may be due to the differences in depth to uppermost aquifer material. Lower nitrate-nitrogen concentrations would be expected in areas with deeper aquifer materials (20 to 50 feet in subunits 4 and 6) for two reasons. First, less surficially applied nitrogen fertilizers would be transported to deeper depths. Also, low oxygen conditions are typically more prevalent at deeper depths; thus, denitrifying conditions should be more prevalent at deeper depths as well. The sulfate concentrations appear to be similar except for subunit 4 (Figure 5.14), which has higher concentrations. Many wells in subunit 4 are completed in Pennsylvanian and Mississippian bedrock, which may contain sulfate-bearing minerals such as pyrite and gypsum.

Time-Series Sampling Program—Anions and Cations

Anion and cation concentrations for the time-series sampling program are reported in Table 5.17. The number of samples reported here are generally fewer than the 215 pesticide samples, primarily because some samples were not analyzed due to instrument problems at the IDA laboratory. In addition, some ions (bromide, fluoride, nitrite-nitrogen, phosphate, and potassium) had a considerable number of samples at concentrations below the method reporting limit. Box plots (Figure 5.15) show the distribution of the concentration data for the selected ions within each of the six subunits. These plots include a log axis for the concentration data and exclude the samples reported at less than method reporting limits. For most ions, the concentrations generally vary across the subunits and vary by one or two orders of magnitude. When tested using the Kruskal-Wallis test, the distributions of chloride, nitrate-nitrogen, sulfate, calcium, magnesium
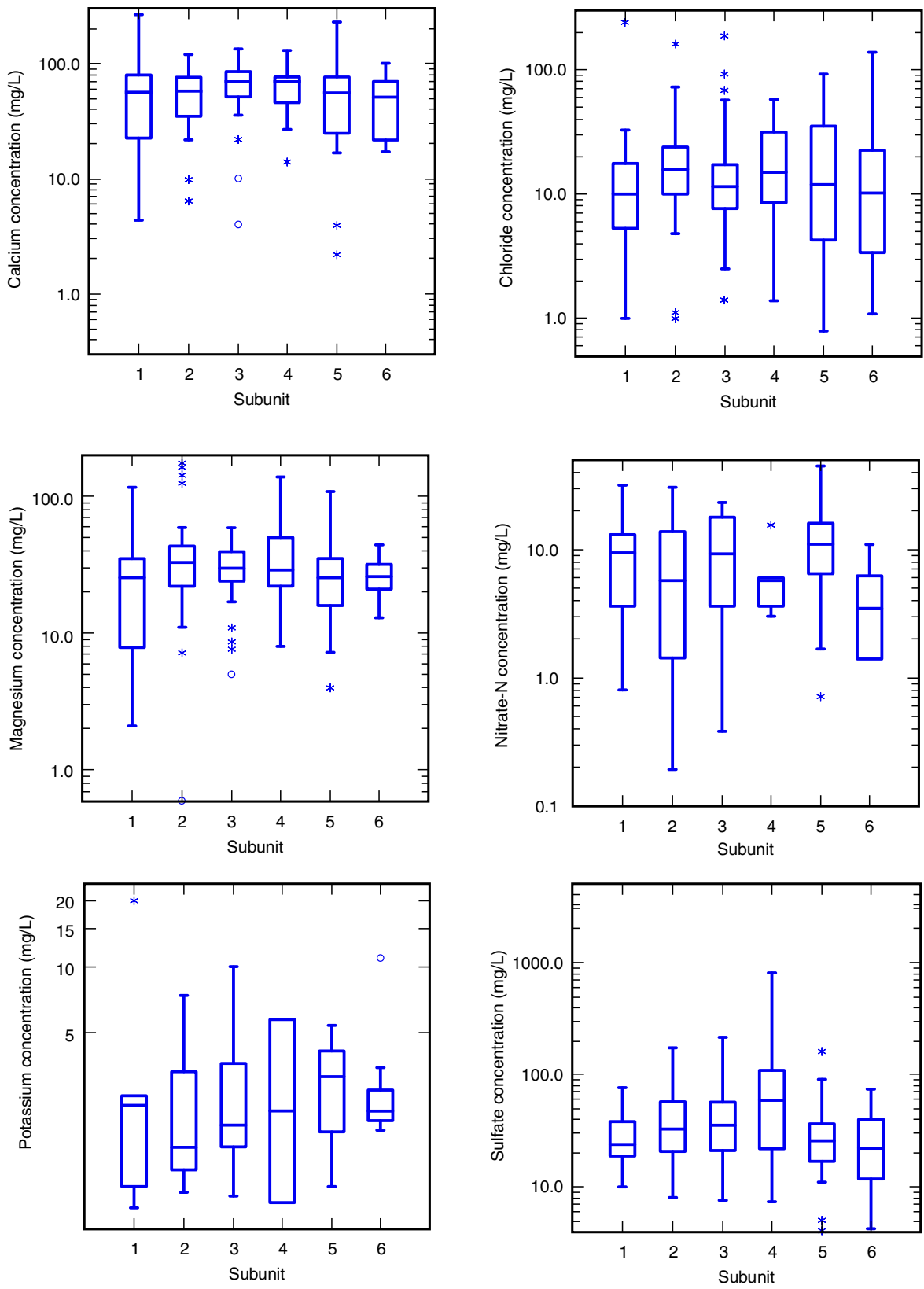
Figure 5.14 *Box plot of calcium, magnesium, potassium, chloride, nitrate-N, and sulfate concentrations (excluding censored values) for the one-time samples. *, 1.5 times the Hspread (interquartile range); o, points more than 3 times the Hspread.*
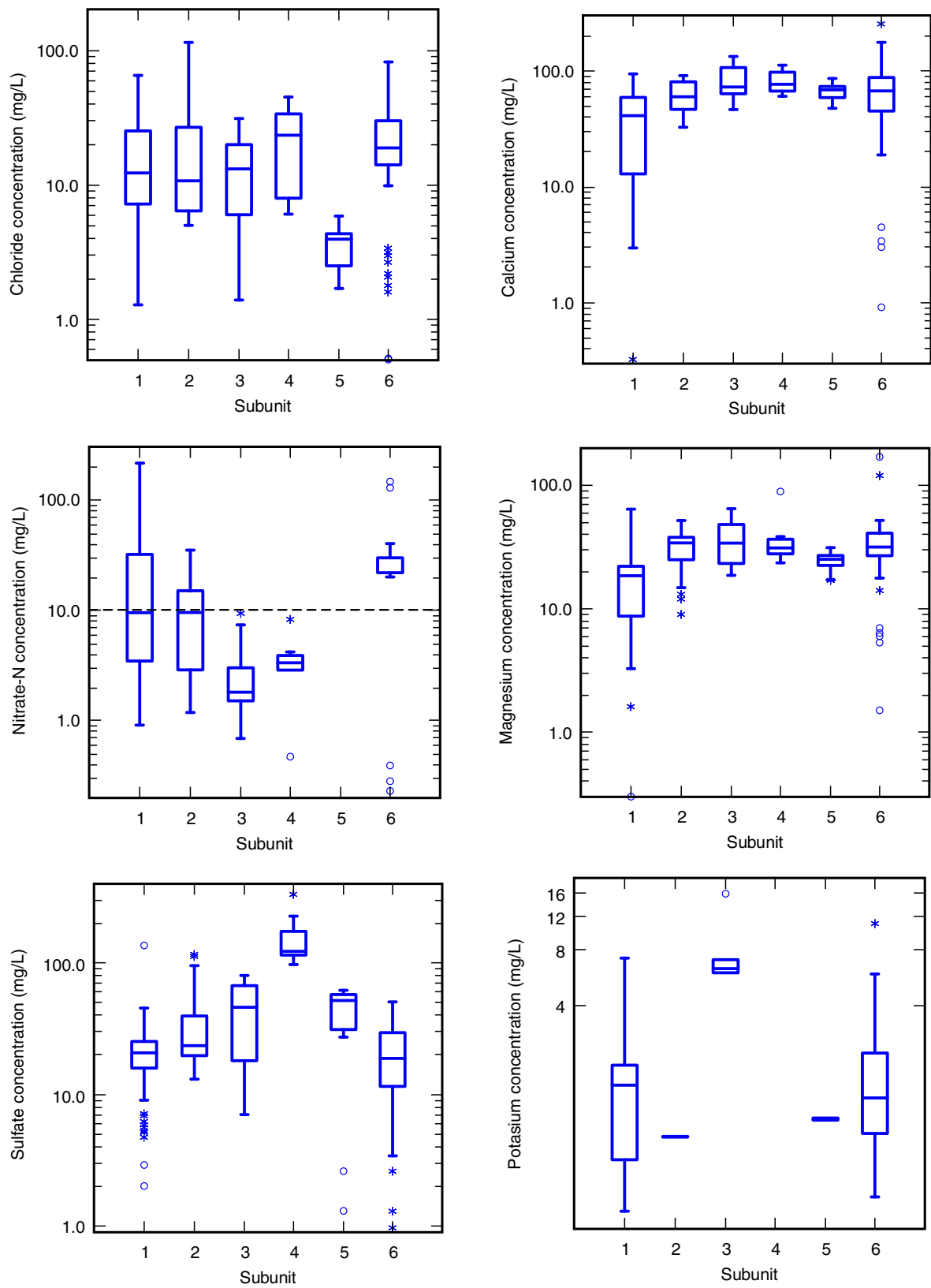
Figure 5.15 *Box plot of chloride, nitrate-N, sulfate, calcium, magnesium, and potassium concentrations (excluding censored values) for the time-series samples.*

and potassium concentrations failed the null hypothesis ($p \leq 0.01$), indicating that the tested distributions for at least one subunit differed significantly from the other subunits.

Table 5.17 Major cations and anions for samples from the time-series sampling program.

Ion	Samples (no.)	Samples <MRL* (no.)	Concentration (mg/L)		
			Median	Minimum	Maximum
Bromide	191	191	<1.3	<1.3	<1.3
Calcium	201	1	63.0	<1.9	255
Magnesium	201	1	28.0	<1.9	171
Potassium	189	135	<2.4	<2.4	16
Chloride	201	4	15.0	<1.4	114
Fluoride	191	188	<0.76	<0.76	1.02
Nitrate-N	200	69	2.94	<0.23	218
Nitrite-N	190	169	<0.72	<0.72	0.99
Phosphate	184	184	<0.93	<0.93	<0.93
Sulfate	201	15	22.0	<1.9	331

* MRL, method reporting limit.

The median ion concentrations for the time-series and one-time sampling programs are essentially equal, except for nitrate-N (Tables 5.16 and 5.17). The median nitrate-N concentrations for the time-series samples were approximately twice the concentration of the one-time samples. The differences in the range of ion concentrations in each subunit for the two sampling programs are likely due to differences in the number and the distribution of the wells sampled. Twenty-one wells were sampled in the time-series sampling program, and 159 wells were sampled in the one-time sampling program. While the one-time sampling program collected samples nearly uniformly from all subunits, samples for the time-series samples were concentrated in subunits 1 and 6 (see Table 5.9).

Table 5.18 Linear regression models for anion and cation concentrations from the time-series sampling program.

Ion	Slope	p	R^2
Calcium	0.030	<0.00005	0.096
Magnesium	0.0098	0.0092	0.034
Chloride	−0.012	0.0004	0.062
Nitrate-N	−0.0043	0.0002	0.070
Sulfate	0.0537	<0.00005	0.19

To evaluate temporal trends in the ion concentrations, linear regression models were fit using SYSTAT Version 9.0 to the anion and cation concentrations with respect to sampling date. The model results for these statistically significant models ($p < 0.01$) are shown in Table 5.18. The slope's sign indicates the direction of the linear trend. A positive slope means an increasing

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temporal trend, and a negative slope means a decreasing temporal trend. The coefficient of determination (R^2) for these linear models is less than 20% and usually less than 10%. In other words, these models explain less than 20% of the variation in the data. In addition, the modeled slopes are quite small, suggesting little change over time. Linear regression models were fit to the calcium, nitrate-nitrogen, and sulfate for individual wells with more than 20 samples (1-14-251, 1-7-278, and 6-45-921). The results were similar to the models for all time-series data (Table 5.18): the slopes had the same sign and similar p- and R^2-values.

CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Numerous studies have been reported on pesticides in well water. For almost all studies that covered a broad geographic area, samples were collected from water-supply wells, either public or domestic wells. In our present study, dedicated monitoring wells were sampled. These wells were located on the perimeter of agricultural production fields (primarily corn and soybeans) where the only known source of pesticides were those used in normal agricultural production. Thus, this study was designed to generate data with a unique perspective on the occurrence of pesticides in the shallow groundwater of rural, agricultural settings.

The data from the one-time and time-series sampling programs indicated the following:

- Pesticides were detected in 16 to 18% of the samples. Atrazine was the most commonly detected pesticide, followed by metolachlor, butylate, and bromacil. Only one sample had a pesticide concentration (atrazine) that exceeded a federal drinking water standard. Most concentrations were less than 1 µg/L. Although we sampled dedicated monitoring wells, the pesticides detected and the preponderance of low concentrations agree with results from domestic, water-well sampling studies.

- Pesticide occurrence was dependent on the depth to uppermost aquifer material. Pesticide occurrence was three times more common in samples where depth to aquifer material was less than 20 feet than at 20 to 50 feet. These data show that pesticide occurrence is more likely at depths to the uppermost aquifer material that are shallower than previously shown (Schock et al., 1992).

- Pesticide occurrence was not dependent on the soils and hydrogeologic factors as defined by the six subunits. If "occurrence" is defined as used by Schock et al. (1992) to be one of agriculturally related chemical occurrence (a pesticide detection or nitrate-nitrogen above 10 mg/L), then occurrence is dependent on the six subunits. However, even using this definition of occurrence, occurrence showed a stronger dependence on depth to uppermost aquifer material (hydrogeologic factor) than on the soils and hydrogeological factors.

- Pesticide occurrence was generally dependent on sampling time. Post-application time frames (June through October) versus other time frames (November through May) showed the strongest temporal relationship. Pesticide occurrence during post-application months was three times higher than during other months. This dependence on sampling time was due to the subunit 1, 2, 3, and 5 wells (depth to uppermost aquifer material less than 20 feet), because pesticide occurrence in the subunit 4 and 6 wells (depth to uppermost aquifer material at 20 to 50 feet) did not vary with sampling time.

- No trends were observed in pesticide occurrence or atrazine concentrations over the duration of the one-time sampling program.

- For individual wells, the time-series data suggested that pesticide occurrence was generally constant over time. Wells with a pesticide occurrence were likely to have additional pesticide occurrences. Conversely, wells with no pesticide occurrence were likely to have no pesticide occurrence when sampled repeatedly.

- The anion and cation concentrations for both sampling programs had similar median and range of concentrations. The median nitrate-nitrogen concentration for both programs was less than 3.0 mg/L, which is well below the 10 mg/L of maximum contaminant level for nitrate-nitrogen. The concentrations of nitrate and sulfate were not uniform across the six subunits.

Based on the neural network analysis of the one-time sampling data, the time of sample collection and well depth appeared to be the most sensitive parameters in predicting pesticide concentration. Depth to uppermost aquifer material and depth to water also were significant. Aquifer sensitivity to contamination and pesticide leaching class were not able to predict contamination potential independently; however, their presence with other input parameters improved the predictive power of the neural network.

Results from neural network analysis and more conventional statistical analysis agree except for the significance of well depth. Well depth was determined to be a significant factor by the neural network, but not by conventional statistical analysis. This difference may be due to slight differences in the data analyzed—pesticide concentration was used for neural network analysis, but pesticide occurrence was used for conventional statistical analysis, reflecting the additional analytical power in numerical (pesticide concentration) versus binary (pesticide occurrence) data.

Recommendations

Additional study of the temporal variations of pesticide occurrence is needed to define temporal trends. The wells in this network could be sampled to satisfy this need. Wells from areas where the depth to uppermost aquifer material is less than 20 feet may be the best wells to sample for this purpose because of the higher pesticide occurrence observed for these wells in the one-time sampling program. This type of study requires consistency in the wells sampled, sampling methods, sampling interval, and analytes.

Pesticide degradates should be included in the list of analytes in all future sampling. As other researchers have shown (Kolpin et al., 2000; Morrow, 2003; Mills and McMillan, 2004), pesticide degradates generally are found more frequently and at higher concentrations than the parent compounds. Thus, to provide a more complete picture of pesticides in Illinois groundwater, pesticide degradates need to be included in future sampling.

Additional research on both the soils and hydrogeologic properties should be conducted to improve the statewide map of aquifer sensitivity to contamination by pesticide leaching. Installation of additional monitoring wells for this network should be suspended until soil characteristics can be incorporated in the aquifer sensitivity map in a meaningful way. The map tested in this project included three leaching properties (hydraulic conductivity, the amount of organic matter of individual soil layers, and drainage class category) for the soil associations. Median values for these three factors were used to develop the tested map. In a modeling study, Scheibe and Yabusaki (1998) found that bulk groundwater flow depends on mean hydraulic conductivity values, but contaminant transport is strongly impacted by the existence and connectedness of extreme-valued hydraulic conductivities.

Thus, we may be able to improve the map by incorporating extreme values of the soil leaching properties rather than the median values used. In addition, neural network analysis could be

used to identify soil and other factors that improve the ability to predict pesticide concentration in the project samples and ultimately the statewide map of aquifer sensitivity to contamination by pesticide leaching. The hydrogeologic property, depth to uppermost aquifer material, could be improved by more accurately delineating those areas where the depth to uppermost aquifer is between 20 and 50 feet.

Once these recommendations have been addressed, samples from the monitoring well network should continue to be collected, and these data should be analyzed and interpreted on a regular basis.

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