

PILOT STUDY: AGRICULTURAL CHEMICALS IN RURAL, PRIVATE WELLS IN ILLINOIS



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Department of Energy and Natural Resources
ILLINOIS STATE GEOLOGICAL SURVEY
ILLINOIS STATE WATER SURVEY

PILOT STUDY: AGRICULTURAL CHEMICALS IN RURAL, PRIVATE WELLS IN ILLINOIS

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EXECUTIVE SUMMARY

Background

In the Illinois Groundwater Protection Act of 1987 (PA 85-863), the state legislature mandated that the Illinois Department of Energy and Natural Resources (DENR) conduct an "ongoing program of basic and applied research relating to groundwater," including an evaluation of pesticide impacts upon groundwater. "Such evaluation shall include the general location and extent of any contamination of groundwaters resulting from pesticide use. . . . Priority shall be given to those areas of the State where pesticides are utilized most intensively." In response to this mandate, the Illinois State Water Survey (ISWS) and the Illinois State Geological Survey (ISGS), divisions of DENR, developed a plan to assess the occurrence of agricultural chemicals in rural, private wells on a statewide basis (McKenna et al. 1989). In response to the concerns regarding the proposed statewide survey, a separate pilot study was designed, based on the recommended statewide survey, to produce tangible, documented results of well-water sampling and to demonstrate the validity of the survey design.

The legislative mandate addressed the pesticide impacts on groundwater. The proposed statewide plan and the pilot study will focus on groundwater drawn from rural, private wells. This approach will maximize data acquisition on the potential for exposure of the rural residents of Illinois to agricultural chemicals (pesticides and nitrogen fertilizers) through drinking water; it will also minimize sample collection costs. Inferences drawn from this project are valid for groundwater drawn from rural, private wells and not from other sources.

Project Description

The pilot study was conducted jointly by the ISWS and ISGS, with contributions by the Illinois Department of Agriculture (IDOA) and the Illinois Department of Public Health (IDPH). Key elements included

- defining the sample population as private, drinking-water wells in rural Illinois;
- using stratified random sampling based on potential for contamination of shallow groundwater as approximated by depth to the uppermost aquifer material;
- sampling wells in five areas that represented four distinct hydrogeologic environments and were approximately 36 square miles (equivalent to a legal township) in size;
- randomly selecting wells within each of the five study areas;
- scheduling well sampling to address temporal variability of pesticides in groundwater;
- characterizing the agricultural practices, hydrology, land use, and shallow hydrogeology of the study areas;
- selecting analytes on the basis of their use for corn and soybean production in Illinois and potential to leach to groundwater;
- using analytical methods from the United States Environmental Protection Agency's (USEPA) National Pesticide Survey (NPS);
- using and, as needed, revising all protocols and procedures of the recommended statewide survey;
- developing the information and data management programs for the pilot study and the recommended statewide survey;
- statistically analyzing and interpreting the pilot study results.

One purpose of the proposed statewide survey was to estimate the occurrence of agricultural chemicals, chiefly those used in the production of corn and soybeans, in rural, private wells. Compared with public water-supply wells, rural, private wells are located closer to the fields where agricultural chemicals are applied, and the quality of water from private wells is monitored less frequently and less thoroughly.

Wells were sampled according to a stratified random sampling scheme. In this type of sampling scheme, the wells are first stratified or categorized and then the wells in these strata or categories are randomly sampled. In the pilot study, the rural, private wells were categorized by the depth to the uppermost aquifer material. Stratified random sampling provides data for developing a statistically valid estimate of the occurrence of agricultural chemicals in rural, private wells and developing an estimate of occurrence in each category. The estimates of the various categories can then be statistically analyzed, providing additional information about the occurrence of agricultural chemicals. A key objective of the pilot study was to test the validity of this stratification variable.

The following criteria were used to select the five study areas:

- geologic setting,
- well type,
- land use,
- proximity to the investigators' headquarters (Champaign, Illinois),
- availability of data for characterization,
- percentage of land in corn and soybean production,
- cooperation of local agencies and area residents,
- contiguous areas larger than 35 square miles,
- well density.

The first two criteria were used to differentiate the selected study areas. All study areas met the remaining criteria. The location and geologic setting of the five study areas are given in the table below. The geologic setting, as defined by the depth to uppermost aquifer material, was unique for each of four study areas. The Effingham County study area was included to study the effect of well type on the occurrence of agricultural chemicals in rural, private wells.

Areas included in the pilot study.

Depth to uppermost aquifer material (ft)	County	Location ^a
< 5	Mason	T 22 N, R 6 W
5 to 20	Kankakee	T 31 & 32 N, R 12 & 13 E
20 to 50	Livingston	T 25 & 26 N, R 6 & 7 E, T 26 N, R 8 E
> 50	Piatt	T 19 N, R 5 E
> 50	Effingham	T 7 N, R 7 E

^a Study areas occupy all or part of the townships listed.

Well-water samples were collected from 48 private wells in each area (240 wells total). The wells sampled were selected from a complete list of private wells, which was compiled during a well inventory of each study area. Wells in each area were sampled twice a month for 12 months (March 1990 to February 1991) to avoid temporal bias in our observations of the occurrence of agricultural chemicals in the well water. In addition, wells were sampled with strict adherence to a written protocol to ensure the collection of high-quality and uniform samples. It is important to note that the pilot study is not a substitute for the recommended statewide survey. Rather, it was an effective way to refine the procedures and protocols of the statewide survey, another objective of the pilot study.

The well users/owners, whose wells were selected for sampling in the pilot study, were interviewed by ISWS/ISGS staff prior to well sampling. (For convenience, we will use the term "well user" in place of "well user/owner.") The well user was interviewed regarding well construction, possible well contamination, and land use around the well. In addition, farmers were asked about their use of agricultural chemicals during the past 5 years.

Detailed characterization, described in Barnhardt et al. (1992), was undertaken, to help understand the land use, agricultural practices, hydrology, and shallow hydrogeology of each study area. The characterization served several purposes. The most important outcome of the characterization effort may be a deeper understanding of what is involved in developing basic information about wells and land-use patterns across the range of hydrogeologic environments in Illinois. This understanding helped the pilot study team make some valuable recommendations about the level of detail needed for the characterization in the recommended statewide survey.

The well-water samples were analyzed for 39 agricultural chemicals, using USEPA NPS Methods 1, 2, 3, 4, 5, and 9. These compounds were selected on the basis of their use in the production of corn and soybeans, their detection in well-water or groundwater by other researchers, and the availability of analytical methods.

Target analytes in the pilot study.

Method 1

alachlor, atrazine, butylate, carboxin, chlorpropham, diazinon, disulfoton, EPTC, ethoprop, metolachlor, metribuzin, simazine, terbufos, vernolate

Method 2

aldrin, α -chlordane, γ -chlordane, dieldrin, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, p,p'-DDT, propachlor, trifluralin

Method 3

2,4-D, 2,4-DB, bentazon, chloramben, dicamba, dinoseb, picloram

Method 4

carbofuran phenol, cyanazine, desethylatrazine, linuron

Method 5

carbaryl, carbofuran

Method 9

N O_3^- + NO_2^- as N

Considerable effort was expended on the implementation of the six analytical methods. Chemical method implementation included purchasing, installing, setting up, and calibrating the instruments, as well as debugging the methods with field samples, establishing estimated detection limits, determining average percent recoveries, implementing quality assurance/quality control (QA/QC) methods, and extracting and preparing samples.

A comprehensive, PC-based information and data management system was developed for the pilot study. The system has the capability to generate a master form used for printing a multi-part form that tracks sampling materials, forms for recording field measurements, and labels for the sample bottles. The system was designed to allow for tracking the chemical laboratory activities and sample movement, and to generate reports for QA/QC purposes. The system stores information gathered in all phases of the study, processes that information, and produces reports. It also allows the project staff to format information and analytical chemical results for statistical and interpretive analysis.

Results, Discussion, and Conclusions

One or more agricultural chemicals were detected at or above the minimum reporting level (MRL) in 55 out of 240 (23%) samples. The occurrence of agricultural chemicals in rural, private wells varied from 0% in the Piatt County study area to 46% in the Effingham County

study area. The results from the study areas with drilled or driven wells are in agreement with the results predicted using the map of potential for contamination by agricultural chemicals from McKenna et al. (1989).

The results from the study area with dug or bored wells (Effingham County) were not predictable using the potential for contamination map (McKenna et al. 1989). The Effingham County and Piatt County study areas are in the same category of potential for contamination; however, the occurrence of agricultural chemicals is dramatically different in wells in these two areas. This difference demonstrates the impact of well type on the occurrence of agricultural chemicals in rural, private drinking-water wells.

Nitrate occurred most frequently. In addition to nitrate, ten other agricultural chemicals were detected above their respective MRLs. From a practical standpoint, α -chlordane and γ -chlordane are considered to be the same compound, so the number of agricultural chemicals detected above the MRL, including nitrate, was reduced from eleven to ten. However, the remaining 28 agricultural chemicals included as analytes for this study were not detected above their respective MRLs. Only nitrate (42 occurrences) and atrazine (one occurrence) had one or more occurrences above their respective maximum contaminant level established by the federal government.

Comparing research results with those from similar studies is a standard practice and can help place research results in perspective. The results of the pilot study were compared with results from USEPA's National Pesticide Survey (USEPA 1990) and Iowa's State-Wide Rural Well-Water Survey (SWRL) (Kross et al. 1990). However, after evaluating the purpose and design of these studies, along with the technical details of the chemical analysis and the definition of the sample populations, we found that the results of these three studies are not comparable. Comparing results of the pilot study with other surveys of agricultural chemicals in well water must be done cautiously.

The analytical chemistry results were statistically analyzed to gain additional insight into the occurrence of agricultural chemicals in rural, private wells. Inferences drawn from this analysis are valid for the wells sampled in the pilot study, but may not be valid for other wells. The statistical analysis included the use of hypothesis testing and two nonparametric techniques, contingency tables and logistic regression.

The analysis indicates that some parameters have a greater influence than others on the occurrence of contaminants in rural, private water wells. Occurrence is most strongly related to study area, well type, well depth, and well cover. These parameters point to the well as the most important parameter for defining the occurrence. These results, however, must be put in the proper perspective. The study area incorporates information regarding well type and hydrogeologic setting. Well depth and type of well cover can be related to type of well and ultimately to the study area.

The results of the pilot study provide estimates of the probability of occurrence of agricultural chemicals in rural, private wells in areas that represent the four categories of contamination potential of the recommended statewide survey and in areas where water is obtained from dug or bored wells. Consequently, it has been possible to update the procedures in the recommended survey and optimize the number of samples necessary for it, while maintaining the same levels of confidence and precision.

The primary conclusion is that the stratification variable, depth to the uppermost aquifer material, is useful for predicting the occurrence of agricultural chemicals in drilled or driven, private wells in rural Illinois. Thus, the occurrence of agricultural chemicals is not uniform across different hydrogeologic environments, and the recommended statewide survey using

stratification by hydrogeologic environment is warranted. In addition, the potential for contamination map, based on depth to the uppermost aquifer material (McKenna et al. 1989), should be a reasonable guide for the design of the recommended statewide survey for drilled or driven wells. The statistical analysis indicates that certain categories may be combined. Such a combination could reduce the cost of a statewide survey, but might not be desirable if the intended use of the results calls for the level of detail originally recommended. A great deal of variation exists in the occurrence of the various agricultural chemicals. Thus, the general knowledge regarding the potential for contamination by agricultural chemicals of an area does not mean that every site within an area has an equal potential for contamination.

Depth to the uppermost aquifer, was not useful for predicting the occurrence of agricultural chemicals for dug or bored wells. The dug or bored wells sampled in the Effingham County study area were shown to have the highest frequency of occurrence of agricultural chemicals. Dug or bored wells generally draw water from thin, discontinuous geologic materials that are not considered aquifer materials as defined in this report.

Well depth was shown to be a very significant predictor of occurrence of agricultural chemicals in rural, private, drinking-water wells. The occurrence of agricultural chemicals in deep (≥ 50 feet deep) wells was shown to be significantly lower than the occurrence in shallow (< 50 feet deep) wells. In addition, for drilled or driven wells, the concentration of nitrate generally, but not always, decreases with depth. For drilled or driven wells, the rate of occurrence also generally decreases as the depth to the uppermost aquifer materials increases.

The pilot study provided an opportunity to test and improve all the procedures and protocols to be used in the proposed statewide survey. These improvements are described throughout the report and should be applicable to any sampling program having a regional scope and/or focusing on agricultural chemicals.

A danger in conducting a pilot study is that the full-scale project will not be conducted because funding agencies are satisfied with the results of the pilot study. This can often lead to misapplication of data and analyses. Some people may consider the results of a pilot study as if the results were developed from a full-scale project. For this project, the area covered in the pilot study was small in comparison with the area of the entire state: about 180 square miles of the more than 80,000 square miles of total area in Illinois. Only 240 samples were collected within this small area. The size of the study areas and the number of samples collected were appropriate for the purposes for which they were intended. This pilot study fulfilled all its goals, but it is not a substitute for the recommended state survey. It indicates that there may indeed be problems with pesticides and nitrate contamination in well-water in Illinois, and therefore that the recommended statewide survey is needed.

ACKNOWLEDGMENTS

The authors thank the numerous well owners and well users for their cooperation throughout this project. The Agricultural Stabilization and Conservation Service (ASCS), Soil Conservation Service (SCS), and Cooperative Extension Service (CES) all provided data for this project and helped introduce and explain the project to the residents of the study areas. Walter F. Black, Michelle R. Brown, and Vincent J. Garcia of the Illinois Department of Agriculture (IDOA), under the direction of Warren D. Goetsch, conducted the chemical analyses for National Pesticide Survey (NPS) Methods 4 and 5. Robert G. Brown, IDOA, worked on the initial stages of this project. Dr. Thomas Long of the Illinois Department of Public Health provided comments for the well users/owners regarding the potential health effects for any occurrences of agricultural chemicals. The Illinois State Geological Survey (ISGS) and Illinois State Water Survey (ISWS) relayed these comments, along with the results of the chemical analyses, to the well users and owners. Dr. Thomas J. Bicki helped set up meetings with county officials and representatives of the offices of the ASCS, SCS, and CES to develop the understanding and cooperation that made this project possible. Dr. Dennis Cox and the staff of the Illinois Statistics Office at the University of Illinois assisted in development of the well selection procedure and developed equations needed for statistical analysis of project results.

Sue Bachman of the ISWS performed the nitrate determinations (NPS Method 9) for the project. Eleanor Hopke, Carolyn Hohenboken, Patti Isaacs-Hansen, Holly Wilper, and Kaye Surratt were responsible for chemical analyses and data handling for NPS Method 1. Mary R. Greenpool and Donald A. Keefer of the ISGS provided data, through the manipulation of the Geographic Information System, needed for refining the well selection procedure for the proposed statewide survey and assisted in inventorying and sampling wells. Dennis P. McKenna of the ISGS played an integral part in planning the pilot study. Matthew H. Riggs of the ISGS assisted in the well inventory, well sampling, and geologic characterization during the early phase of the project. Samuel V. Panno and Madalene R. Cartwright of the ISGS assisted in inventorying and sampling wells. Many technical reviewers at the ISGS and ISWS provided suggestions to improve this report. The editorial staff, under the supervision of Ellen Wolf at the ISGS, edited and typeset the report and the staffs at the ISGS and ISWS contributed to the development of the GIS components of the study.

This project was funded by the Illinois Department of Energy and Natural Resources, with David M. Baker serving as project manager, and the Illinois Environmental Protection Agency, with Robert Clarke and, later, Richard Cobb serving as project manager. Financial support was provided from the Environmental Protection Trust Fund.

INTRODUCTION

The Illinois Groundwater Protection Act of 1987 (PA 85-863) (IGPA) mandated that the Illinois Department of Energy and Natural Resources (DENR) conduct an "ongoing program of basic and applied research relating to groundwater," including an evaluation of pesticide impacts upon groundwater. "Such evaluation shall include the general location and extent of any contamination of groundwaters resulting from pesticide use. . . . Priority shall be given to those areas of the State where pesticides are utilized most intensively." In response to this legislative mandate, the Illinois State Water Survey (ISWS) and the Illinois State Geological Survey (ISGS), divisions of DENR, developed a plan to assess the occurrence of agricultural chemicals in rural, private wells on a statewide basis (McKenna et al. 1989). The recommended survey addressed the following question: what percentage of rural, private wells in Illinois is contaminated with the agricultural chemicals most commonly used for production of corn and soybeans? In this report, the term "agricultural chemicals" refers to pesticides and nitrogen fertilizers.

The Interagency Coordinating Committee on Groundwater (ICCG), formed under the IGPA, is charged with coordinating the efforts of the state agencies under the directives of the IGPA. In recognition of the limited knowledge of the extent of agricultural chemicals in Illinois groundwater, the ICCG members from the Illinois Environmental Protection Agency (IEPA), the Illinois Department of Agriculture (IDOA), and the Illinois Department of Public Health (IDPH) requested this pilot study. The study had two main goals. First, it would field test and evaluate various components of the experimental design recommended in the ISGS-ISWS Cooperative Groundwater Report 11, *Agricultural Chemicals in Rural, Private Wells in Illinois: Recommendations for the Design of a Statewide Survey* (McKenna et al. 1989), to streamline the experimental design and make it more economically feasible, and therefore more attractive to the State. Second, it would begin to determine the frequency of occurrence and the probable range of concentrations of agricultural chemicals in rural, private wells in representative hydrogeologic settings.

The legislative mandate addressed the pesticide impacts on groundwater. The pilot study and the proposed statewide plan focus on groundwater drawn from rural, private wells. This approach will maximize acquisition of data on the potential for exposure of the rural residents of Illinois to agricultural chemicals through drinking water and minimize sample collection costs. Inferences drawn from this project, however, are valid for groundwater drawn from rural, private wells, and not from other sources.

- defining the sample population as private, drinking-water wells in rural Illinois;
- using stratified random sampling based on potential for contamination of shallow groundwater as approximated by depth to the uppermost aquifer material;
- sampling wells in five areas that represented four distinct hydrogeologic environments and were approximately 36 square miles (equivalent to a legal township) in size;
- randomly selecting wells within each of the five study areas;
- scheduling well sampling to address temporal variability of pesticides in groundwater;
- characterizing the agricultural practices, hydrology, land use, and shallow hydrogeology of the study areas;
- selecting analytes on the basis of their use for corn and soybean production in Illinois and potential to leach to groundwater;
- using analytical methods from the United States Environmental Protection Agency's (USEPA) National Pesticide Survey (NPS);
- using and, as needed, revising all protocols and procedures of the recommended statewide survey;
- developing the information and data management programs;
- statistically analyzing and interpreting results.

Wells were sampled according to a stratified random sampling scheme. In this type of scheme, the wells are first stratified or categorized, and the wells in those strata or categories are then randomly sampled. In the pilot study, the rural, private wells were categorized by depth to the uppermost aquifer material. The pilot study included a category for an area with dug or bored wells, a category not included in the recommended statewide survey. The statewide survey plan recommended that a separate survey and/or monitoring system be established to address these wells because they were thought to be highly susceptible because of their design. These wells were included in the pilot study to investigate whether there is a difference in the occurrence of agricultural chemicals between dug and bored wells and drilled wells.

The pilot study was conducted jointly by the ISWS and ISGS, with contributions by the IDOA and IDPH. The ISWS and ISGS were responsible for implementing the pilot study and, based on results of the pilot study, for suggesting modifications to the recommended statewide survey. The IDOA volunteered to conduct chemical analyses for two chemical methods that were beyond the budget capabilities of the ISWS and ISGS. The IDPH agreed to review chemical analytical results and report their assessment of the health risks posed by agricultural chemicals found in well-water samples. The IDPH reviewed information that did not include the name of the well users/owners, or the locations of the wells, ensuring the anonymity of the well owner/user. (For convenience, the term "well user" will be used in place of "well user/owner" in this report.)

Pilot Study Plan

The pilot study plan is the organized description of the protocols, programs, and efforts needed to conduct the project. The plan describes the methods for the selection of target analytes, the selection of sample sites, the process for well inventorying, the selection of wells, the process of the well user interview, the selection of the sampling period, the procedures for several field activities (including sample collection, sample transport, and sample tracking), the methods of chemical analyses, and the interpretation and reporting of the results of chemical analyses. Each element of the plan is presented later in this document and includes the changes made from the original recommended statewide plan during the pilot study.

One important feature of the pilot study plan is the test of the hypothesis that depth to the uppermost aquifer material is a key factor in defining the susceptibility of groundwater to contamination from agricultural chemicals. Sampling environments were selected so that other major criteria were equal in each of the five areas. The statistical design of the pilot study differed from that of the recommended statewide survey because the purpose of the pilot study was to test this hypothesis, and the purpose of the recommended statewide survey was to determine the status of agricultural chemicals in rural, private wells.

Over a 1-year period, samples were collected from 48 private wells in each of the township-sized areas for a total of 240 samples. The wells sampled were selected from a complete list of private wells in each study area. The list was developed during the well-inventory phase of the study. Prior to sampling, the well user was interviewed regarding well construction, possible contamination from point sources, and land use around the well. To avoid temporal bias in our observations of the occurrence of agricultural chemicals in the well waters, the wells were sampled as follows. In each area, a total of 48 wells was sampled. Two different wells were sampled on each sampling trip. There were two sampling trips per month to each of the five areas over the 12-month period. Each well was sampled only once, with strict adherence to a written protocol to ensure the collection of high-quality and uniform samples. The personnel collecting samples were trained and practiced with the sampling equipment before sampling began.

Sample tracking was developed as part of the information system to track each sample from materials preparation process in the laboratory, to the field, and back to the laboratory. In the

laboratories, the samples were analyzed using USEPA analytical methods and standard quality assurance/quality control (QA/QC) procedures.

The pilot study was not a substitute for the recommended statewide survey. Rather, it was an effective way to refine the procedures and protocols for the statewide survey. It was also an efficient way to estimate the number of occurrences of target analytes that might be expected in the statewide survey for a given hydrogeologic environment. This estimate may reduce the number of samples needed for the statewide survey.

SELECTION OF TARGET ANALYTES

Target analytes were selected on the basis of their use in corn and soybean production in Illinois, their occurrence in well water or groundwater as shown by previous research, and the availability of methods for chemical analysis. Samples were analyzed for 39 agricultural chemicals, which are listed in table 1. Trade names for the target analytes are available in Pike et al. (1991).

Although identified as a concern by McKenna et al. (1989), chemicals used exclusively for lawn care were not included as target analytes. These compounds are used most intensively in urban and suburban settings. In the pilot study, only wells in rural areas were sampled; therefore, a separate study is needed to address the issue of lawn-care chemicals.

SELECTION OF THE STUDY AREAS

Five areas were selected, representing four distinct hydrogeologic environments and ranging from 35 to 49 square miles in size. These areas were selected using a two-step process. First, a statewide screening was conducted, using the Illinois Geographic Information System (GIS). A detailed check of potential sites followed, using records available to ISGS and ISWS staff. No field checking was done. Figure 1 shows the areas selected for the study. More specific descriptions of the areas are provided in table 2.

Selection Criteria

The following criteria were used to select study areas for the pilot study:

- geologic setting;
- well type;
- land use;
- proximity to investigators' headquarters (Champaign, Illinois),
- availability of data for characterization of the land use, agricultural practices, hydrology, and shallow hydrogeology;
- percentage of land in corn and soybean production;
- cooperation of local agencies and area residents;
- contiguous areas larger than 35 square miles;
- well density.

The criteria were derived from the recommended statewide survey. The first two criteria were used to differentiate the areas to be selected into the five categories. All areas satisfied the remaining criteria. The criteria focus on specific characterization of water samples drawn from private wells in rural Illinois for agricultural chemicals, as well as other factors, including cost and availability of data.

Geologic setting As described by McKenna et al. (1989), the potential for contamination of shallow aquifers from agricultural chemicals was mapped on the basis of depth from land surface to the uppermost aquifer material. The Stack-Unit Map of Illinois (Berg and Kempton 1988) was used as a base. The map information was divided, from highest to lowest potential

Table 1 Target analytes and their estimated detection, minimum quantitation, minimum reporting, and health advisory limits.

Analyte	Type ^a	EDL ^b (µg/L)	MQL ^c (µg/L) ^c	MRL ^d (µg/L)	HAL or MCL ^e (µg/L)
Method 1					
alachlor	H	0.38	1.5	0.75	2
atrazine	H	0.08	0.30	0.15	3
butylate	H	0.15	0.60	0.30	350
carboxin	F	0.25	1.0	0.50	700
chlorpropham	H	0.20	0.80	0.40	—
diazinon ^g	I	—	—	—	0.6
disulfoton ^g	I	—	—	—	0.3
EPTC	H	0.08	0.30	0.15	0.15
ethoprop	I	0.03	0.12	0.06	—
metolachlor	H	0.38	1.5	0.75	100
metribuzin	H	0.20	0.80	0.40	200
simazine	H	0.08	0.29	0.15	1
terbufos ^g	I	—	—	—	0.9
vernolate	H	0.10	0.38	0.19	—
Method 2					
aldrin	I	0.016	0.080	0.040	—
α-chlordane	I	0.019	0.095	0.048	2
γ-chlordane	I	0.019	0.095	0.048	2
dieldrin	I	0.016	0.080	0.040	—
endrin	I	0.015	0.075	0.038	2
endrin aldehyde	D	0.055	0.28	0.14	—
heptachlor	I	0.011	0.055	0.028	0.4
heptachlor epoxide	D	0.020	0.10	0.050	0.2
p,p'-DDT	I	0.020	0.10	0.050	—
propachlor	H	0.064	0.32	0.16	90
trifluralin	H	0.026	0.13	0.065	5
Method 3					
2,4-D	H	0.16	0.8	0.40	70
2,4-DB	H	2.0	10	5.1	—
bentazon	H	0.32	1.6	0.79	20
chloramben	H	0.21	1.0	0.52	100
dicamba	H	0.06	0.3	0.15	200
dinoseb	H	0.21	1.0	0.52	7
picloram	H	0.30	1.5	0.76	500
Method 4					
carbofuran phenol	D	130	650	325	—
cyanazine	H	16.8	84	42	10
desethylatrazine	D	13.8	69	35	—
linuron	H	3.0	15	7.5	—
Method 5					
carbaryl	I	2	6	3	700
carbofuran	I	3	9	4.5	40
Method 9					
NO ₃ ⁻ + NO ₂ ⁻ as N	—	20	60f	30 ^f	10,000

^a D: degradation product; F: fungicide; H: herbicide; and I: insecticide.

^b EDL : estimated detection limit.

^c MQL : minimum quantitation limit = NPS factor times EDL.

^d MRL : minimum reporting limit = half the MQL.

^e HAL : USEPA lifetime Health Advisory Limit (USEPA 1990); MCL = Maximum Contaminant Level. Those compounds without a HAL or MCL are marked by "—".

^f For nitrate, the MCL, not the MRL, was used for the interpretation of the analytical results.

^g The results for this analyte are qualitative only.

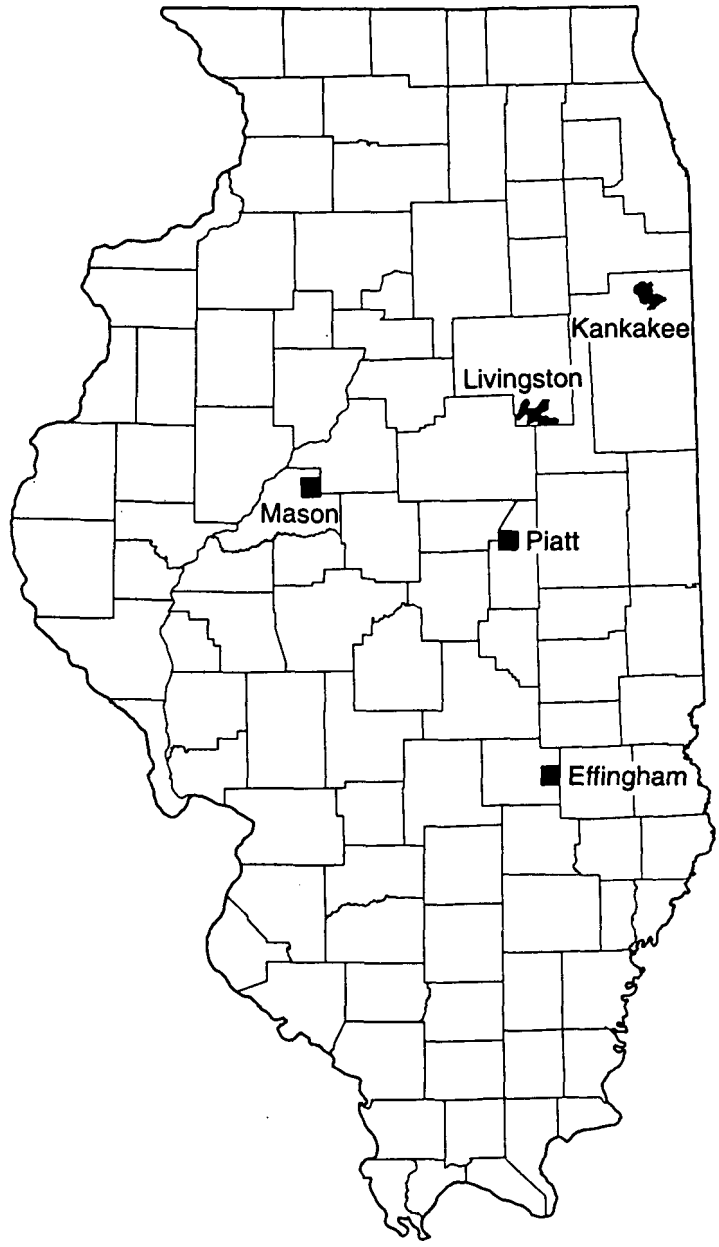


Figure 1 Location of pilot study areas.

for aquifer contamination, into four categories: (1) top of aquifer material within 5 feet of land surface, (2) top of aquifer material between 5 and 20 feet of land surface, (3) top of aquifer material between 20 to 50 feet of land surface, (4) no aquifer material within 50 feet of land surface.

The first four areas listed in table 2 (Mason, Kankakee, Livingston, and Piatt Counties) were selected such that the predominant soil types were Mollisols and the Quaternary deposits were Wisconsinan age. The fifth area selected (Effingham County) has predominantly Alfisols and its Quaternary deposits are of Illinoian age. Alfisols contain less organic matter than Mollisols.

Well type The recommended statewide survey was designed to sample drilled wells. The predominant well type of each area was determined using the WELLFAX database (National

Table 2 Areas included in the pilot study.

County	Location ^a	Depth to uppermost aquifer material (ft)	% in State ^b
Mason	T22N, R6W	< 5	15.6
Kankakee	T31 & 32N, R12 & 13E	5 to 20	13.6
Livingston	T25 & 26N, R6 & 7E, T26N, R8E	20 to 50	9.5
Piatt	T19N, R5E	> 50	52.3
Effingham	T7N, R7E	> 50	— ^c

^a A study area may occupy all or part of a township.

^b Percentage of land area in Illinois within this category. Values do not equal 100% because land area of non-rural areas are not listed.

^c Not reported for this area because it is a subset of the Piatt County study area.

Water Well Association 1986). Less than 33% of wells were dug or bored wells in the first four areas. The fifth area was included in the pilot study to estimate the importance of well type on the occurrence of agricultural chemicals. It was used for a comparison between the large-diameter dug and bored wells and the drilled wells of the other four study areas. Dug and bored wells are inherently more susceptible to contamination than drilled wells because they are shallower and have larger diameter openings, allowing the possibility of greater infiltration from surface contaminants. More than 67% of wells were dug and bored wells in the fifth area.

Land use The focus of the recommended statewide survey was to sample rural, private wells. “Rural” was defined as all areas except incorporated areas with a population greater than 2,500. Forested or other natural areas greater than 1 square mile were also excluded from “rural” areas (McKenna et al. 1989).

Proximity to investigator’s headquarters (Champaign, Illinois) This factor was included to help control travel costs. A maximum distance of 100 miles from Champaign was chosen so that field work would not require overnight travel.

Availability of data for characterization The availability of data was considered in the selection of the study areas. Essential data for characterization included a modern soil survey, geologic data, and hydrologic information. Areas with more available data were favored over areas lacking data. The detailed characterization of all five areas appears in Barnhardt et al. (1992). Some aspects of the characterization performed for the pilot study involved much greater effort than will be feasible during the recommended statewide survey. These tasks were undertaken intentionally to determine which were realistic within the constraints of time, labor, and cost for the recommended statewide survey. Suggestions for changes are made in the characterization section of this report.

Percentage of land in corn and soybean production In terms of total volume of agricultural chemicals used, the major uses of agricultural chemicals in Illinois are in the production of corn and soybeans. Consequently, areas were chosen that had greater than 50% of the land area in corn and soybean production. Crop production data were obtained from the IDOA (1978).

Cooperation of local agencies and area residents The cooperation of local agencies, such as the Cooperative Extension Service, the Soil Conservation Service, Agricultural Stabilization and Conservation Service, and county public health departments, was vital for securing the cooperation of area residents and obtaining the data necessary for characterization. The cooperation of the area residents was essential to sample their water-supply wells. To obtain the necessary cooperation, presentations were given in each selected locality to county officials. Articles describing the project were published in local newspapers. In some areas, the

agricultural extension agent sent letters to farmers to explain the process and encourage participation.

Contiguous areas greater than 35 square miles and well density These criteria were included to ensure that the selected areas contained the minimum of at least 60 wells estimated to satisfy the needs of the project. Data on well density were obtained from the WELL-FAX database (NWWA 1986).

WELL INVENTORY

In each study area, an inventory of all rural, private, drinking-water wells was made. Each residence was identified, and the drinking-water supply was determined. Initially, an effort was made to identify residences from aerial photographs, plat books, and topographic maps. This effort had limited success because of the lack of availability of current materials. Survey staff members then visited and traveled the roads of each study area, marking new dwellings on a topographic map, crossing off abandoned or burned houses, and stopping at each rural residence or farmstead. When residents were at home, a staff member briefly described the pilot study and gave the resident a fact sheet (appendix A). Residents were asked to provide the following information: name, address, phone number, well type, and the year the well was constructed. Renters were asked to provide the name, address, and phone number of the owner. When residents could not be contacted at home, a fact sheet was left at the dwelling; information was sometimes provided by neighbors.

A high degree of participation was necessary to obtain good statistical results. This participation was sought by presenting the benefits of the study to the residents and the mechanics of the study in a clear and personal way. Staff members conducting the inventory emphasized that the chemical analyses were at no cost to the resident and that site-specific results would only be revealed to the well user and owner. Many residents were aware of the study through information in local newspapers or in newsletters distributed by county agricultural agencies. Confidentiality and prior notice from a familiar source were very important factors in securing the cooperation of the well users.

Each residence was considered a potential well site, except where more than one residence used the same well. In those cases, the residences were grouped together and numbered as one site. The owner of the land or the individual designated to have responsibility for the well was the individual interviewed. Each well site was assigned a site code number. Only wells with the potential to meet our sample population criteria were assigned a number in order to avoid introducing a bias. Vacant houses were not considered suitable unless they could potentially be occupied during the sampling period. Field teams used their judgement to determine if a vacant structure had the potential to be occupied during the study. Sometimes owners were contacted to inquire if they had intentions of leasing or living on the property. Results of the well inventory are presented in table 3. For the reasons mentioned, there were fewer suitable sites than there were wells.

The inventory did not account for changes in the population during the study. In one study area, one house was physically moved into the area and two new houses were constructed during the sampling period. Home sales, fires, winter vacations, and other problems that affected the sample population were encountered during the study. To allow for these problems, a larger number of well sites were randomly selected than were required to be sampled.

The procedures used to inventory wells worked well. Most of the residents contacted participated in the initial well inventory. Although effective, the method was labor intensive. For example, in the Mason County study area, which includes approximately 36 square miles, a total of 162 potential well sites were identified and visited. These visits took place during five

Table 3 Results of the initial well inventory.

Category	County				
	Mason	Kankakee	Livingston	Piatt	Effingham
No. of potential well sites	162	188	164	104	136
No. of contacted	134	133	145	85	106
No. of potentially suitable	151	177	155	87	134
Well type ^a					
% Drilled/driven	61	29	65	68	1
% Bored/dug	0	0	6	0	90
% Unknown	39	71	29	32	9
Residence type ^a					
No. of active farms	51	120	100	37	74
No. of rural residences	71	43	45	47	47
No. of unclassified	40	25	19	20	15

^a Based on the number of potential well sites in each study area.

different trips and required approximately 120 hours to complete. The estimated cost for conducting the initial inventory in Mason County was approximately \$2000, or about \$12 per site. Suggestions for changing this process are made in the recommendations section.

WELL SELECTION

Wells to be sampled were selected from the list of potentially suitable wells compiled during the well inventory. Wells were randomly selected in each study area. All wells inventoried in an area were numbered sequentially. A computer code was used to generate 75 random numbers for each study area. The first 48 of these wells were selected, and their users were contacted for interviewing and sampling. The remaining 27 wells were designated as alternates. An alternate was selected if a well user declined to participate in the study. The wells were sampled in the same order as the random numbers were generated. For example, if the first random number generated was 67, then the well assigned the number 67 would have been sampled first.

The procedure for well selection in the recommended statewide survey has been revised, based on the experiences of the pilot study, from the procedure proposed by McKenna et al. (1989). The revised procedure is more involved than the selection procedure used for the pilot study and includes the following steps.

- Using the GIS, identify all sections, approximately 1 square mile in area, in rural Illinois covered by each of the four categories identified in table 2.
- Select those sections that comprise only one category.
- Randomly select 200 sections for each category.
- Determine the total area of each category in the state.
- List and number all wells meeting the definition of the sample population in the selected sections for each category.
- Randomly select two wells per section per category. If there are fewer than 384 wells per category, randomly select additional wells from sections with three or more wells.

These steps are written under the assumption that 384 wells are to be sampled in each category (McKenna et al. 1989). The sample size for the recommended statewide survey may change, however, based on the results of this pilot study.

INTERVIEW PROCESS

The well users whose wells were selected for sampling were interviewed by ISGS or ISWS staff prior to well sampling. Questionnaires were developed for the recommended statewide survey; they were similar in design to those used by the USEPA during the NPS. The first questionnaire was for all participants. The second questionnaire was for participants residing on active farm sites. Information about the well site and land use in the area around the well was gathered for use during the data interpretation portion of the pilot study. Data on agricultural chemical use were also collected. The information was to be used to help determine what types of activities influence groundwater quality. After the interviews were completed, project staff members conferred to revise the questionnaires for use in the recommended statewide survey project. The revised questionnaires appear in appendix B of this report.

The questionnaires were administered to an adult member of each residence selected for sampling. The first part of the first questionnaire dealt with activities and features near the well head and well construction and history. The second part of the first questionnaire addressed potential sources of pesticides and nitrate around the well. Information was also collected from rural residents and farmers on non-commercial use of pesticides and nitrogen near the well site. In the second questionnaire, active farmers were asked for information about their practices with respect to pesticides and nitrogen fertilizers during the past 5 years.

During the interview, a detailed sketch of the well site and the surrounding area was drawn. The sketch included buildings, wells, and other features that might impact the quality of the water reaching the well. These features included pesticide mixing points, septic systems, underground storage tanks, ditches, ponds, and the location of spills or other reported incidents. The sketch also showed roads, driveways, and other significant information to help the sampling teams locate the exact sampling point.

During the interview, staff members received permission from an adult resident for the sampling team to have access to the well site for sample collection. An example of the well-site access permission form used is shown in figure 2. The form was signed by an adult resident and was to be used in the event that anyone questioned the presence of the sampling team on the property. The well user could still change his or her mind about participating in the study if he or she so desired.

The Department of Energy and Natural Resources (DENR) is conducting a survey of Illinois rural private water supply Wells. The objective of the survey is to determine the occurrence of pesticides in those wells. Your well is one of those randomly selected to be included in the survey. As part of the survey, staff from the DENR will be collecting a set of water samples from the well. If you agree to participate, you will be given a report of the results of the chemical analyses performed on your well. This information will not be released in any way that will link the results from your well to your name and address. You will be contacted approximately two weeks before the DENR staff visits your well. It will not be necessary for you to be present during the sampling unless you so desire.

If you agree to participate, please read and sign the following:

I give permission to the DENR to have access to my property in order to collect water samples at my well for the Agricultural Chemicals in Rural Private Water Supply Pilot Study. I understand that I will be contacted in advance of the sample collection date to arrange the visit.

Signature _____ Date _____

Figure 2 Well-site access permission form.

SELECTION OF SAMPLING PERIOD

The well-sampling period was selected to avoid any temporal bias and to accommodate the quantity of samples the laboratories could analyze at one time. Published research results (McKenna et al. 1988, Hallberg 1986) indicated that the occurrence of agricultural chemicals in water wells would vary temporally. The exact temporal variation could not be predicted due to limited information. Therefore, well-water samples from each area were collected at nearly equal intervals for 1 year, sampling each well only once. The number of samples to be collected during each sampling trip was determined by the capacity of the laboratories to analyze the field samples and associated QA/QC samples.

Fifteen samples (ten field and five QA/QC) were collected from wells in the five study areas for each sampling trip. Two sampling trips were made each month. Samples were collected on Monday and Tuesday of the week. In the event of a Monday holiday, samples were collected on Tuesday and Wednesday. Sampling began the week of March 3, 1990 and was completed the week of February 18, 1991.

FIELD-RELATED PROCEDURES

Throughout the study, the field-related procedures were tested and revised as necessary to refine the procedures for the recommended statewide survey. As a result, some major and many subtle modifications of the protocols have been made. The use of a multiple-part form for tracking the materials and sample transfer was found to be efficient and is an example of a subtle modification.

Field-Sampling Protocol

The ISWS and ISGS developed a comprehensive sample collection protocol for the field-sampling teams. The protocol includes notification of the well users of the sampling date, and it allows for the preparation of the sample labels. The Sample Coordinator from the ISWS, with cooperation from the ISGS team, updated the protocol over the course of the project in response to changes required in the field. It was expected that suggestions for improvements of this protocol would be made by the sampling teams as they encountered problems or discovered unexpected situations in the field. The final version of the protocol, revised from the original, evolved throughout the study and is listed below.

Sampling-trip preparation and date confirmation The random sampling order was generated for each of the five study areas and a letter of notification was sent to each appropriate well user informing him or her of the approximate sampling time (e.g., spring 1990, summer 1990). About 2 weeks before a sampling trip, each well user was called and informed of the specific sampling date. At this time, any necessary special arrangements were made, such as planning to sample at a time when someone would be at home, to give samplers access to an inside tap, or to restrain pets. Site residents who could not be reached by phone were notified by mail. If a site owner needed to change the sampling date, his or her schedule was accommodated whenever possible. The Project Information Officer at the ISWS was notified of any change in sampling dates.

Preparation of sampling kits Each analytical laboratory was responsible for providing clean sample containers prepared with any necessary sample preservative. During the project, a change was made such that preservatives for use in Methods 1 and 3 were added in the field. Laboratory personnel who provided containers with sample preservatives to the field teams signed the sample-tracking forms (fig. 3), and the sample containers were delivered to the ISWS. Personnel delivering sample containers signed the sample-tracking forms. Each sample bottle was labeled at the ISWS laboratory, and the appropriate bottles were organized into sampling kits. One kit was prepared for each study area and the required kits were given to the

Method No. - Sample Trip No.

Sample Number _____

Initial Material Preparation _____
 Released by: _____ Agency _____
 Received by: _____ Agency _____
 Date: _____ Time _____

Materials Prepared For Sampling Teams **METHOD NO. BOTTLES TYPE PRESERVATIVE OTHER**
 ___ 1 _____
 ___ 2 _____
 ___ 3 _____
 ___ 4 _____
 ___ 5 _____
 ___ 9 _____

Released by: _____ Agency _____
 Received by: _____ Agency _____

Samples Collected & Transported Collected by: _____ Agency _____
 Received by: _____ Agency _____
 Date: _____ Time _____
 Comments on sample condition _____

Any alternative sites sampled: ___ Yes ___ No
 Have all bottles from the two sampling teams been accounted for?
 ___ Yes ___ No

Samples Transferred To Laboratory Released by: _____ Agency _____
 Received by: _____ Agency _____
 Date: _____ Time _____

Comments on sample condition _____

Figure 3 Sample-tracking form.

sampling crews. Spare bottles were supplied in case of accidental breakage during the trip. A schematic diagram describing the transfer of bottles and samples and the use of the sample-tracking forms is depicted in figure 4.

On-Site Procedures

Arrival at a site Upon arrival at the site, the sampling crew reminded the well user that sampling was to take place. The following information was recorded on the well-sampling information sheet (fig. 5): date and time of arrival of the field team, site ID and random number, sampling personnel, environmental conditions, and any additional information that could have an impact on the integrity of the samples.

Equipment setup The spigot sampled was first rinsed thoroughly with deionized water. A Y-adaptor was also rinsed and attached to the spigot, with the ball valve in both sides of the adaptor closed. A garden hose was then attached to one end of the adaptor. The spigot was

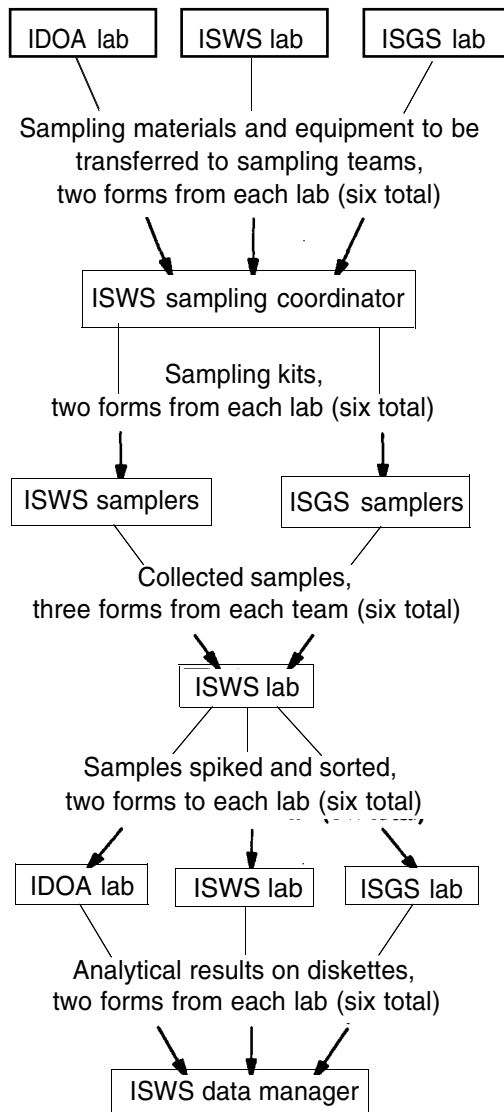


Figure 4 Transfer scheme for samples.

turned on and the ball valve opened such that water flowed through the garden hose to an appropriate drainage area. The time that the spigot was turned on was recorded on the well-sampling information sheet. The flow rate through the garden hose was measured using a graduated bucket and stopwatch, and the information was recorded. After the flow rate was measured, water was sent through the flow-through cell.

On the remaining end of the Y-adaptor, a step-down connector was used to attach Teflon tubing to the flow-through cell from the spigot. All sections of the Teflon tubing used were rinsed with deionized water. This tubing was covered with pipe insulation to minimize changes in the water temperature during sample collection. The remaining equipment was set up on a sheet of clean plastic, both for cleanliness and to protect the property.

Preparation of flow-through cell components The sampling flow-through cells were a slightly modified version of the cell developed by the ISWS (Garske and Schock 1985). The original sampling cell was invented and patented for use in a study to evaluate the frequency of

sampling needed for statistically sound evaluations of groundwater with respect to various chemical parameters (Barcelona et al. 1989). The cell was modified for the pilot study by changing from a multiple-source input to a single-source setup. The original cell also included a redox potential measurement, whereas this one did not (see fig. 6). Finally, this cell used a digital readout conductance meter instead of the manual Wheatstone bridge system previously used. The cell has three probes, which allow dual sample collection and constant parameter checking during the flushing of the well.

The ISWS flow-through cell provides simultaneous measurement of pH, specific conductance, and temperature under conditions as close to in situ as practical. The flow-through cell is equipped with four electrodes: a Ross Sure-Flow (Orion No. 8165BN) combination pH electrode, an Orion (No. 8156BN) combination pH electrode, an Orion (No. 917001) automatic temperature compensation sensor probe, and a VWR Scientific (No. 525) platinum specific conductance probe. For pH measurements, the Ross Sure-Flow electrode was the primary electrode. The other pH electrode is a general purpose model and was intended as a backup. (Please note that the use of trade names is for the purpose of description only and does not imply endorsement by either the ISWS or ISGS.)

pH calibration Before each sampling session, the pH electrode was standardized against two buffers of pH values that bracketed the expected sample pH (e.g., pH 4 and 7, or pH 7 and 10). Buffer solutions traceable to the National Institute for Standards and Technology (NIST)

Well Identification No. _____ Random No. _____

Well User _____

Well Location _____

Sample Collectors _____

Sampling Date _____ Arrival Time _____

Environmental Conditions: Temp _____ Wind _____

Cloud Cover (%) _____ Precipitation _____

Other Conditions (Dust, pesticide spraying, etc.) _____

Time Spigot Turned On _____

Flow Rate Through Garden Hose _____

Comments: _____

Figure 5 Information sheet for well sampling.

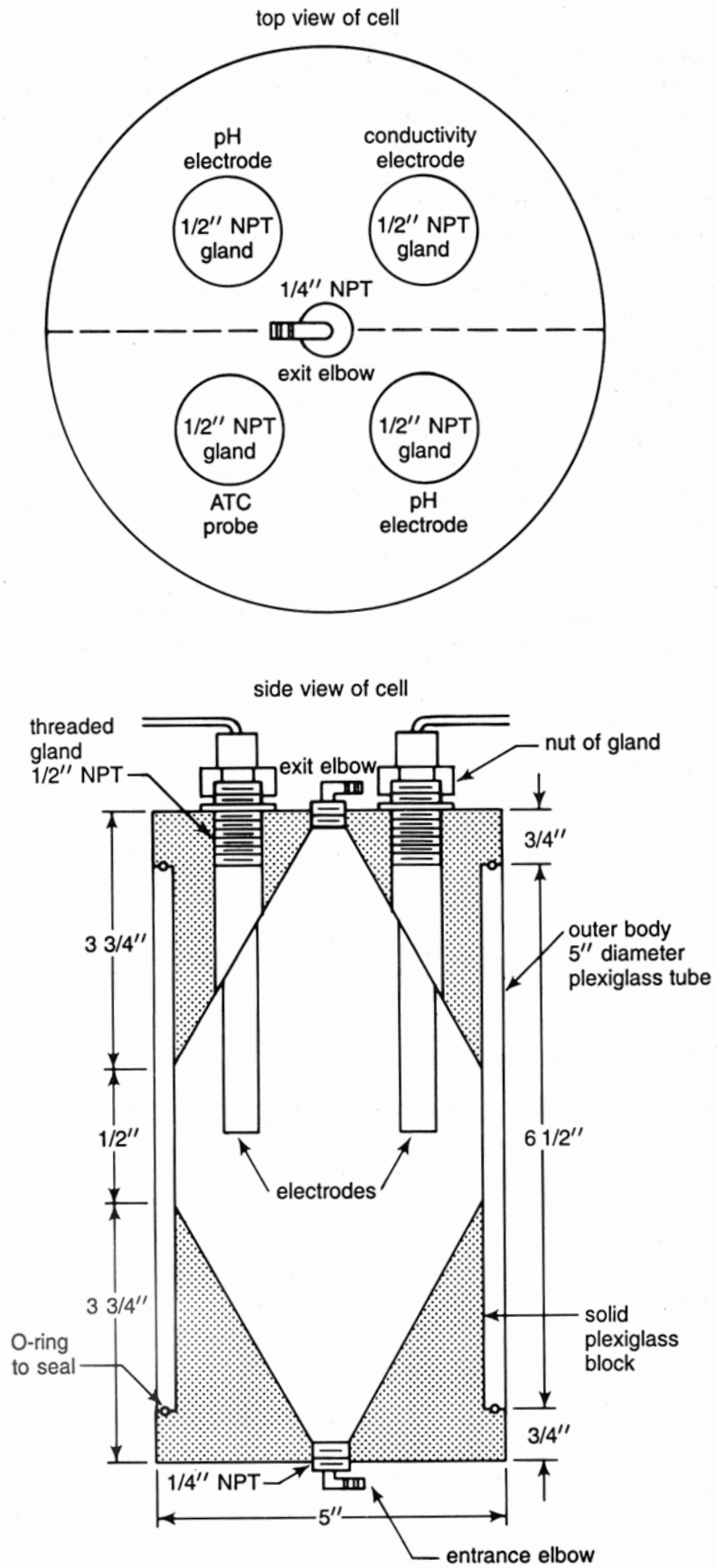


Figure 6 Schematic of the sampling cell (drawing not to scale).

Well Identification No. _____ Random No. _____

pH Buffer Used _____ Buffer Lot No. _____

pH Buffer Used _____ Buffer Lot No. _____

Time Flow Started Through Sample Cell _____

Flow Rate Through Sample Cell _____

Record Readings Below Until Stable and at End of Test

Time	Temperature	pH	Conductance
t ₀	_____	_____	_____
t ₅	_____	_____	_____
t ₁₀	_____	_____	_____
t ₁₅	_____	_____	_____
t ₂₀	_____	_____	_____
t ₂₅	_____	_____	_____
t ₃₀	_____	_____	_____
Post Sample	_____	_____	_____

Sampling Start Time _____ Sampling End Time _____

Figure 7 Well-purging record sheet.

(Fisher Scientific, color-coded, pH 4, 7, 10) were obtained in 500-mL lots. Portions of buffer solution sufficient for a single calibration were sealed in 25-mL glass vials at the ISWS laboratory to isolate them from the atmosphere until use. The specific lot numbers of the buffers used at a given well site were noted on the well-purging record (fig. 7). The pH meter was calibrated according to the manufacturer's instructions.

Conductance calibration The specific conductance probe was calibrated at each well site against a standard of known specific conductance. Standard conductance solutions were prepared in each laboratory by serial dilution using class-A volumetric glassware and double-deionized water. Stock solutions were initially provided at the time of the purchase of the probe. Additional stock solutions were prepared using reagent grade analytical salt (potassium chloride). Each new lot of calibration standard was verified by comparison with NIST or USEPA reference standards, as well as by comparison with previous lots of standard. The conductance meter was calibrated according to the manufacturer's instructions.

Well purging A sampling protocol was used to obtain samples chemically representative of the well water, not the distribution system. Purging was verified for each well site at the time of sampling by monitoring the well-purging parameters: pH, specific conductance, and temperature. The monitoring was conducted by using the ISWS flow-through cell until all the parameters had stabilized, indicating that the distribution system had been flushed.

Once the pH and conductance calibration procedures were completed, water flow was started through the cell by opening the ball valve on the Y-adaptor. The time water flow began was recorded on the well-purging record (fig. 7), as was the measured flow rate through the cell. The minimum rate of flow through the cell was 1 liter per minute, if possible.

After flow through the cell was initiated, the sampling crew monitored the purging parameters and recorded them at approximately 5-minute intervals on the well-purging record. Sample collection began once all of the parameters had stabilized to within ± 0.05 pH, $\pm 5\%$ change in conductance, and $\pm 0.5^\circ$ C for three successive readings (i.e., a 10-minute interval). If consistent readings were not obtained after 30 minutes of purging, the purging was stopped and sampling begun.

While the purging process was being monitored, well water was allowed to discharge through the hose at as high a flow rate as possible. Well-purging flow rates were reduced when the owner so requested or during the summer months when the water level of the well was suspected to be low.

Sample collection Once the well-purging parameters became stable, samples for each of the six analytical methods were collected. Each sampling team was provided with an information sheet that listed the random sample bottle numbers used at each site, including the type(s) of QA/QC samples, if any, to be collected.

To expedite the sample-handling procedure, all sample containers were brought to the field thoroughly cleaned, labeled, and, except for Methods 1 and 3, containing any required preservative. The specific types of sample containers used for each analytical method are listed in table 4.

Samples were collected ahead of the flow-through cell. A valve switch on the outside of the flow cell was used to divert flow from the cell to the sample-filling tube. Before filling the sample containers, the sampling personnel put on a pair of clean surgical gloves. The flow rate through the Teflon tubing was then reduced to avoid splashing and overfilling. The starting time of sampling was recorded on the well-purging record. Each sample container was filled to a predetermined mark, keeping the sample tubing as close to the mouth of the bottle as possible without touching it. Preservation chemicals for NPS Methods 1 and 3 were added to the samples from individual vials prepared by the respective analytical laboratories. Each container was capped tightly and shaken to ensure that the sample water was mixed with the chemical preservative.

After filling all of the sample containers, the sampling team recorded the time of completion and again routed the water through the flow-through cell. Final pH, conductance, and temperature readings were recorded after flushing the stagnant water from the cell.

QA/QC sample collection Three types of QA/QC samples were collected: field blank, field duplicate, and spike. Field blanks were collected at one randomly selected site per day by each team for a total of three field blanks per sampling trip. Samples designated as field blanks for each method were filled in the field from bottles of reagent-grade water supplied by each analytical laboratory. Handling of the field blanks was otherwise the same as for the well-water samples.

Field duplicates are two separate samples collected at the same place and time. The simultaneous collection of duplicate samples was accomplished using a tee-union at the end of the sample tubing. One site per sampling trip was randomly selected for the collection of field duplicates.

Table 4 Sample preservation and handling according to analytical method.

Method	Preservative ^a	Volume (mL)	Bottle type ^b	Sample volume
NPS-1	Dichloromethane	2.5	A	1 L
NPS-2	Mercuric chloride	1.0	B	1 L
NPS-3	Dichloromethane	5.0	B	1 L
NPS-4	Mercuric chloride	1.0	B	1 L
NPS-5	pH buffer	2.5	C	40 mL
NPS-9	Sulfuric acid	0.25	D	125 mL

^a Dichloromethane: pesticide grade.
 Mercuric chloride: 1 g reagent grade HgCl₂ dissolved in 1 L deionized water.
 pH buffer: 100 mL of 1 M potassium acetate solution plus 156 mL of 1 M chloroacetic acid solution.
 Sulfuric acid: double-distilled, concentrated H₂SO₄.

^b A: 1-L Amber glass with PTFE-lined cap.
 B: 1-L Clear borosilicate glass with PTFE-lined cap.
 C: Amber glass vial with PTFE-lined septum.
 D: High density polyethylene.

One site per sampling trip was randomly selected for analytical spiking. These samples also required simultaneous collection with the well sample. If a case arose where a field duplicate and a spike were to be collected at the same well site, the duplicate was collected simultaneously with the well sample and the spiked sample was collected immediately following. For the health and safety of the sampling personnel and greater accuracy, spiking was performed in the laboratory.

Sample transport and transfer Once a sample was collected, it was immediately placed in a plastic ziplock bag and then placed in an ice chest to maintain sample integrity. Certain of the target analytes are unstable and may decompose upon excessive exposure to heat or light.

The samples were transported back to the ISWS laboratory at the completion of sampling, and each sample was accounted for on the sample-tracking forms. Any comments on the condition of the samples as received were recorded. The samples were sorted according to analytical method, and designated samples were spiked.

After being spiked, the samples were transferred to the individual laboratories for analysis. Receipt of the samples was acknowledged by a laboratory staff member on the sample-tracking form. The last copy of these forms was sent to the ISWS Project Information Officer, and notification of sampling of alternate sites, if any, was made at that time.

Sample spiking A staff member not directly involved in the chemical analysis was responsible for spiking all samples, regardless of the analytical method. Each laboratory performing a set of analyses provided an appropriate spiking solution. Pipettes, syringes, and other laboratory apparatus used for sample spiking were dedicated for each analytical method.

Samples for Method 9 were spiked by diluting an aliquot of 1000-mg/L standard nitrate stock to a volume of 50 mL in a class-A volumetric flask. All other samples (Methods 1 through 5) were spiked by directly adding an aliquot of stock spike solution to the sample container. The volume of sample into which the spike was added was determined at the ISWS laboratory. The target spike concentration for each analyte was approximately ten times the estimated detection limit (EDL).

CHEMICAL ANALYSIS

The development of the methods of chemical analysis included the following steps:

- purchasing, installing, setting up, and calibrating equipment,
- debugging methods using field samples,
- estimating detection limits,
- determining average percent recoveries,
- implementing QA/QC methods,
- extracting and preparing of samples.

Analytical Methods

Groundwater and quality-control samples were analyzed following USEPA NPS Methods 1, 2, 3, 4, 5, and 9. Work began using the methods as described in USEPA (1987). During the study, the methods were progressively updated and clarified by the USEPA and its contractors.

In 1988, USEPA Water Quality Method 507 was derived from NPS 1, 508 from NPS 2, 515.1 from NPS 3, and 531.1 from NPS 5 (USEPA 1988). NPS Method 9 was originally based on USEPA Method 353.2 and was not changed during the study. For the sake of simplicity and consistency, the NPS designations are retained in this report.

NPS Method 1 (USEPA Method 507) NPS Method 1 involves the determination of nitrogen- and phosphorus-containing pesticides in groundwater by gas chromatography (GC) with a nitrogen-phosphorus detector (NPD). The water sample is preserved with mercuric chloride and refrigeration. A measured volume of water, approximately 1 liter, is spiked with a surrogate standard, 1,3-dimethyl-2nitrobenzene (1,3-D-2-N), and buffered to pH 7. Sodium chloride is dissolved in the water to aid in the subsequent extraction of the analytes into dichloromethane (methylene chloride). The water and the dichloromethane phases are separated after solvent extraction. Trace amounts of water are removed from the dichloromethane phase with anhydrous sodium sulfate, and the solvent volume is decreased to about 2 mL by distillation. The remaining dichloromethane is exchanged with methyl tert-butyl ether (MTBE). The internal standard, triphenyl phosphate, is added to the sample prior to capillary-column GC.

NPS Method 2 (USEPA Method 508) NPS Method 2 involves the determination of chlorinated pesticides in groundwater by GC with an electron capture detector (ECD). The water sample is preserved with mercuric chloride and refrigeration. A measured volume of water, approximately 1 liter, is spiked with a surrogate standard, 4,4'-dichlorobiphenyl (4,4'-DCB) and buffered to pH 7. Sodium chloride is dissolved in the water to aid in the subsequent extraction of the pesticide analytes into dichloromethane. The water and dichloromethane phases are separated after solvent extraction. The dichloromethane phase is dried with anhydrous sodium sulfate, and the solvent volume is decreased to about 2 mL by distillation. The remaining dichloromethane is exchanged with MTBE. The internal standard, pentachloronitrobenzene (PCNB), is added to the sample prior to capillary column GC.

NPS Method 3 (USEPA Method 515.1) NPS Method 3 involves the determination of chlorinated acids in groundwater by GC with an ECD. The water sample is preserved with mercuric chloride and refrigeration. The sample, approximately 1 liter, is spiked with a surrogate standard, 2,4-dichlorophenylacetic acid (2,4-DCAA). Sodium chloride is added to the water to aid in the extraction of the pesticide analytes. The sample pH is adjusted to 12 with sodium hydroxide to hydrolyze the organic acid esters. Interfering organic compounds are removed from the water by extraction into dichloromethane. The organic phase is discarded and the remaining aqueous phase is acidified. The chlorinated acids are then extracted into ethyl ether. The volume of ethyl ether is reduced, and the remaining ethyl ether is replaced by MTBE and distillation of the ethyl ether. The organic acid analytes are methylated using diazomethane. Excess derivatizing reagent is removed and interfering compounds are then removed by

passing the sample through a Florisil column. The internal standard, 4,4'-dibromooctafluorobiphenyl (4,4'-DBOB), is added to the sample prior to capillary-column GC.

NPS Method 4 NPS Method 4 involves the determination of pesticides in water by high performance liquid chromatography (HPLC) with UV detection. The water sample is preserved with dichloromethane and refrigeration. A measured volume, approximately 1 liter, of sample is spiked with carbazole (surrogate standard) and buffered to pH 7. Sodium chloride is dissolved in the sample to aid the extraction and the sample extracted with dichloromethane. The extract is dried with sodium sulfate, concentrated, and the solvent is exchanged with methanol. The methanol is adjusted to 5 mL and spiked with an ethylbenzene internal standard before analysis by HPLC.

NPS Method 5 (USEPA Method 531.1) NPS Method 5 involves the measurement of N-methylcarbamoyloximes and N-methylcarbamates in groundwater by direct aqueous injection HPLC with post-column derivatization. The water sample is preserved with monochloroacetic acid buffer and refrigeration. The sample is filtered and an aliquot is injected onto a reverse-phase HPLC column where the analytes are separated by gradient elution chromatography. After elution, the analytes are hydrolyzed and reacted with o-phthalaldehyde (OPA) and 2-mercaptoethanol to form derivatives detectable by fluorescence monitoring. The internal standard is 4-bromo-3,5-dimethylphenyl-N-methylcarbamate.

NPS Method 9 (USEPA Method 353.2) NPS Method 9 involves the determination of nitrate-nitrogen in groundwater by automated cadmium reduction and colorimetry. Water samples are preserved with 2 mL sulfuric acid per liter and then refrigerated. Automated flow-injection analysis (Lachat FIA system using QuikChem Method 10-107-04-1-A) quantitatively reduces nitrate to nitrite by passage of the sample through a "copperized" cadmium column. The nitrite formed by this reduction, including any nitrite originally present in the sample, is diazotized with sulfanilamide and then coupled to N-(1-naphthyl)-ethylenediamine dihydrochloride. The concentration of water-soluble magenta dye produced is quantified by measuring its absorbance at 520 nm. Nitrite is determined in a second aliquot of sample without passing the aliquot through the cadmium reduction column. Nitrate concentration is then calculated by difference.

Identification and Quantitation

Unavailable reference standards The original pilot study proposal (McKenna et al. 1989) anticipated that disulfoton sulfone and sulfoxide would be analyzed by Method 1, acifluorfen be analyzed by Method 3, and metribuzin degradates by Method 4. However, analytical standards were unavailable from the USEPA or commercial suppliers. Therefore, it was not possible to quantitate these analytes.

Detection and reporting limits The NPS methods define the estimated detection limit (EDL) as the minimum analyte concentration above zero that can be measured and reported with confidence that the concentration is greater than zero. The EDL for each analyte is computed in two ways, and the method that yields the higher detection limit is used. In the first computation, the standard deviation of n (where $n \geq 4$) determinations of the concentration of the analyte is multiplied by the Student t value appropriate for a 99% confidence level and $n-1$ degrees of freedom. In the second method, the EDL is the minimum initial analyte concentration in a water sample that will give a signal-to-noise ratio of 5 in the chromatograms.

The instructions in the NPS methods for determining the EDL based on standard deviation were unclear because the standard deviation is dependent on analyte concentration. The concentration at which to calculate the standard deviation in the first method was not clearly defined in the 1987 NPS method descriptions. Therefore, the second method was used for calculating the EDL. These values were determined using the primary-column results for extracts from fortified distilled deionized water. The method detection limit (MDL) used in

this study for nitrate-nitrogen was three times the standard deviation of a mean low-level concentration.

In the National Pesticide Survey Phase I Report (USEPA 1990), the minimum quantitation limit (MQL) is defined as four times the EDL for Method 1, it is five times the EDL for Methods 2, 3 and 4, and it is three times the EDL for Methods 5 and 9. The minimum reporting limit (MRL) was defined as one-half of the MQL. These definitions have been adopted in this study, and the respective values for each analyte in this study are shown in table 1. Concentrations above the MQL are reported as quantitative results. Those values below the MQL but above the MRL are reported as detected, but without quantitation. Concentrations below the MRL are not reported.

Analyte quantitation The 1987 NPS method descriptions did not specify how to resolve quantitative differences between primary and confirmation column concentration results. In the NPS Phase I Report (USEPA 1990), however, the following criterion was given.

"Quantitative results were reported, if the concentration determined on the confirmation column agreed within 25% of that determined on the primary column. If this requirement was met, the quantitative results determined on the primary column were reported. If this requirement was not met, and for analytes determined using a GC method, the presence of the analyte was confirmed by GC/MS, and the detection of the analyte was reported without quantification."

This criterion was used for reporting pilot study results.

Analyte identification Retention time of a single analyte peak on a single GC column is insufficient to identify a component in a complex environmental sample, such as the water samples analyzed in this study. For a minimum level of certainty, a tentatively identified analyte peak must also elute at the expected time on another GC column with a dissimilar stationary phase. Elution within the expected time windows on two columns increases the probability that an unknown peak is a target analyte, but it is still not conclusive. In the NPS, only 82.5% of the analyte identifications based upon dual elution times were confirmable by mass spectrometry.

The staff of the Hazardous Waste Research and Information Center (HWRIC) of the DENR assisted in confirming tentative detections for various analytes in Methods 1 and 3. The confirmations were completed using either full-scan or selected-ion-monitoring (SIM) mass spectrometry. The detections determined by retention times that were confirmable by monitoring three or four characteristic ions (SIM) are shown in table 5; the detections confirmable in full-scan mode are also shown. The degree of certainty for confirming detections varied according to method. The greatest degree of certainty was achieved with the full-scan, followed by SIM and dual-column GC. Identifications of Methods 2 and 3 analytes were checked by using the Joint Survey Hewlett-Packard Model 5890 GC coupled to a 5988A MS. Positive detections of bentazon in extracts were confirmed in full-scan mode. Picloram was determined in several extracts by dual capillary column GC. Because the concentrations of picloram, in all but one case, were below the GC/MS detection limit, its presence was confirmed in only one extract using the VG Tribrid GC/MS at HWRIC in full-scan mode. Mass spectra of field-sample analytes were compared with standard spectra and with a NIST library file. Because of questions regarding the possible occurrence of simazine in some of the field samples, particular attention was given to confirming those detections. A mass spectrum for a simazine standard is compared in figure 8 and table 6 with that of an analyte in two field-sample extracts. The mass spectra indicate that the compounds in the field sample were in fact simazine.

Modifications to NPS Methods

The methods of chemical analysis were improved throughout the course of the study. The following modifications improved the analytical methods.

Table 5 Degree of certainty of confirmation for target analytes reported in field samples.

Sample ID No.	Dual-column GC retention times	Selected-ion monitoring GC/MS	Full-scan GC/MS
0822	atrazine	atrazine	— ^a
0869	atrazine	atrazine	atrazine
1830	α -chlordane	α -chlordane	—
	γ -chlordane	γ -chlordane	—
1855	picloram	—	—
2221	atrazine	atrazine	atrazine
	metribuzin	metribuzin	metribuzin
	picloram	—	—
	simazine	simazine	simazine
2122	picloram	—	picloram
2893	bentazon	—	bentazon
3156	picloram	—	—
3170	atrazine	atrazine	—
3375	atrazine	atrazine	atrazine
3474	bentazon	—	bentazon
4035	picloram	—	—
4584	atrazine	atrazine	—
4622	atrazine	atrazine	—
4665	atrazine	atrazine	atrazine
	picloram	—	—
4667	chlorpropham	chlorpropham	chlorpropham
4684	atrazine	—	—
	bentazon	—	bentazon
	metribuzin	—	—
5540	atrazine	atrazine	atrazine
	simazine	simazine	simazine
6225	atrazine	atrazine	atrazine
7660	picloram	—	—
8277	picloram	—	—
8520	bentazon	—	bentazon
8942	picloram	—	—
8772	atrazine	atrazine	atrazine

^abelow the instrument detection limit.

GC conditions The NPS GC methods (Methods 1, 2, and 3) recommend that the GC oven be programmed from 60° to 300°C at 4° per minute. To take full advantage of timed split injection of Method 1, the initial oven temperature was set 15° below the boiling point of MTBE, at 40°C, with a 5-minute initial hold time. This procedure increased the sensitivity and minimized the magnitude of the solvent disturbance on early eluting peaks. Optimal injector temperature for the Method 1 target analytes was found to be 270°C, rather than 250°C. The higher temperature improved peak shapes without significant diminution of any peak area due to thermal decomposition. For all three GC methods, the stationary phase of the capillary columns bled excessively at 300°C, causing signal noise and decreasing column life. Lower maximum oven temperatures were used to ameliorate this problem (table 7). No loss of peak separation was observed; column bleed decreased, and a flatter baseline was obtained.

Method 1 extractions and separatory funnel tumbler A unique separatory funnel tumbler was designed and built to get the best extraction efficiency and reproducibility possible (fig. 9). This device has the advantage of thorough end-over-end mixing without requiring both tumbler bottles and separatory funnels. The design allows the funnels to be vented, the phases to rate, and the organic layers to be withdrawn without removing the funnels from the tumbler.

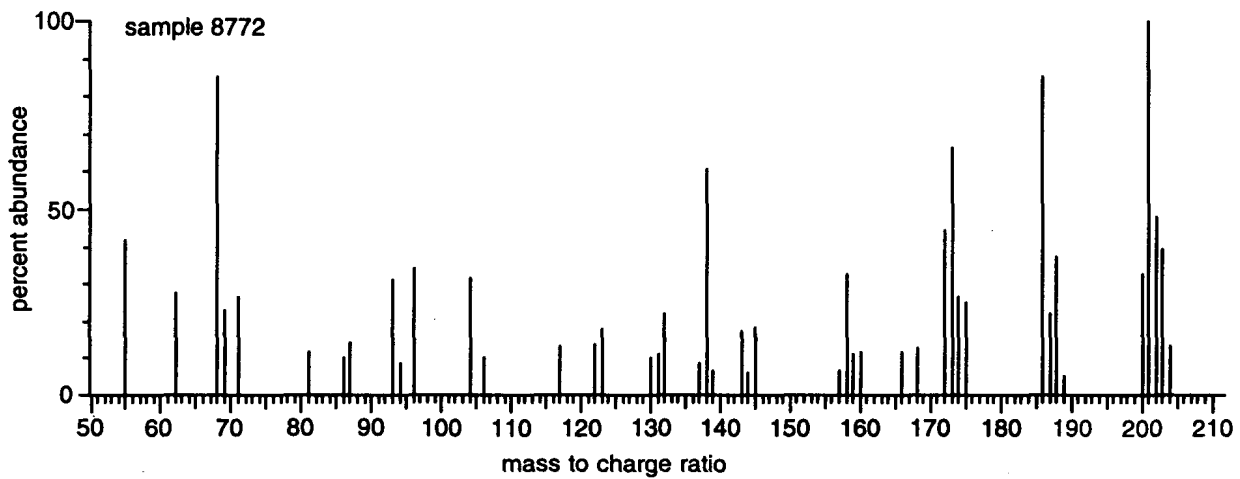
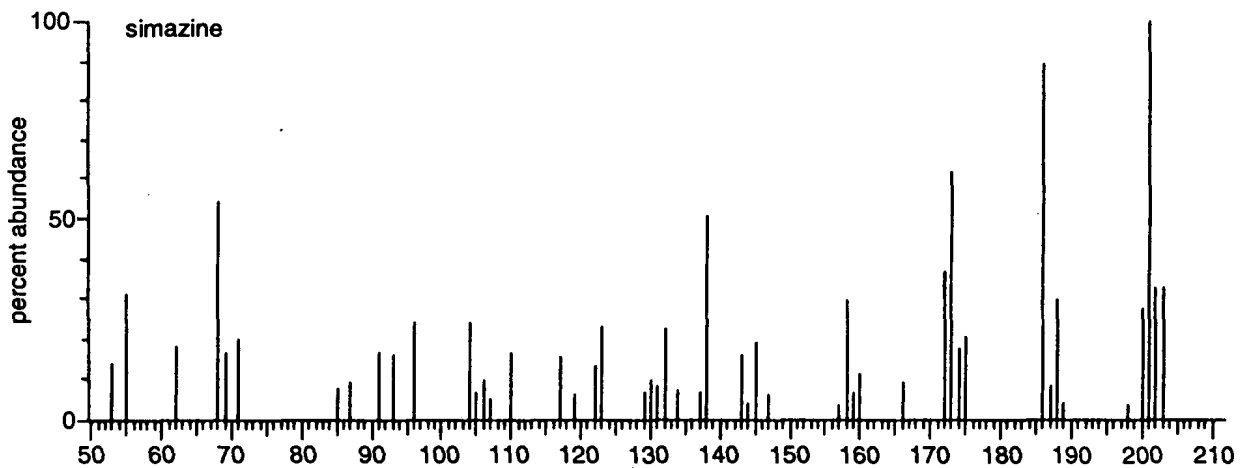
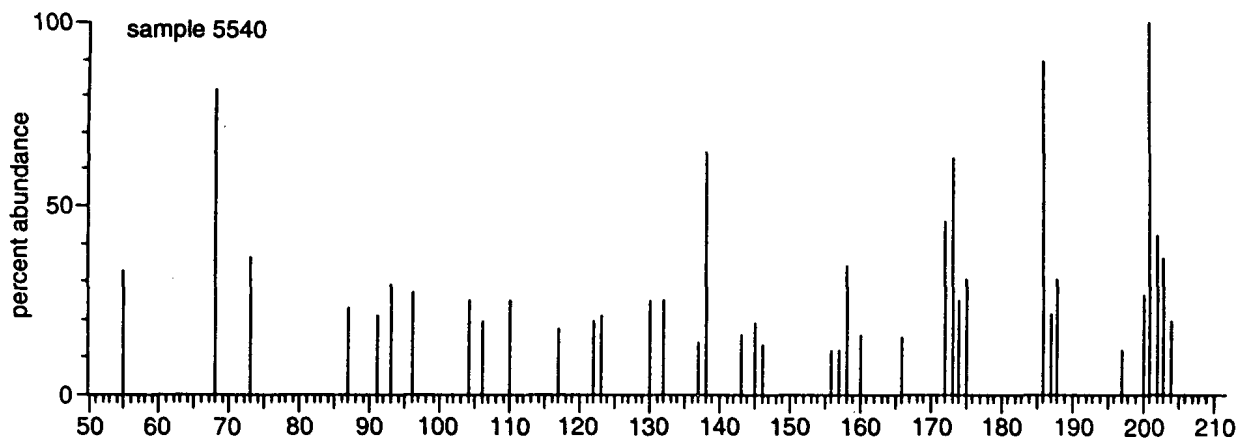


Figure 8 Mass spectra of simazine and two representative field extracts.

Table 6 Mass and intensity entry statistics for mass spectra of simazine and two representative field extracts (see fig. 8).

Mass	Intensity		
	Simazine	Sample 5540	Sample 8772
53	44	—	—
55	101	106	136
62	57	—	89
68	176	266	278
69	53	—	74
71	64	—	86
73	—	117	—
81	—	—	38
85	24	—	—
86	—	—	33
87	29	74	45
91	53	67	—
93	50	94	100
94	—	—	28
96	78	87	111
104	77	80	103
105	21	—	—
106	30	62	33
107	16	—	—
110	53	81	—
117	49	55	42
119	19	—	—
122	42	63	44
123	74	68	57
129	20	—	—
130	31	81	33
131	26	—	36
132	72	81	70
134	23	—	—
137	21	44	28
138	164	210	198
139	—	—	21
143	50	50	55
144	12	—	19
145	60	61	59
146	—	43	—
147	19	—	—
156	—	38	—
157	11	37	21
158	95	111	106
159	21	—	36
160	36	50	38
166	29	49	38
168	—	—	41
172	119	149	144
173	201	205	216
174	55	81	85
175	66	99	80
186	290	293	278
187	26	69	71
188	95	99	120
189	12	—	16
197	—	37	—
198	11	—	—
200	89	86	106
201	325	325	325
202	105	137	156
203	106	117	127
204	—	62	43

Table 7 Summary of GC conditions used in the pilot study.

Method	Injector temp (°C)	Detector temp (°C)	Purge time (min)	Initial oven temp (°C)	Hold time (min)	Ramp	Final temp (°C)
NPS 1	270	300	0.8	40	5	multi-step	290
NPS 2	250	320	0.45	60	0	4°/min	250
NPS 3	250	320	0.45	60	0	4°/min	250

The apparatus fits entirely within a fume hood with the sash at any desired position. Tumbling speed is continuously variable from 0 to 30 rpm. The maximum speed was used, duplicating the rate suggested in the NPS methods for a bottle tumbler. To get a thorough extraction, each sample was extracted with three successive 100-mL volumes of dichloromethane, rather than with the single 300-mL volume suggested in the USEPA method.

Method 2 surrogate standard concentration Method 2 states that 50 µL of the surrogate standard spiking solution (4,4'-DCB at 500 µg/mL) should be added to each water sample. If none of the surrogate standard is lost during processing of the sample, the concentration of 4,4'-DCB in the final MTBE extract would be 5.0 µg/mL. This concentration was found to be too high for our system. The 4,4'-DCB elutes at almost the same time as the internal standard, PCNB. At the recommended concentration, the 4,4'-DCB peak is much larger than the PCNB peak. Under these conditions, the surrogate standard peak can be improperly identified by the integrator as the internal standard peak. This occurs because the integrator seeks the largest peak within the specified retention-time window and identifies that as the internal standard peak. Consequently, it was found that 50 µL of a solution containing 50 µg/mL of the 4,4'-DCB was preferable (final concentration of 0.5 µg/mL in the MTBE extract). The average percent recovery of 4,4'-DCB in spiked field samples was 93%.

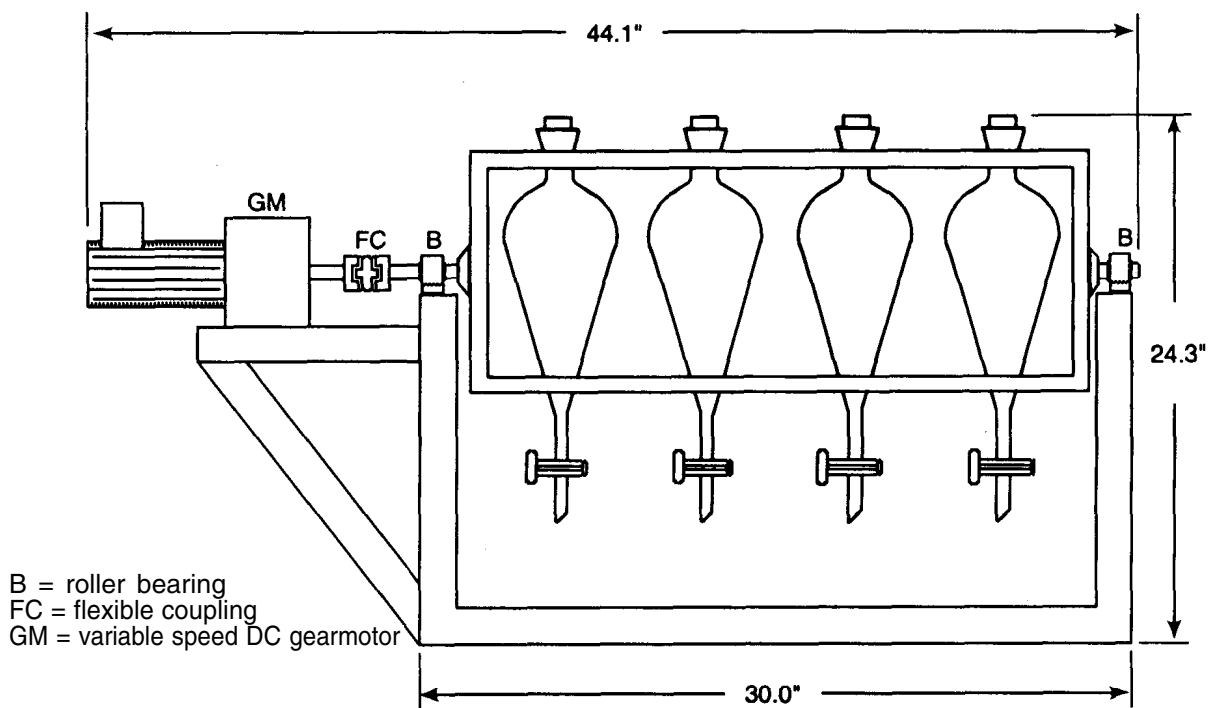


Figure 9 Separatory-funnel apparatus.

Method 4 HPLC column The primary column was the DuPont (now Mac Mod) Zorbax ODS stated in the method. The confirmation column was changed to the J&W Accusphere cyano column on the advice of Kent Sorrell of the USEPA Environmental Monitoring Systems Laboratory (Cincinnati, OH). Use of the cyano confirmation column required a change of solvents to an acetonitrile-water gradient.

Method 5 HPLC conditions A 500- μ L sample loop was used in place of the 400- μ L sample loop suggested in the method. The following changes to the method were made at the suggestion of the supplier of the post-column derivatization apparatus (Pickering Laboratories): boric acid was used instead of sodium borate, the amount of OPA was increased to 0.5 g, and 1 mL of 2-mercaptoethanol was used in place of a 1:1 mixture of acetonitrile and 2-mercaptoethanol.

Sample preservation with dichloromethane Mercuric chloride was the recommended preservative for Methods 1, 2, and 3. This compound produces several extraneous peaks in the chromatogram that may interfere with desired analyte peaks when electron capture detection is used.

Dichloromethane was tested as an alternative to mercuric chloride on the recommendation of Dr. William Foreman of the U.S. Geological Survey (USGS), Water Resources Division. In addition to slowing microbial metabolism, dichloromethane sequesters the organic analytes away from the aqueous phase, significantly slowing their hydrolysis. A comparison of the extraction recoveries with the two preservatives for Method 1 analytes spiked into natural groundwater is given in table 8. In most cases, recovery using dichloromethane was as good as or better than recovery using mercuric chloride.

Dichloromethane was found to be as effective a preservative as mercuric chloride for Method 3 analytes, on the basis of the recovery of analytes spiked in groundwater after holding times of 0 and 14 days (table 9). With the exception of dinoseb, the percent recoveries of the Method 3 analytes were as good as or better when dichloromethane was used than when mercuric chloride was used. Chromatograms of laboratory controls with dichloromethane and with mercuric chloride are shown in figure 10. An interference peak with a retention time of approximately 23.5 minutes masks the surrogate peak.

Quality Control and Quality Assurance

Several quality-control procedures were conducted throughout the study. The results of these procedures inform and assure the user of the data of the levels of accuracy and precision attained during the research.

Assessment of surrogate standard recovery A surrogate standard is a compound that is added in known amount to each sample, fortified sample, calibration standard, laboratory control standard, or reagent blank. The surrogate compound should not otherwise be found in a sample, should be chemically similar to the target analytes, and should behave in a similar manner during extraction and analysis. Surrogate standards are used to detect problems in extraction, work-up, or analysis. There are no surrogate standards for Methods 5 and 9, which use direct injection without an extraction step.

The percent recovery of the surrogate compound should be between 70% and 130% of the theoretical value. Only four of nearly 400 samples failed on the basis of unacceptable surrogate standard recovery in Method 2, and only one failed in Method 3. There were six samples for Method 2 and one sample for Method 3 for which surrogate standards were omitted from the sample.

Assessment of internal standard An internal standard was added in known amount to each sample, standard, and blank. The internal standard used for each Method was not an analyte

Table 8 Comparison of the effectiveness of the sample preservatives for Method 1.

Analyte	Preservative	Average % recovery at			
		0 weeks	1 week	2 weeks	3 weeks
1,3-D-2-N	DCM	90	70	64	63
	HgCl ₂	87	73	64	60
alachlor	DCM	90	65	61	63
	HgCl ₂	87	65	59	62
atrazine	DCM	96	73	69	67
	HgCl ₂	93	73	65	68
butylate	DCM	90	67	61	60
	HgCl ₂	85	67	62	60
carboxin	DCM	85	69	62	65
	HgCl ₂	88	69	61	63
chlorpropham	DCM	118	78	79	71
	HgCl ₂	112	77	74	70
diazinon	DCM	91	74	70	65
	HgCl ₂	86	0	0	0
disulfoton	DCM	93	69	67	64
	HgCl ₂	78	0	0	0
EPTC	DCM	89	68	62	61
	HgCl ₂	89	68	63	60
ethoprop	DCM	96	76	77	71
	HgCl ₂	92	77	79	69
metolachlor	DCM	89	70	66	66
	HgCl ₂	80	70	63	68
metribuzin	DCM	91	66	65	62
	HgCl ₂	89	65	64	62
simazine	DCM	98	73	62	64
	HgCl ₂	94	74	77	70
terbufos	DCM	93	63	54	47
	HgCl ₂	15	0	0	0
vernolate	DCM	95	68	61	62
	HgCl ₂	91	67	61	60

Analytes were spiked at 10 times EDL into natural groundwater. Results are the average for duplicates.

found in the sample, but it was similar to the target analytes. It was used to calculate the concentrations of target analytes in each sample. To be acceptable, the peak area for the internal standard in each sample must be within $\pm 30\%$ of the average peak area for the internal standards in the most recently analyzed calibration standards.

Assessment of laboratory contamination To demonstrate that all laboratory ware used in sample preparation was clean and that reagents were free of significant interferences, a liter of reagent water was extracted in parallel with each batch of samples. If a peak appeared within the retention-time window for any target analyte, then corrective action was taken. For Method 1, a very small peak sometimes fell within the retention-time window for chlorpropham on the primary column, but never on the confirmation column. The concentration of the interfering peaks exceeded the integration threshold but was always less than the EDL. The quantity of contaminant present was too small for GC/MS identification, even when the extract was concentrated 20-fold. No interfering peak appeared in the retention-time window of any analyte determined in this study by either Method 2 or 3. Reagent blanks for Method 9 were compensated for during the daily instrument calibration procedure.

Assessment of GC and HPLC performance Chromatographic performance was assessed by analyzing an instrument quality-control standard containing compounds chosen to test

Table 9 Comparison of the effectiveness of the sample preservative for Method 3.^a

Analyte	Preservative	0 weeks		2 weeks	
		R ^b (%)	S _R	R (%)	S _R
2,4-D	DCM	120	2.0	106	2.7
	HgCl ₂	106	1.4	112	0.6
2,4-DB	DCM	121	3.3	110	3.4
	HgCl ₂	99	1.7	99	0.4
2,4-DCAA	DCM	107	1.8	94	1.8
	HgCl ₂	93	1.4	103	2.1
bentazon	DCM	98	3.0	86	1.8
	HgCl ₂	94	1.5	94	0.7
chloramben	DCM	97	2.7	90	2.2
	HgCl ₂	88	6.3	88	7.1
dicamba	DCM	111	2.1	92	2.1
	HgCl ₂	97	1.0	122	3.8
dinoseb	DCM	45	2.1	47	2.7
	HgCl ₂	71	5.6	67	2.0
picloram	DCM	100	17.0	107	7.8
	HgCl ₂	110	1.6	145	1.5

^a Recoveries of method 3 analytes are spiked at eight times EDL (except picloram: 12 times EDL in DCM and 5.7 times EDL in HgCl₂) into groundwater (average of four and five replicates for DCM and HgCl₂, respectively).

^b R: average percent recovery.

^c S_R: standard deviation of percent recovery.

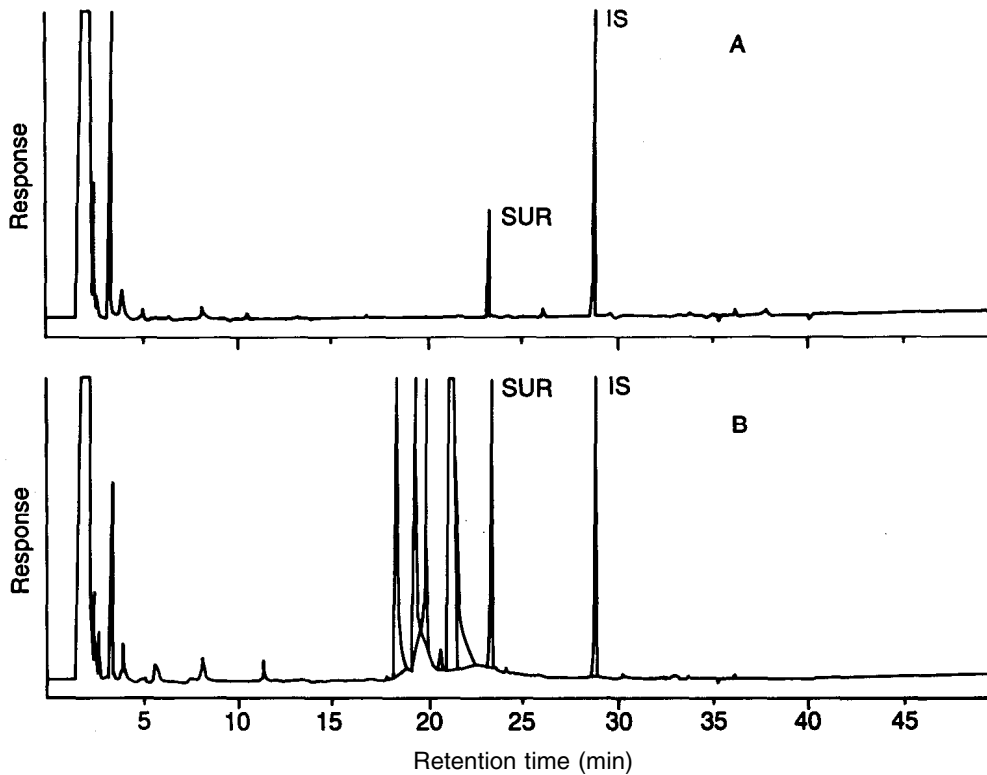


Figure 10 GC chromatograms of laboratory controls with dichloromethane (A) and mercuric chloride (B) as preservative (IS: internal standard; SUR: surrogate).

detector sensitivity, peak shape, and chromatographic resolution prior to each sample set. Whenever an instrument QC test failed, corrective action was taken before proceeding with sample analyses.

Laboratory control samples and fortified field samples At least one laboratory control standard was analyzed with each set of samples to assess the effectiveness of the extraction, concentration, and solvent exchange processes. The laboratory control standard was prepared by fortifying reagent water with appropriate target analytes at known concentrations of approximately ten times the respective EDL value given in the 1987 NPS descriptions.

The composition of field samples was not determined prior to fortification. Therefore, it was not possible to adjust the fortification amounts accordingly, as the USEPA procedures recommend. To obtain valid results, the amount of an analyte added should be two to five times the respective background concentration. Certain field samples fortified with Method 1 analytes contained complex assemblages of detectable analytes at appreciable concentrations prior to fortification. Therefore, recovery percentages from fortified field samples were more variable than were those from laboratory control samples. Certain field samples contained detectable quantities of analytes that eluted near or with target analytes and/or internal standard peaks, making quantitation less reliable. For Methods 2, 3, 4, and 5, the field samples that were fortified did not contain appreciable background analyte concentrations, so the results for individual analytes in both types of samples were similar.

The average percent recovery and relative standard deviation of the percent recovery for each target analyte are compared in table 10 for all laboratory control samples and fortified field samples.

Analysis of field duplicates Ten percent of all field locations were randomly selected for duplicate sampling and analysis. The person performing the analysis was unaware of which samples were duplicates. No duplicated field sample for Method 2, 3, 4, or 5 contained a target analyte above the detection limit. One Method 1 field sample did not show any atrazine although the duplicate contained atrazine below the MQL. The results for Method 9 duplicates with detections above the MQL are compared in table 11. The differences are generally small except for concentrations greater than 100 mg/L. The greater variability for the samples with higher concentrations (> 100 mg/L NO₃-N) results from multiple dilutions required to bring the sample concentrations within the dynamic range of the instrument.

External checks on laboratory performance Ideally, all quantitation standards should be compared with quality-control check standards initially and then quarterly. However, neither USEPA nor commercial suppliers made such check standards available during this study.

The ISWS laboratory participated in a performance comparison with ten other laboratories that routinely analyze water samples for certain Method 1 target analytes. Because the round-robin testing used actual field samples, the true analyte concentrations in each were unknown. Instead, in each case, the median from the eleven values reported was taken as the standard of comparison. Figure 11 shows our results plotted against those median values for the five target analytes detected in the round-robin samples. ISWS results were at or slightly above the median value for each of the five target analytes.

A quality-control sample obtained from Mr. Robert Maxey, USEPA (Bay St. Louis, MS) was analyzed for Method 3 analytes. As shown in table 12, only the chloramben percent recovery fell outside the desired $\pm 30\%$ range.

Table 10 Percent extract recoveries—analytes from laboratory control standards and matrix sample fortified at approximately 10 times EDL.

Analyte	Laboratory control			Fortified matrix		
	n ^a	R ^b (%)	RSD ^c (%)	n	R (%)	RSD (%)
Method 1						
1,3-D-2-N (surrogate)	63	92	25	23	88	15
alachlor	63	93	18	23	86	17
atrazine	63	96	17	23	95	35
butylate	63	90	19	23	88	21
carboxin	63	92	17	23	87	17
chlorpropham	63	101	17	23	95	28
diazinon ^d	63	94	18	23	79	22
disulfoton ^d	63	90	18	23	84	17
EPTC	63	93	17	23	109	37
ethoprop	63	93	17	23	93	30
metolachlor	63	96	18	23	86	16
metribuzin	63	91	17	23	85	32
simazine	63	97	17	23	84	15
terbufos ^d	63	92	18	23	57	49
vernolate	63	92	19	23	88	15
Method 2						
4,4-DCB(surrogate)	36	93	10	24	93	10
aldrin	37	44	34	24	69	12
α-chlordane	37	132	14	24	132	16
γ-chlordane	37	89	9	24	90	11
dieldrin	37	89	10	24	90	12
endrin	37	110	14	24	133	8
endrin aldehyde	37	98	18	24	103	27
heptachlor	37	69	11	24	67	11
heptachlor epoxide	37	88	9	24	89	9
p,p'-DDT	37	123	69	24	135	94
propachlor	37	98	25	24	97	26
trifluralin	36	92	11	24	92	9
Method 3						
2,4-D	49	115	18	24	118	17
2,4-DB	49	103	16	24	105	19
2,4-DCAA(surrogate)	49	100	8	24	100	10
bentazon	49	95	12	24	89	10
chloramben	49	70	17	24	73	18
dicamba	49	109	12	24	109	12
dinoseb	49	51	29	24	54	33
picloram	49	112	38	24	122	36
Method 4						
carbofuran phenol	— ^e	—	—	19	81	23
cyanazine	—	—	—	23	87	23
deethylatrazine	—	—	—	23	82	23
linuron	—	—	—	23	82	23
Method 5						
carbaryl	24	112	31	22	127	32
carbofuran	24	127	40	22	115	27
Method 9						
NO ₃ ⁻ + NO ₂ ⁻ as N	31	97	3	24	97	11

^a n: number of replicates.

^b R: average percent recovery.

^c RSD: relative standard deviation of percent recovery.

^d Analyte is qualitative only.

^e No laboratory fortified spike samples were analyzed.

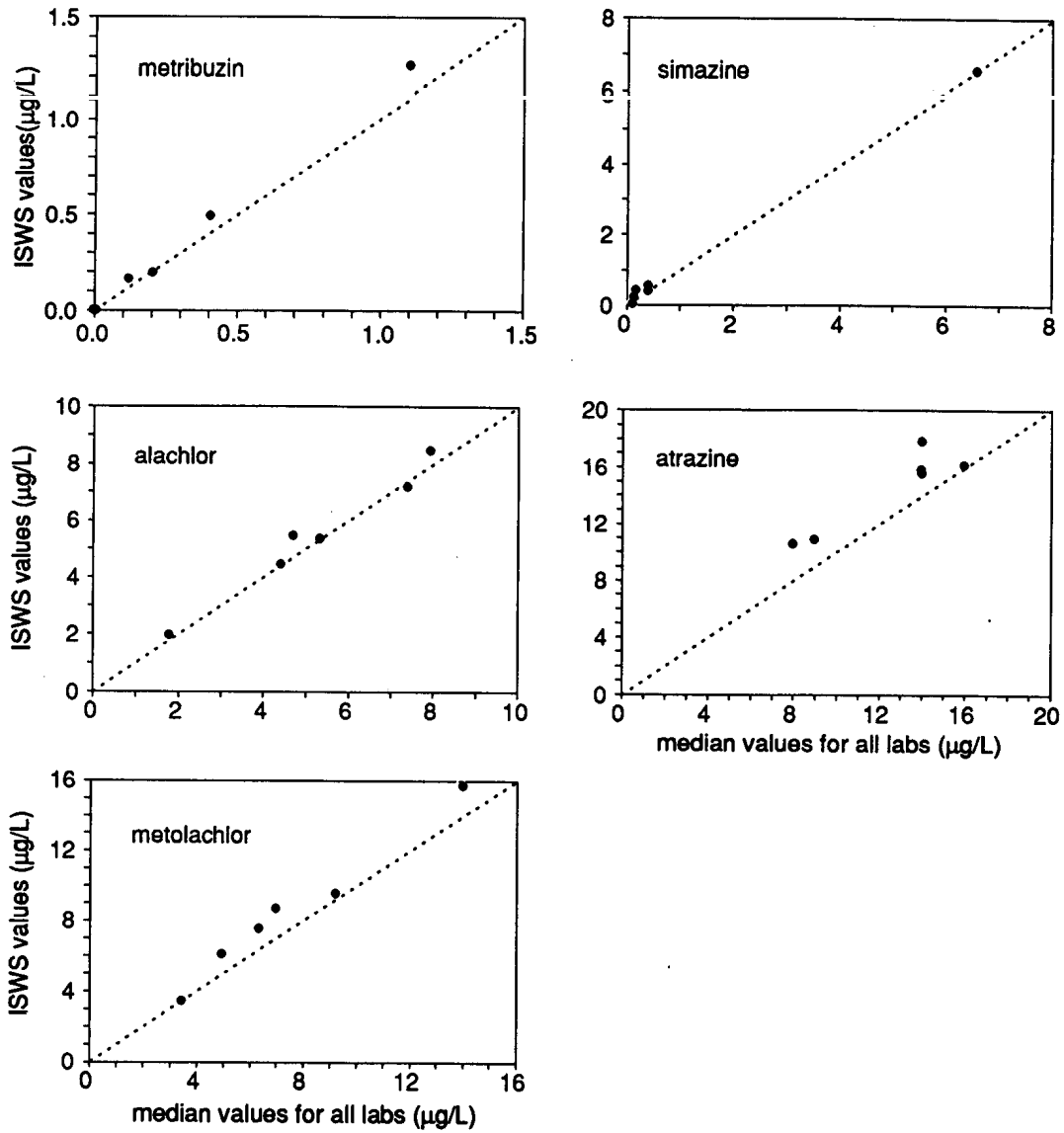


Figure 11 Comparison of round-robin testing results.

Table 11 Results for nitrate analyses of duplicate field samples.^a

First sample	Second sample	Difference
1.59	1.53	0.06
38.24	36.24	2.00
0.51	0.49	0.02
10.07	10.41	0.34
10.60	10.56	0.04
58.34	64.77	6.43
10.94	10.99	0.05
63.14	63.45	0.31
145.71	153.30	7.59
87.09	92.48	5.39
42.64	43.62	0.98
138.11	115.67	22.44
153.46	93.43	60.03
23.80	27.01	3.21
0.87	0.87	0.00
83.42	81.41	2.01

^a Concentrations are mg/L as NO₃⁻-N.

Table 12 Percent recoveries for performance and evaluation standard from fortified reagent water.

Analyte	Expected conc. (µg/L)	Observed conc. (µg/L)	n ^a	R ^b (%)	S _R ^c	RSD ^d (%)
2,4-DCAA	5.0	5.2	8	104	4.4	4.2
dicamba	0.4	0.38	8	95	1.3	1.3
2,4-D	0.6	0.62	8	103	1.7	1.6
chloramben	2.8	1.2	8	42	4.6	10.0
dinoseb	2.2	1.6	8	71	1.4	1.9
bentazon	1.5	1.3	8	88	1.3	1.5
picloram	1.1	1.4	8	128	5.5	4.3

^a n: number of replicates.

^b R: average percent recovery.

^c S_R: standard deviation of percent recovery.

^d RSD: relative standard deviation of percent recovery.

Sample Losses and QC Failures

The sample losses and other categories of procedural errors affecting field samples are summarized in table 13. The extraction methods were more prone to difficulties than were the simpler, direct injection methods.

Time and Material Requirements

A minimum of two investigators working full-time for 3 days was required in Method 1 to extract and work-up each set of 15 field samples and the associated laboratory controls. Gas chromatography analysis of the 15 extracts and 12 QC samples, plus the daily calibrations, required from 4 to 5 days for one person working full-time. Bottle and other glassware preparation required approximately one person for 1 day of each 2-week cycle of sample sets. Major expenses beyond the original acquisition of instruments included instrument servicing, NPD bead replacements, and high-purity gases and solvents. Thus, a total of about 12 man-days was required for each set of samples analyzed using Method 1.

Table 13 Percentages of laboratory QC failures for 360 pilot study field QA/QC samples.

Problem	Method (%)					
	1	2	3	4	5	9
Complete loss of field sample	0	1.7	1.7	1.4	0	0
Partial loss of field sample during lab work-up	9	0.8	1.9	2.5	0.6	NA
Instrument failure	0	0	0	0	3.9	0
Failure to add surrogate standard to field sample	1	1.4	0	0	0	NA

NA: not applicable.

A minimum of 8 hours was required in Method 2 for the complete extraction, preparation, condensation, and addition of internal standard for 15 field samples plus one laboratory control. For each set of 16 samples, 112 pieces of glassware must be washed and baked in accordance with the NPS methods. Glassware preparation required approximately 6 to 7 hours for washing and approximately 8 hours for complete baking. Additional labor was required for data analysis and interpretation. Thus, about 4 man-days were required for each sample set analyzed using Method 2.

A minimum of 20 hours was required in Method 3 for the complete preparation of 15 field samples and 3 laboratory controls. For each set of 18 samples, 162 pieces of glassware must be washed and baked in accordance with the NPS methods. Glassware preparation and baking required approximately 16 hours. Data analysis and interpretation of 18 samples and 5 instrument QA/QC samples required about 30 hours. Thus, about 8 man-days were required for each sample set analyzed using Method 3.

A minimum of 8 hours was necessary in Method 4 for the extraction, preparation, and addition of internal standard for 15 field samples and one laboratory control. Glassware preparation required approximately 6 hours. For data analysis and reporting, 24 hours were required. Approximately 5 man-days were required for every 16 samples (one set) analyzed using Method 4.

In Method 9, one person was required to work 2 days during each 2-week cycle. Only comparatively minor expenses beyond the original cost of the instrumentation were incurred.

General Chemical Recommendations

One of the basic objectives of the pilot study was to suggest improvements for the recommended statewide study of agricultural chemicals in groundwater. Our suggestions regarding the chemical analysis aspects of future studies are summarized below.

Analyte confirmation All tentative analyte identifications based on GC or HPLC retention times should be confirmed promptly by mass spectrometry. There is a question about whether use of a confirmation column is worthwhile in terms of time or expense when MS confirmation is available. In the GC methods, the flow of sample from the injector was split to the primary and confirmation columns to permit simultaneous analyses. Although doing so saved considerable instrument time, it also necessitated using a compromise oven temperature program that was not optimal for either column. Thus, it was more difficult to resolve closely eluting peaks than it would have been if conditions were optimized for a single column. It was also suspected that the split ratio between parallel columns probably varied slightly from one injection to another, adversely affecting quantitation. Use of a second NPD in Method 1 doubled the expense for the collector assemblies of replacement detectors, which cost \$90 each and were replaced approximately every 2 weeks.

Spiking field samples As discussed above, field samples should not be fortified to check for matrix interference until a corresponding unfortified field sample has been analyzed and the

background concentrations are known. At that time, appropriate concentrations of analyte spikes can be added.

Spare field samples Because the entire 1-liter sample collected for each method is extracted in Methods 1, 2, 3, and 4, there is no allowance for breakage or other loss of sample during transport, storage, or laboratory work-up. If duplicate field samples were collected for each method at each site, a spare would always be available if necessary. It would also be desirable to analyze the duplicate sample whenever one or more target analytes are detected in a primary field sample. The 10% rate of random duplication used during the pilot study was not sufficient to check precision for three of the four methods that detected quantifiable concentrations of target analytes in field samples.

Back-up instrumentation and personnel Serious delays were caused by equipment and personnel problems in each of the three participating laboratories during the course of the pilot study. For a statewide study, with even greater throughput demands, it is imperative to have complete back-up instrument and data systems and at least three analysts with experience in each analytical method. Videotapes would be helpful in demonstrating each step in sample preparation to facilitate the training of replacement laboratory analysts.

Internal standard for Method 1 Nitrogen-phosphorus selective detectors are inherently unstable when operated at the sensitivity levels required for the pilot study analyses. One source of that instability involves unequal changes in the relative sensitivities to nitrogen and phosphorus as a detector bead ages. Triphenyl phosphate (used as the internal standard in the NPS method) does not contain nitrogen, and therefore is not the best choice for quantifying analytes that do not contain phosphorus. It is suggested that the GC data system chosen for Method 1 have the capability to simultaneously use at least two internal standards. A second internal standard, such as 1,3-dimethyl-4-nitrobenzene, should be used to quantify nitrogen-containing analytes.

Choice of Target Analytes

Certain analytes were difficult to determine reliably, and some, for other reasons, may not be suitable choices for a statewide survey. In addition, certain widely used pesticides that were not chosen as targets for the pilot study should be considered for inclusion in follow-up studies.

Aldrin Recoveries were poor for this Method 2 analyte, as determined by laboratory control samples. The compound is known to degrade to dieldrin in the environment. Aldrin has not been used in the United States for many years (World Health Organization 1989, Budaveri 1989). Aldrin was not detected in the pilot study and should not be included as a target analyte for the recommended statewide survey because of its rapid conversion to dieldrin in the environment, the lack of reliable quantitation in our laboratory, and its discontinuation of use in the United States.

Chloramben and dinoseb The precision and accuracy of dinoseb determination by NPS Method 3 were poor, and marginally acceptable for chloramben, as measured by the average percent recovery and relative standard deviations (table 10). Method 3 is qualitative to semi-quantitative for dinoseb, and is marginally acceptable for chloramben. Improved methods for their determinations should be sought. There was one detection of chloramben above its MRL and no detection of dinoseb above its MRL.

Heptachlor The percent recovery of heptachlor using Method 2 was relatively low in laboratory control samples and in spiked field samples (table 10). Heptachlor has been banned for agricultural food uses in the United States since 1975 (Federal Register 1975). Its half-life is 1 to 3 days under typical environmental conditions. One of the heptachlor degradates is heptachlor epoxide, another compound determined by Method 2. The epoxide has a longer half-life,

which is on the order of years (USEPA 1979). Heptachlor was not detected in any field sample analyzed during this study. For all of the above reasons, heptachlor should not be included in the recommended statewide survey.

Picloram This compound was among the compounds most frequently detected during the pilot study. Its quantitation using Method 3, however, lacks precision (table 10). Because it occurs in Illinois groundwater, picloram should be retained in further studies, but an improved method for its determination should be developed.

Additional Target Analytes for Subsequent Studies

A number of potential target analytes were not selected for the pilot study. In most cases, this was because the analytes were comparatively new, and suitable analytical methods had not been tested when the pilot study was planned. Possible additions for subsequent studies in Illinois include the following: dimethyltetrachlorophthalate degradates (DCPAM), 4,4'-DDD, 4,4'-DDE, pendimethalin, ethafluralin, glyphosate, clomazone, and bromoxynil.

DCPAM can be determined using Method 3. In the recently completed USEPA National Pesticide Survey, DCPAM was second only to nitrate in the number of detections in groundwater samples. The results were initially attributed to suburban applications of yard weed control chemicals. These types of chemicals were not considered in the original pilot study plan. Therefore, it was not part of the original pilot study plan to monitor the occurrence of this herbicide degradate. In view of the NPS results, however, Method 3 extracts were reanalyzed. Because the sample extracts at the time of analysis ranged from 3 to 14 months old, the accuracy of DCPAM quantitation is uncertain. If DCPAM or its parent compounds are used in Illinois agricultural settings on a regular, wide-spread basis, DCPAM should be included in further studies of agricultural chemicals in Illinois well-water.

DDD and DDE are degradates of p,p'-DDT and are highly stable in the environment. These analytes can be determined using Method 2. Although use of the parent compound has been banned in the United States since 1973, DDT and its degradates are extremely persistent. The estimated half-life for DDT is more than 150 years under direct photolysis (USEPA 1979). This warrants the inclusion of DDT and its degradates in further studies.

Extract Volume and Storage

Methods 1, 2, 3, and 4 specify that the sample extracts should be diluted to a final volume of 5 mL following concentration and solvent exchange. A smaller final volume, such as 1 mL, would enhance sensitivity proportionately without greatly increasing the uncertainty of the volume measurement. Any imprecision introduced by measuring a smaller volume would be compensated for by the internal standard.

Partial evaporation of the solvent from extract vials during storage was a common problem, especially when analyses were repeated beyond the recommended 2-week time limit. It is critical that caps and seals be tightened carefully and rechecked after the vials have been refrigerated for several hours.

Evaluation of Solid-Phase Extraction

Liquid-liquid extraction (LLE) has serious disadvantages, which make it worthwhile to seek an alternative extraction technique for Methods 1, 2, 3, and 4. Separatory funnels are awkward to use and difficult to clean properly. Emulsion formation increases work-up times and decreases analyte recoveries. Dichloromethane is a chlorinated solvent and a suspected carcinogen (Sittig 1985) and requires special precautions during storage, use, and disposal. Liquid-liquid extraction of each 1-liter water sample requires 300 mL of dichloromethane. The bulk of this solvent evaporates into the air during the extract concentration and solvent exchange steps. Although

Table 14 Results of solid-phase extraction of Method 1 target analytes from reagent water.^a

Analyte	Conc (μ g/L)	n	Average recovery (%)	Std dev.	RSD (%)
1,3-D-2-N	12.8	10	59	5.3	8.9
alachlor	3.9	10	95	6.2	6.5
atrazine	1.3	10	88	6.3	7.1
butylate	1.5	10	83	7.5	9.1
carboxin	6.2	10	69	7.3	10.5
chlorpropham	5.1	10	106	7.5	7.1
diazinon	2.6	10	85	4.8	5.6
disulfoton	3.1	10	62	5.6	9.1
EPTC	2.6	10	87	7.3	8.5
ethoprop	1.9	10	94	3.0	3.3
metolachlor	7.7	10	96	5.9	6.2
metribuzin	1.4	10	71	9.7	13.7
simazine	0.6	10	90	7.9	8.7
terbufos	5.0	10	67	11.5	17.1
vernolate	1.3	10	81	8.2	10.1

^a The water samples contained no preservative.

solvent recovery is possible using additional equipment, significant problems remain, including safety, storage, and waste disposal.

Target analytes can instead be extracted by passing the water sample through a bed of solid particles coated with lipophilic groups, such as C_{18} . Such solid-phase extraction (SPE) does not require large volumes of chlorinated solvents. As little as 5 mL of less toxic solvents, such as ethyl acetate, are required for each liter of water extracted. No bulky separatory funnels or shakers are required, and no troublesome emulsion layers are formed. It requires less hood space and is simpler to clean glassware. Solid-phase extraction requires as little as 30 minutes to prepare a concentrate ready for injection, as compared with 3 hours for LLE and Kuderna-Danish concentration. Elimination of the concentration and solvent exchange steps not only saves time, but also eliminates one of the major causes of sample loss.

Our preliminary Method 1 analyte recoveries using SPE from fortified, reagent water are summarized in table 14. The recovery of the surrogate standard, 1,3-D-2-N, with SPE is low (59%), but another more suitable surrogate could easily be used. Recoveries for metribuzin (71%) and carboxin (69%) are marginal, but no doubt the SPE conditions can be modified to improve the percentages. Disulfoton and terbufos are problematic by SPE, as they also are by Method 1 with mercuric chloride preservation, because it is not possible to add dichloromethane to samples prior to extraction. In any case, it appears improbable that disulfoton, terbufos, or other rapidly hydrolyzable analytes persist very long in natural water samples, unless the initial concentration is extremely high. Although more developmental work remains, SPE looks extremely promising.

INFORMATION SYSTEM

A comprehensive information and data management system was developed for the pilot study. The system had the capability to generate a master form used to print a multi-part form for tracking sampling materials, forms to record field measurements, and labels for the sample bottles. The system was designed to allow for tracking the chemical laboratory activities and to generate reports for QA/QC purposes. The system stored all of the information gathered in all phases of the study, processed that information, and produced reports. It also allowed the

project staff to format general and analytical chemical information for later statistical and interpretive analysis.

System Basis

A system was needed to document all phases of the project. The necessary forms were initially designed during the development of the plan for the recommended statewide survey. The software necessary to print these forms with the required numbers for tracking was developed during the pilot study. The data-entry software displayed screens that mimicked these forms for ease of data entry. Tables of the data from the entry forms were stored with the unique well-site number. The information gathered during the well-site inventory phase and well-user interview phase was cross-referenced using the same identification number. This system allowed us to relate the information in several tables, and more importantly, allowed us to keep the locations of the sites, names of well users, and other privileged information separate and confidential.

The analytical chemistry information was organized and processed allowing its immediate use by the chemists and later use by staff for interpretation of results. The requirements for reporting and tracking of the QA/QC results were included in the analytical method protocols published by the USEPA. The software needed for recording, standardizing, checking, and reporting was developed by the pilot study staff. The programs needed were very complex and required a series of steps to convert a variety of data structures to a standard format for processing. These prescribed forms and requirements became the basis of the information system.

The information management system is unique among project-tracking systems because of its capability to relate chemical results, site survey information, and interview information, as well as generate forms and track, check, and report results. This comprehensive system was originally intended to become a stand-alone system that could be adapted to other studies with little effort. Because of personnel changes prior to completion of the documentation and changing analytical instrumentation, the basic system became more and more complex. The final system is adaptable to other projects, but adaptation would require significant effort.

Software and Hardware Requirements

The information management system was developed on the R:Base software package for IBM or IBM-compatible personal computers (PCs). Each PC had at least a 20-megabyte (MB) hard disk to store the software package, files custom-developed for the system, and data. The main system with all of the data and production files eventually required 40 MB of disk storage. The project manager was the only individual who could connect all parts of the data. The laboratory managers had all of the software and files to carry out the chemical tasks, but did not have the names or locations of sample sites or other information about the sites. The database could be queried for information regarding the site and for interview information for general patterns and factors that might have influenced the chemical results. Only the project manager could relate the site information to the individual sites or well users after the results had been returned to the users. At the end of the pilot study, information relating data to a specific site was destroyed, as part of the agreement made with the well users in return for their participation.

Site Database

The information system consisted of a series of tables that fell into two groups. The first group of tables contained the information from the site survey and the interview with the well user. Information in these tables included the unique site number, location, site status (whether the site was an active farm or a rural residence), well type, well depth, and year of construction. Where applicable, these tables also contained data regarding well-water treatment, topography

of the well site, well-head protection, presence of livestock, and manure applications near the well. In addition, well-specific information such as the geologic material(s) in which the well was finished, well casing, well screens, pump capacity, and history was in these tables. The system also contained records of agricultural chemical use, including the use, mixing, storage, and disposal of all pesticides, herbicides, and nitrogen fertilizers within the past 5 years.

Chemical Database

The chemistry portion of the information system was designed to standardize the format of all data coming from different laboratory equipment systems. The design made it possible to check the laboratory QA/QC programs. The system reformatted files from several gas chromatographs, a flow injection analyzer, and an HPLC. After reformatting, files were loaded into the appropriate table in the information system.

Types of data maintained by the chemical database The main menu of the information system presented the user with five options. Each option represents a different type of data maintained in the system as a separate table: sample-tracking information, instrument calibration and sample quality-control data, analyte concentration results, retention times, and areas of the chromatogram that were integrated by the instrument.

The sample-tracking screens allowed the laboratory sample manager to document the materials (e.g., sample bottles) leaving the laboratory for sampling and the materials being returned after sampling. The sample-tracking system mimicked the multi-part paper form that accompanied each set of bottles.

Instrument calibration data and sample quality-control information documented calibration and quality-control analyses completed by each laboratory working on the project. Quality-control data included results from surrogate standards, laboratory control samples, and spiked samples. The system calculated the percent recovery of analytes in each sample analysis.

The analyte concentration screen allowed the laboratory manager to view the data from the laboratory instruments. The data from the files received from the laboratory could not be altered by the project manager. Comment fields and hand-calculated concentration fields were available to the laboratory manager or quality assurance officer if he or she suspected errors in the results reported by the instrumentation. When a gas chromatograph was used, the results from both the primary and confirmation columns were maintained in the database in separate tables.

The backup-data utility of the management system allowed the laboratory manager to copy data to his laboratory system. A copy of the files from each laboratory was appended to the central set on the project computer. This was the only place where all of the results from all the laboratories for the project were combined and maintained.

CHARACTERIZATION

Characterization of geologic sediments is a major component in assessing the potential for contamination of an area from agricultural chemicals. The hydrogeologic settings of the pilot study, derived from the Stack-Unit Geologic Map of Illinois (Berg and Kempton 1988), were appropriate for establishing the potential vulnerability stratifications at a statewide scale. The average distance from the land surface to the top of the uppermost aquifer material was used to differentiate the four vulnerability groups. This translates into a range of depths when each category, or strata, is examined more closely. Therefore, a detailed characterization was undertaken to help understand the hydrogeology of each of the study areas (Barnhardt et al. 1992).

The characterization served several purposes. First, it allowed a better interpretation of the chemical analytical results of the study. Second, it demonstrated that within each hydrogeologic category the variability of certain parameters, such as land use or local infrastructure, was great enough that the impact on the chemical results could not be readily determined. Third, it made clear that the availability of basic information is not the same in all areas. Records, such as well logs and land-use patterns, are more likely to be documented in places with a long-standing administrative structure. In rural areas where land ownership has not changed hands very often, even such basic information as age of well and location of abandoned wells may not be known. The most important outcome of the characterization effort may be a deeper understanding of how much is involved in determining the basic information about wells and land-use patterns across the range of hydrogeologic environments in Illinois. This understanding helped the pilot study team to make some valuable recommendations about the level of characterization necessary for the recommended statewide survey.

All available topographic, geologic, and soil survey maps were used to characterize the five study areas and to create a subset of the Geographical Information System (GIS) for all of these maps. Selected cultural, topographic, geologic, hydrologic, and soil survey information was digitized or enhanced on various base maps. The location of each water well on record for each study area was verified when possible, and the driller's log for each well was interpreted to form a better picture of the subsurface geology on a local scale. A version of a stack-unit map to a depth of 50 feet and bedrock topography, drift thickness, parent materials/soils, and terrane maps were produced for each area. A final version of all these maps was not necessarily produced for each study area because the maps were often quite similar, and one map could convey the necessary information.

Streamlining the geologic characterization methodology to eliminate redundancy was desirable because one of the objectives was to evaluate the economic feasibility of a statewide survey. Because the pilot study was designed to test procedures and methodologies that would be applied in a statewide survey, emphasis was placed on using all available databases. No additional fieldwork was conducted other than the actual water sampling and selected reconnaissance trips to identify industrial, commercial, and agricultural activities, and to interview residents in the study areas. Existing water wells were used for sampling. This design focused the characterization effort on interpreting the existing geologic database, which consists of drill logs from private, municipal, and commercial water wells, drill logs from coal, oil, and gas borings, highway and bridge borings, reports, maps, and unpublished data housed at the ISGS and ISWS. Additional information was obtained from the U.S. Department of Agriculture-Soil Conservation Service county soil survey reports.

Difficulties in the Characterization Efforts

The selection of the five study areas was made on the basis of hydrogeologic classification. The quality and quantity of geologic and hydrologic data varied considerably for the five areas. This variation will probably be even greater in the recommended statewide survey. Some of the study areas had been recently examined by research projects, but minimal geologic and hydrologic information was available for others. One serious concern is the different map scales of the original source information. Map scales ranged from 1:15,840 (soil survey map) to 1:250,000 (state stack-unit map). The pilot study used 1:24,000-scale topographic maps for preliminary geologic mapping. The scale of the GIS maps generated ranged from about 1:62,000 to 1:100,000. Because map detail and readability are concerns for researchers and planners, the reliability of drawing information from those maps, and basing decisions on that information, is also a concern.

Although in some cases considerable detail was generalized for the final map, more complete, current, geologic and hydrologic information was needed in all five areas. The most common problem encountered was the lack of detailed, verifiable, drillers' logs for water wells. Often, the

verifiable wells were clustered in a small area or lacked detailed geologic information. These problems are an indication of those to be expected in a statewide survey. It will be impossible for the statewide survey research team to look at the subsurface information at the same level of detail as the pilot study characterization team did. The statewide survey team will have to look at enough information to assure themselves that the potential for vulnerability to agricultural chemical contamination is the same across the areas included in any one category of vulnerability.

The incorporation of ISGS work on the glacial stratigraphic framework, mapping, and other published ISGS research assisted in extrapolating geologic units into the study areas and allowed some interpretations to be made. The accuracy and detail of the extrapolation is obviously related to the detail of the research upon which it is based, but the detail was generally sufficient to meet the needs of the pilot study. Neither the pilot study nor the recommended statewide survey will replace the need for detailed, site-specific studies when questions are asked concerning the siting of landfills or the disposal of hazardous wastes. However, sufficient information appears to be available in the current geologic database to allow for generalized mapping and interpretation of geologic sediments and their role in the potential for contamination by agricultural chemicals. Generalizations and extrapolations, however, were necessary in developing base maps. The difference between estimating the potential for contamination and attempting to determine the source of that contamination if it is found is great. On a statewide basis, this difference will be even more important because the generalizations will be made across larger areas. The characterization report (Barnhardt et al. 1992) should be consulted for detailed explanations of the characterization process.

RESULTS AND ANALYSIS

Occurrence of Agricultural Chemicals

The following results are given in terms of an occurrence, which is defined for this study as the presence of one or more analytes above some specified concentration in a well-water sample. The concentration used to define an occurrence was the MRL, following the approach of the USEPA in its NPS. The 39 analytes and their respective EDL, MQL, and MRL for the pilot study are listed in table 1. It also lists the health advisory limit (HAL) or the maximum contaminant level (MCL) for each analyte. The MRL for nitrate was replaced by its MCL, 10.0 mg/L, reported as nitrogen.

The number of occurrences of agricultural chemicals is listed by study area in table 15. One or more agricultural chemicals were detected at or above the MRL in 55 out of 240 (23%) samples. The number of occurrences was highest in the Effingham County study area (22) and lowest in the Piatt County study area (no occurrences).

The results listed in table 15 for areas with drilled and driven wells are in agreement with the results that would be predicted using the map of potential for contamination by agricultural chemicals (McKenna et al. 1989). For study areas with drilled or driven wells, the number of occurrences was highest in Kankakee and Mason Counties. The Kankakee and Mason County study areas represent areas with a depth to the uppermost aquifer material of 5 to 20 feet and less than 5 feet below the ground surface, respectively. As will be shown, the difference in occurrences for these two study areas is not statistically significant. The number of occurrences from the Livingston County study area (20 to 50 feet to the uppermost aquifer material) is significantly lower than those from Kankakee and Mason. The number of occurrences in the Piatt County study area (>50 feet to the uppermost aquifer material) is significantly lower than in Livingston.

The highest number of occurrences was found in the area with dug and bored wells (Effingham County). The potential for contamination in these areas is not predictable using the potential for

Table 15 Occurrence of one or more targeted agricultural chemicals in the five study areas.

County	Number of occurrences	Number of samples	Percent occurrence
Effingham	22	48	46
Kankakee	18	48	38
Mason	11	48	23
Livingston	4	48	8
Piatt	0	48	0
Total	55	240	23

Table 16 Occurrence of nitrate in the five study areas.

County	Number of occurrences	Number of samples	Percent occurrence
Effingham	19	48	40
Kankakee	14	48	29
Mason	7	48	15
Livingston	2	48	4
Piatt	0	48	0
Total	42	240	18

Table 17 Occurrence of one or more pesticides in the five study areas.

County	Number of occurrences	Number of samples	Percent occurrence
Effingham	11	48	23
Kankakee	6	48	13
Mason	4	48	8
Livingston	3	48	6
Piatt	0	48	0
Total	24	240	10

contamination map of McKenna et al. (1989) because dug or bored wells generally do not obtain water from geologic materials qualifying as "aquifer materials." Instead, these wells obtain water from thin and discontinuous geologic materials.

The occurrence of nitrate and the occurrence of pesticides by study area are presented in tables 16 and 17, respectively. Table 16 provides the number of wells with an occurrence of nitrate, including wells with nitrate only and those with nitrate and another agricultural chemical. Table 17 provides the number of wells with an occurrence of a pesticide, including wells with pesticide only and those with pesticide and nitrate. The sums of the figures in tables 16 and 17 may not equal the figures in table 15 because both nitrate and pesticides occur in some wells.

Ten agricultural chemicals were detected at or above the MRL (i.e., high enough to be classified as an occurrence) (table 18, listed by county in table 19). Of the ten detected compounds, four were detected by NPS Method 1. One compound ((α -chlordane and γ -chlordane are both considered chlordane for this report) was detected by NPS Method 2. Four compounds were detected by NPS Method 3, and one was detected by NPS Method 9. The target analytes for NPS Methods 4 and 5 were not detected.

Table 18 Agricultural chemicals detected.

Compound	NPS method	Number of occurrences	MRL ^a (µg/L)	Concentration ^b		No. of high occurrences ^c	HAL or MCL ^d (µg/L)
				low	high		
nitrate	9	42	30.0 ^e	11,000	58,000	42	10,000*
DCPAM ^f	3	18	0.24	NA ^f	NA ^f	0	4000
atrazine	1	11	0.15	0.15	3.8	1*	3*
picloram	3	10	0.76	0.82	4.2	0	500*
bentazon	3	4	0.79	1.7	10	0	20
metribuzin	1	2	0.40	0.71	2.6	0	200
simazine	1	2	0.15	0.24	0.76	0	1*
chloramben	3	1	0.52	NA ^g	0.95	0	100
chlordane	2	1	0.048	NA	0.06	0	2*
chlorpropham	1	1	0.40	NA	1.6	0	—

^a Minimum reporting level.

^b Concentration for occurrences, given in µg/L.

^c Number of occurrences exceeding the HAL or MCL.

^d HAL: USEPA lifetime health advisory, MCL: maximum contaminant level (denoted by *).

^e For nitrate, an occurrence is defined as 10,000 µg/L or 10.0 mg/L as nitrogen, which is higher than the minimum reporting level for nitrate-nitrogen.

^f DCPAM is not included in the overall total number of occurrences because this compound was detected in sample extracts stored for a long period of time.

^g Not applicable, only one occurrence of this compound.

Table 19 Agricultural chemicals detected by study area.

County area	Compound	Number of occurrences	Number of high occurrences ^a
Effingham	nitrate	19	19
	DCPAM	8	0
	atrazine	7	1
	picloram	4	0
	bentazon	2	0
	metribuzin	1	0
	simazine	2	0
	chlordane	1	0
Kankakee	nitrate	14	14
	DCPAM	8	0
	atrazine	3	0
	picloram	1	0
	bentazon	1	0
Livingston	nitrate	2	2
	DCPAM	1	0
	atrazine	1	0
	picloram	2	0
	bentazon	1	0
	metribuzin	1	0
	chlorpropham	1	0
Mason	nitrate	7	7
	DCPAM	1	0
	picloram	3	0
	chloramben	1	0
Piatt	none detected		

^a Number of occurrences exceeding the HAL or MCL.

Nitrate-nitrogen was the most frequently detected agricultural chemical, followed by DCPA acid metabolite (DCPAM) (table 18). Only two of the 39 target analytes (nitrate and atrazine) in the pilot study had concentrations exceeding their respective USEPA MCL. DCPA and its degrade, DCPAM, were not included in the original list of target analytes. DCPAM was detected by reanalyzing sample extracts that had been stored for several months, and after the USEPA released its NPS Phase I report. Consequently, the results for DCPAM were qualitative rather than quantitative, and these occurrences were not included in the 55 occurrences given in table 15. The NPS found DCPAM in about 2.5% of its samples from domestic wells (USEPA 1990). The USEPA attributed the occurrence of this compound to suburban pesticide use.

Comparison with Other Studies

Comparing research results with those from similar studies is a standard practice and can help place research results in perspective. The results of the pilot study were compared with the results from Iowa's State-Wide Rural Well-Water Survey (SWRL) and the USEPA's NPS. It was hoped that this comparison could provide some perspective for the pilot study results. For the reasons discussed in the following sections, the results of the pilot study are not directly comparable with the other two surveys.

Iowa's SWRL Iowa's SWRL is a stratified, systematic sample of private, drinking-water supplies. The study was a one-time sampling survey of 686 wells between April 1988 and June 1989, and was designed to determine the percentage of rural, private wells in Iowa affected by environmental contaminants and the proportion of rural residents using contaminated water. Well water was analyzed for environmental contaminants, including nitrate, 27 pesticides, and 5 pesticide metabolites (Kross et al. 1990).

The overall analytical results for the pilot study and SWRL are presented in table 20. The overall occurrence of nitrate and pesticides is similar for all wells, wells less than 50 feet deep, and wells greater than or equal to 50 feet deep. However, the percentage of occurrences in the pilot study was slightly lower. This fact is interesting because the Iowa researchers felt that their percent occurrence was low because they sampled during a drought (Kross et al. 1990). The occurrence of the 14 pesticides common to both studies are listed in table 21.

The occurrence of agricultural chemicals in dug or bored wells was similar in both studies. The occurrence of $\text{NO}_3^- - \text{N} \geq 10 \text{ mg/L}$ was 40% for the pilot study and 38% for the SWRL, and the occurrence of pesticides was 23% for the pilot study and 19% for the SWRL.

Table 20 Cursory comparison of the occurrence of agricultural chemicals in the pilot study with Iowa's State-Wide Rural Well-Water Survey (SWRL)^a (Kross et al. 1990).

Category	% Occurrence	
	Pilot study	SWRL
All wells		
$\text{NO}_3^- - \text{N} > 10 \text{ mg/L}$	17.5	18.3
Pesticides	10.0	13.6
Wells < 50 feet deep		
$\text{NO}_3^- - \text{N} > 10 \text{ mg/L}$	30.3	35.1
Pesticides	13.2	17.9
Wells > 50 feet deep		
$\text{NO}_3^- - \text{N} > 10 \text{ mg/L}$	11.3	12.8
Pesticides	8.1	11.9

^a See text for a discussion of this comparison.

Table 21 Cursory comparison of the occurrence of pesticides from the pilot study and SWRL^a (Kross et al. 1990).

Analyte	% Occurrence	
	Pilot study ^b	SWRL
alachlor	ND ^b	1.2
atrazine	4.6	4.4
butylate	ND	ND
chloramben	0.042	ND
cyanazine	ND	1.2
desethylatrazine	ND	3.5
dicamba	ND	ND
ethoprop	ND	ND
metolachlor	ND	1.5
metribuzin	0.083	1.9
picloram	4.2	0.6
propachlor	ND	0.4
trifluralin	ND	0.4
2,4-D	ND	0.6

^a See text for a discussion of this comparison.

^b ND: the compound was not detected above the MRL.

Two major differences must be considered when comparing results of the pilot study and SWRL. First, the MRLs in the pilot study were greater than the MRLs in the SWRL for most compounds determined in both studies (table 22). Thus, one would expect a lower percentage of occurrence in the pilot study. The comparison would be improved if the results from both studies were compared using common MRLs. Second, a lower percentage of dug or bored wells was sampled in the pilot study than in the SWRL. In Iowa, 34% of the rural, domestic wells are dug or bored (Kross et al. 1990). For the pilot study, 20% of the wells sampled were dug or bored. This lower percentage of high-risk wells in the pilot study would also lead to a lower percentage of occurrence. This comparison, however, does not represent the actual percentage of dug or bored wells in Illinois, because, by design, one of the five areas studied was an area with predominantly dug and bored wells. As these examples indicate, comparing results of different studies is a very difficult endeavor and must be done cautiously.

USEPA NPS The USEPA conducted the National Survey of Pesticides in Drinking Water Wells, which required 5 years to complete. The NPS was the first, and perhaps the most extensive, survey ever undertaken to evaluate the presence of pesticides, pesticide degradates, and nitrate in drinking-water wells across the United States (USEPA 1990). The NPS was actually two surveys: one for community water-supply wells and another for domestic supply wells. Only the results of the domestic wells are discussed here because domestic supply wells were sampled in the pilot study.

The NPS samples were collected from 783 rural, domestic wells from April 1988 through February 1990. Samples were analyzed for nitrate, 101 pesticides, and 25 pesticide degradates, including all of the analytes in the pilot study. The following compounds were detected above the MRL in rural, domestic wells: alachlor, atrazine, bentazon, DCPAM, dibromochloropropane (DBCP), ethylene dibromide (EDB), ethylene thiourea (ETU), γ -HCH (Lindane), nitrate, prometon, and simazine. α -chlordane and γ -chlordane were detected by USEPA laboratories, at concentrations much lower than the respective MRLs, during QA/QC checks (USEPA 1990). It was not clear if α -chlordane and γ -chlordane were detected in samples from rural, domestic wells or community water-supply wells.

Table 22 Comparison of the MRLs from the pilot study, SWRL (Kross et al. 1990), and NPS (USEPA 1990).

Analyte	SWRL MRL (µg/L)	PS MRL (µg/L)	NPS MRL (µg/L)
alachlor	0.02	0.75	0.50
atrazine	0.13	0.15	0.12
bentazon	ND ^a	0.79	0.25
butylate	0.10	0.30	0.30
chloramben	1.00	0.52	NR ^b
chlordane	ND	0.048	0.06
chlorpropham	ND	0.40	0.35
cyanazine	0.12	42	2.4
DCPAM	ND	0.24	0.10
desethylatrazine	0.10	35	2.2
dicamba	0.10	0.15	0.10
ethoprop	0.10	0.06	0.06
metolachlor	0.04	0.75	0.75
metribuzin	0.01	0.40	0.18
picloram	0.10	0.76	0.50
propachlor	0.02	0.16	0.05
simazine	ND	0.15	0.36
trifluralin	0.02	0.065	0.13
2,4-D	0.10	0.40	0.25

^a Not detected or not included in list of analytes.

^b Not reported.

Results of the pilot study and the NPS are listed in table 23. The overall occurrence of nitrate was much lower for the pilot study, but the occurrence of nitrate above the MCL was much greater. The lower overall occurrence of nitrate in the pilot study was most likely due to the definition of occurrence used for nitrate. The minimum concentration for a nitrate occurrence was defined as the concentration greater than or equal to the MCL (10.0 mg/L NO₃ -N) in the pilot study, and greater than the MRL (0.15 mg/L as NO₃ -N) in the NPS. Also, 783 rural wells for the entire country were sampled in the NPS. Of these wells, only 10% were actually on or near active farmland, which is a significant difference between the pilot study and the NPS. For the pilot study, 248 wells were sampled in a total area of approximately 180 square miles. All of the pilot study wells were on or adjacent to farmed land. Compared with the NPS results, the results of the pilot study were based on samples collected from wells that, by nature of the well-selection process, were more representative of the true status of agricultural chemicals in groundwater.

Four pesticides (chloramben, chlordane, chlorpropham, and picloram) were detected in the pilot study, but not in the NPS. The occurrence of pesticides was generally much higher in the pilot study than in the NPS, even though the MRLs in the pilot study were slightly higher for many pesticides. The higher occurrence in the pilot study was probably due to the fact that all samples were collected from areas of intense agricultural production, while, as stated above, samples in the NPS were collected from a broader spectrum of settings.

Analysis of Results

A great number of parameters might influence the results of a study such as the pilot study. This was a study of private, drinking-water wells at a variety of complex sites. Examples of important factors include the type of well, well site, past and present environment of the well, and nearby agricultural practices. The following discussion outlines a few of the parameters and suggests some ways in which they might be related to the occurrence of agricultural chemicals.

Table 23 Cursory comparison of the results from the pilot study and the NPS^a (USEPA 1990).

Analyte	% Occurrence	
	Pilot study ^b	NPS ^c
Nitrate	17.5	57.0
nitrate > MCL	17.5	2.4
nitrate only ^d	12.9	53.8
nitrate & pesticides ^e	4.6	3.2
pesticide only ^f	5.4	1.0
≥ 1 pesticide > MCL or HAL	0.4	0.6
alachlor ^g	0	<0.1
atrazine ^g	4.6	0.7
bentazon ^g	1.7	0.1
chloramben	0.4	ND ^h
chlordane	0.4	ND
chlorpropham ^g	0.4	ND
DCPAM ^g	7.5	2.5
metribuzin ^g	0.8	0.1
picloram ^g	4.2	ND
simazine	0.8	0.2

^a See text for a discussion of this compar

^c Percentage of all rural, domestic wells sampled ison.

^b Percentages based on all 240 samples. for the NPS.

^d Includes samples that contain nitrate only.

^e Includes samples that contain nitrate and pesticides.

^f Includes samples that contain one or more pesticides only.

^g ND: not detected above the MRL.

^h The MRL in the NPS is lower than the MRL in the pilot study.

Precipitation As suggested by the results of Iowa's SWRL, the deviation of precipitation from normal (defined as historic average) during the project has an impact on results. Throughout the five study areas, precipitation during the period of sampling was 43 to 53 inches, or 7 to 15 inches higher than average. The monthly precipitation in the Kankakee County study area (fig. 12) was typical of the five study areas. The monthly precipitation was more than 1.5 inches higher than average (1951-1980) at recording stations near all or most study areas for February 1990 (five areas), May 1990 (four areas), October 1990 (four areas), and December 1990 (four areas). The monthly precipitation was more than 1.5 inches lower than average (1951-1980) at recording stations near four study areas for September 1990.

The occurrence of agricultural chemicals and the monthly precipitation for Kankakee County are shown in figure 13. After a certain time lag, the occurrence of agricultural chemicals may increase because of above-average levels of precipitation; however, additional data and analysis are needed to support any hypotheses based on the limited data presented here. Necessary data would include the amount of daily precipitation and precipitation rates, and data to understand recharge in each hydrogeologic setting. Samples would also have to be collected over shorter time intervals. The much larger data set created through the recommended statewide survey will afford a better opportunity to understand this relationship.

Type of pesticide Samples were analyzed for 33 pesticides (considering the two types of chlordane as one), four pesticide degradates, and nitrate. Samples were analyzed for 19 herbicides, 13 insecticides, and one fungicide. Thirty-two occurrences of nine different pesticides (eight herbicides and one insecticide) were detected in samples from 24 wells. The eight herbicides detected account for 31 of the 32 occurrences of pesticides. A higher number of detections of herbicides may be attributed to a higher volume of herbicide use, as well as their

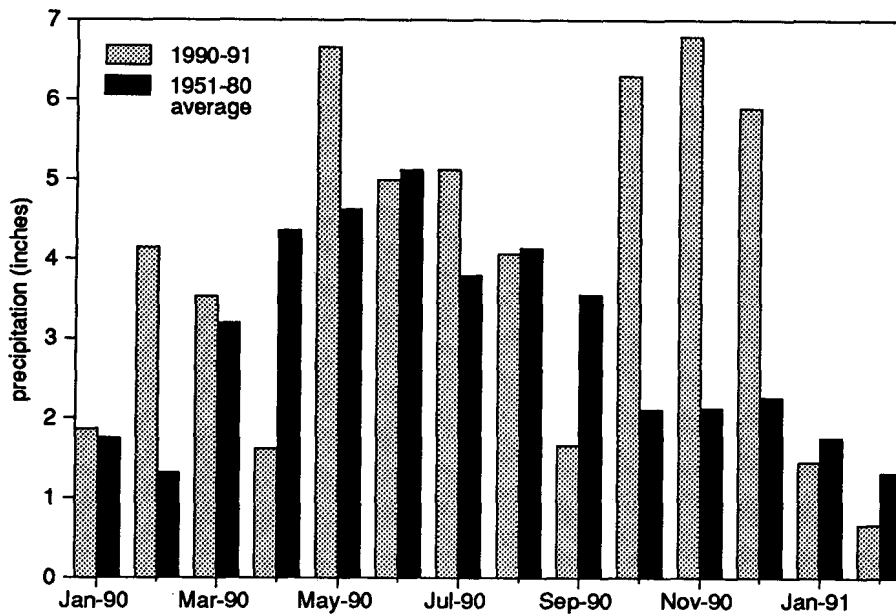


Figure 12 Monthly precipitation rates at station 114603, Kankakee, which is the nearest station to the Kankakee County study area (data from the Midwest Climate Center, ISWS)

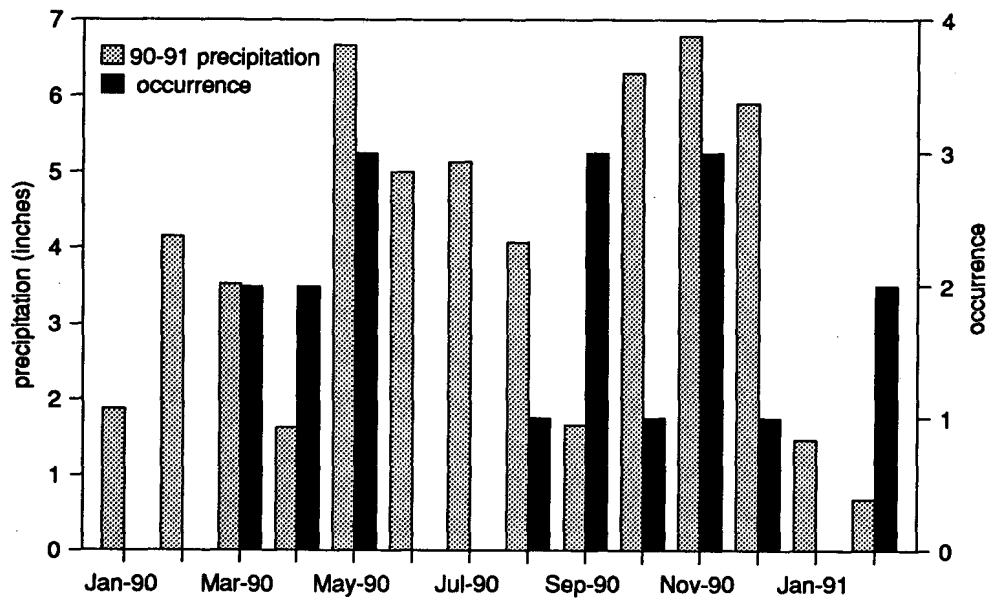


Figure 13 Monthly occurrence and monthly precipitation rates for the Kankakee County study area. The occurrence has a maximum of four (only four wells per month were sampled in each study area).

more widespread applications (Pike et al. 1991) and longer half-lives compared with the half-lives of organophosphorus insecticides. A much larger study, such as the recommended statewide survey, would make it possible to examine with greater confidence the effect of pesticide type.

Pesticide use Atrazine accounted for 11 of the 32 occurrences of pesticide and, for pesticides detected, had the highest reported use in Illinois. More than 9 million acres of cropland, approximately 78% of all corn acreage in the state, was reportedly treated with atrazine in 1990 (Pike et al. 1991).

Picloram accounted for 10 of the 32 occurrences of pesticides, but it was reportedly last used for agricultural purposes in Illinois in 1978 on only 142 acres of pasture and was not used in 1990 (Pike et al. 1991). Picloram is no longer recommended by cooperative extension agents for agricultural use in Illinois due to its persistence, potential for transport in runoff, and toxicity to soybeans (E. L. Knake, personal communication, 1991). Picloram is used by utility companies in Illinois to control brush and weeds along their rights of way (J. Adams, personal communication, 1991; M. Webster, personal communication, 1991). It is also used by the Illinois Department of Transportation in spot treatments to control brush along highways (R. McMullen, personal communication, 1991).

Four of the 32 occurrences of pesticides were bentazon. In 1990, bentazon was applied to 32% of the soybean acreage and 6% of the corn acreage in the State. Metribuzin and simazine each appeared twice in the 32 occurrences of pesticides. Metribuzin was applied to 16% of soybean acreage in Illinois in 1990. Simazine was applied to 1.4% of corn acreage in 1990 (Pike et al. 1991)

There was one occurrence each of chloramben, chlorpropham, and chlordane in the samples collected for this project. Chlorpropham was applied to less than 1% of soybean acreage in Illinois in 1978 (Owen 1980) and there was no reported use in 1990 (Pike et al. 1991). Chloramben was applied to 0.8% of soybean acreage in Illinois in 1990 (Pike et al. 1991), down from 15.2% in 1978 and 39% in 1972 (Pike et al. 1989). Chlordane, an insecticide once used for agricultural insect and residential termite control, is no longer used legally in the United States, and its USEPA registration has been canceled.

The volume of statewide use did not correlate well with the occurrence of pesticides in the pilot study. Several of the pesticides that were not detected, such as metolachlor and dicamba, have a reported use higher than pesticides that were detected. It is not realistic to discuss the volume of use across a state or a large region with respect to the number of detections in discrete sections of that state. The local environment and the conditions of use probably affect the occurrence of contaminants in such a variable way that broad-spectrum averages are meaningless.

Effect of chemical properties of pesticides Cohen et al. (1984) listed criteria to identify pesticides that presented a potential to contaminate groundwater. Some of these criteria are

- water solubility—greater than 30 mg/L,
- adsorption coefficient (K_d), the amount of a compound adsorbed by soil particles compared with the amount of the compound in solution—less than 5 mL/g, and usually less than 1 or 2 mL/g,
- normalized adsorption coefficient (K_{oc}), K_d normalized to a soil's organic matter content—less than 300 to 500 mL/g,
- Henry's law constant—less than 10^{-2} atm-m³/mol,
- soil half-life—greater than 2 to 3 weeks.

Data for these parameters were obtained from McKenna et al. (1989). Five of the eight pesticides detected in the pilot study met all of the above criteria. DCPAM was not a target analyte and these chemical properties were not available for DCPAM, so DCPAM is not discussed here. The other three detected pesticides (chlordane, simazine, and chlorpropham) did not meet the above criteria, but accounted for only four of the 32 occurrences. Simazine has a solubility of 4.98 mg/L, a K_{oc} of 140 mL/g, and a half-life of 75 days. Chlordane has a solubility of 0.056 mg/L, a K_{oc} of 380,000 mL/g, and a reported half-life of 3,500 days. Chlorpropham has a solubility of 88 mg/L, a K_{oc} of 555 mL/g, and a reported half-life of 65 days. Both chlordane and simazine have low solubility and high K_{oc} ; therefore, the predicted soil mobility of these compounds in soil and groundwater is low. Chlorpropham's high K_{oc} indicates a propensity for adsorption by organic matter.

The pesticides detected had solubilities that spanned most of the range of the solubilities of the 33 pesticide analytes. The range of solubilities of detected compounds was from 1,200 mg/L to 0.056 mg/L, and the range of the 33 pesticide analytes was from 7,900 mg/L to 0.002 mg/L. The solubility of the detected pesticides was evenly distributed about the median solubility of the 33 pesticide analytes.

The range of values of K_{oc} for pesticides detected in samples was from 21 to 380,000 mL/g, and K_{oc} for the 33 pesticide analytes ranged from 2.2 to 380,000 mL/g. Six of the eight pesticides detected had a K_{oc} below the median K_{oc} value of the 33 pesticide analytes.

The range of values for half-life in soil of the pesticides detected was from 3,500 days to 30 days. The range for all pesticide analytes was from 5,480 days to 5 days. Six of the eight pesticides detected had a half-life greater than the median half-life of all pesticide analytes.

The degradate of DCPA, or dacthal, was the only pesticide degradate detected in samples. Pesticide degradates that were not detected above their MRL were degradates of atrazine (desethylatrazine), heptachlor (heptachlor epoxide), and carbofuran (carbofuran phenol). However, degradates might be detected in a larger sample from a broader geographic area.

The number of picloram occurrences in samples was disproportionately high compared with the results of the NPS and Iowa's SWRL. Picloram has been shown to leach to groundwater and has been found in surface runoff; however, most published studies were conducted in areas having neither soils nor climate similar to those of Illinois.

A statewide survey in North Dakota studied the occurrence of picloram in rural wells (Lym and Messersmith 1988). Picloram is commonly used on pastures and rights of way in North Dakota. In 1985, picloram was found in samples from 5 of 144 wells. The contaminated wells and 44 additional wells were sampled the following year. Picloram was found only in one of these additional wells. Picloram was found not to leach to groundwater in Texas when applied during a dry year. When applied to the same site the following year when soil moisture was higher, picloram was detected at low concentrations (1 to 4 $\mu\text{g/L}$) in groundwater 11, 41, and 48 days after application (Bovey and Richardson 1991). Off-site vertical and lateral movement was observed from a forested watershed in east-central Alabama, where picloram was applied to control kudzu. Movement of picloram coincided with major rainfall events (Michael et al. 1989). When picloram was applied for roadside weed control in Montana, no off-site movement of picloram was detected (Watson et al. 1989). Vertical leaching of picloram was not detected past 1 meter. Ping et al. (1975) found picloram leached preferentially through macropores. Davidson and Chang (1972) found leaching of picloram increased as pore-water velocity increased, leaching decreased as pore-size decreased, and leaching decreased as bulk-density increased. Studies in Canada on the use of picloram along highways and power line rights of way showed little off-site movement in surface runoff (Sironi et al. 1977, Meru et al. 1990). Neither study attempted to quantify vertical losses from leaching to groundwater. The preliminary results in

this study indicate that picloram should be included as an analyte for the statewide survey. Its persistence makes it important to consider.

High pesticide-use levels in Illinois did not seem to correlate with the pesticides detected in samples for this project. Several of the pesticide analytes not detected in our samples had higher reported levels of use than some pesticide analytes that were detected. Overall, the occurrence of an agricultural chemical cannot be predicted by a single chemical property. The occurrence of an agricultural chemical is controlled by a complex set of processes, and predicting the occurrence requires data for many properties. The size of the data set and bias imposed on by the selection of five small areas for the pilot study might be influencing the results. The recommended statewide survey will afford researchers a better view of the situation.

Effect of well depth Nitrate concentration generally decreased as well depth increased for wells tested in the Mason County study area (fig. 14). This decrease in nitrate concentration with depth was not quite as great for the wells tested in the Livingston County study area (fig. 15), and the relationship was not apparent for wells in the Kankakee County (fig. 16) and Effingham County (fig. 17) study areas.

The occurrence of nitrate and pesticides was much higher in shallow wells (<50 feet deep) than deep wells (≥ 250 feet deep) (table 20). This difference was statistically significant as determined by contingency table analysis. (Contingency table analysis and other types of statistical analysis and their application in this project are discussed in a later section.)

Review of site characteristics The interview sheets contained a vast amount of information ranging from well construction and history to use of agricultural chemicals. For each study area, the data from these sheets were reviewed to identify any patterns in the occurrence of agricultural chemicals. Instead of relying on statistics, the reviewers used a common-sense approach in their analysis. For example, the reviewers tried to relate use, spills, or backsiphoning of agricultural chemicals to occurrences in nearby wells.

This review did not lead to any firm conclusions. For each apparent pattern, evidence to the contrary exists. The occurrence of picloram in the Mason County study area serves as an example of the review of the interview sheets. Three wells, located within 500 feet of one another and near a utility right of way, had occurrences of picloram. The local utility had used picloram along this right of way during the pilot study. However, there were no occurrences of picloram in eight other wells along this right of way and within 500 feet of the three wells with an occurrence of picloram. Although this information indicates a potential link between the occurrence of picloram in the wells and the use of picloram, additional data and analysis are needed to confirm this potential link and explain the nonoccurrence in the other nearby wells.

Nitrate results in the Piatt County study area The number of nitrate occurrences in Piatt County was expected to be low because of the hydrogeologic setting and depth of wells, but zero occurrences was unexpected. Only two of the 48 samples from this area had nitrate concentrations at or above the EDL—the concentrations were 0.027 and 0.023 mg/L. Review of the ISWS water-quality database indicated that these concentrations were typical of other wells near the study area.

Statistical Analysis

The analytical chemistry results were statistically analyzed to gain additional insight into the occurrence of agricultural chemicals in rural, private wells. Inferences drawn from this analysis are valid for the wells sampled as part of the pilot study; extrapolation to other wells may not be valid. Hypothesis testing and two nonparametric techniques were used. The two nonparametric methods were contingency tables and logistic regression. In addition, the concentrations of nitrate were statistically analyzed for temporal variation.

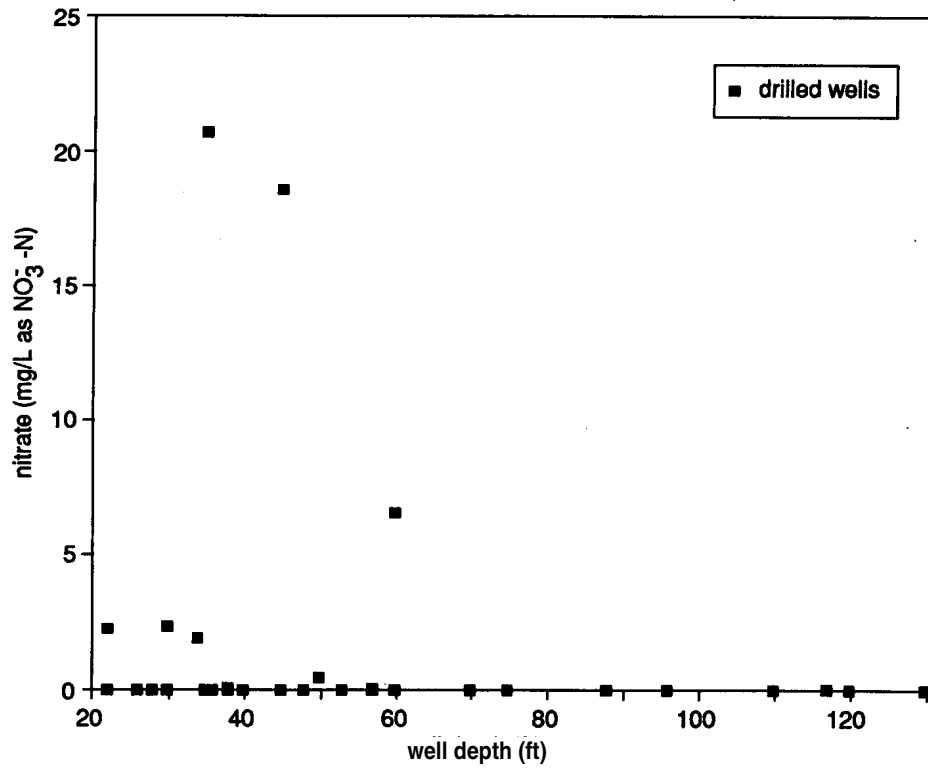


Figure 14 Nitrate concentration plotted against well depth for the Mason County study area.

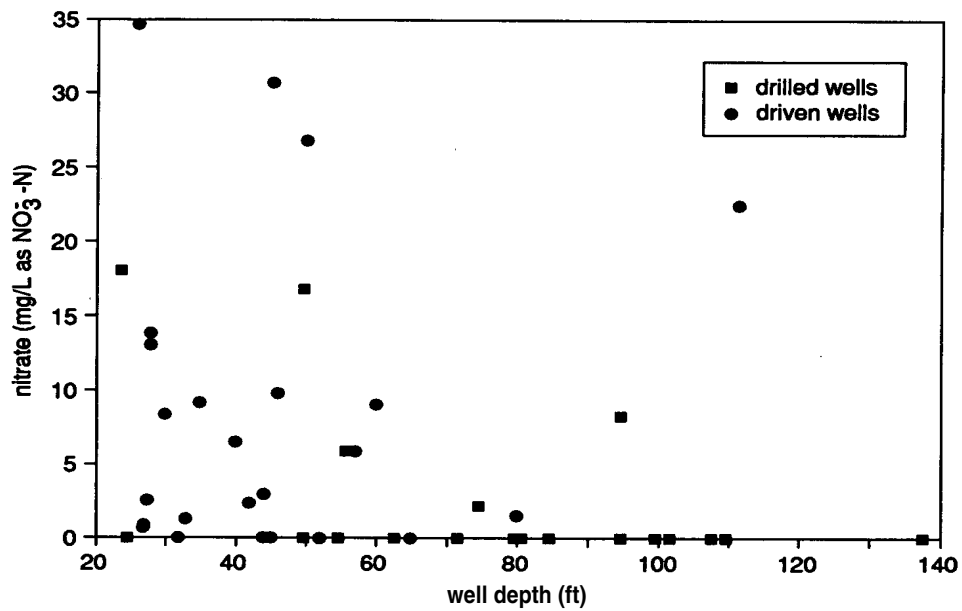


Figure 15 Nitrate concentration plotted against well depth for the Livingston County study area.

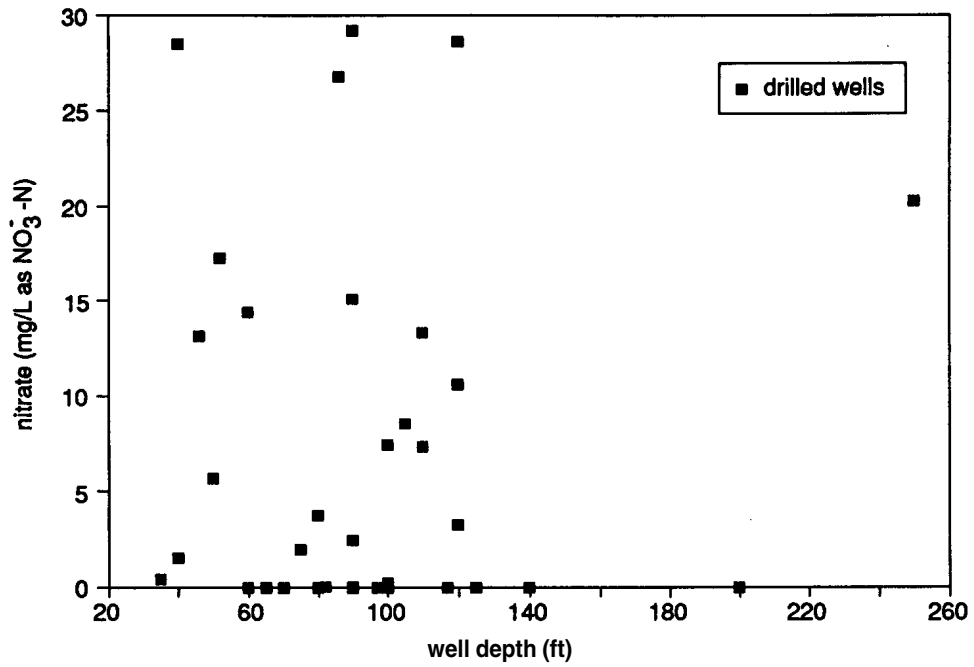


Figure 16 Nitrate concentration plotted against well depth for the Kankakee County study area.

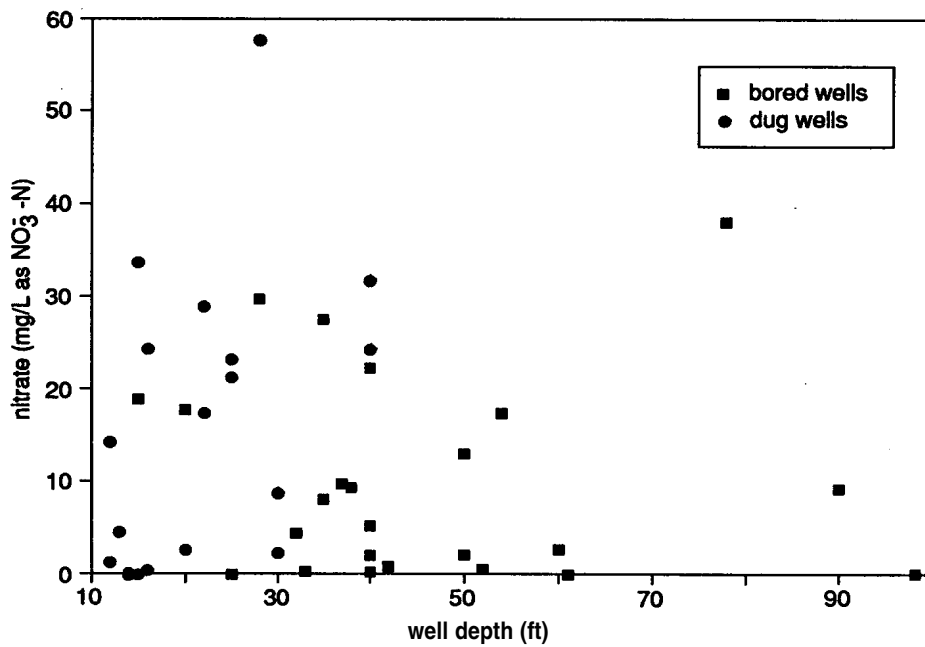


Figure 17 Nitrate concentration plotted against well depth for the Effingham County study area.

Table 24 Occurrence of one or more targeted agricultural chemicals in the five study areas.

Area	Number of occurrences	Number of samples	Proportion	Std dev ^a	95% CI ^b		99.7% CI ^c	
					low	high	low	high
Effingham	22	48	0.46	0.080	0.30	0.62	0.22	0.70
Kankakee	18	48	0.38	0.093	0.19	0.56	0.11	0.66
Mason	11	48	0.23	0.12	0.00	0.46	0.00 ^d	0.58
Livingston	4	48	0.08	0.15	0.00 ^d	0.38	0.00 ^d	0.54
Piatt	0	48	0.00	0.00	0.00	0.00	0.00	0.00
Total	55	240	0.23					

^a Standard deviation (σ) is the positive square root of the variance (σ^2), which is computed using the following equation developed for this project by the Illinois Statistics Office (Amarasinghe and Cox 1990):

$$\sigma_h^2 = \left(1 - \frac{n_h}{N_h}\right) \frac{p_h(1 - p_h)}{n_h - 1}$$

where n_h = number of wells with an occurrence from category h
 N_h = total number of wells in category h
 p_h = proportion of occurrences in category h

^b 95% confidence interval based on 1.96σ .

^c 99.7% confidence interval based on 3σ .

^d Reported as 0.00, computed value is less than 0.00.

Table 25 Results of hypothesis testing-pairwise comparison.

Area a	Area b	$p_a - p_b$ ^a	Test statistic ^b	Statistically different?
Effingham	Kankakee	0.083	0.120	No

^a The absolute value of the proportion in area a minus the proportion in area b.

^b The following test statistic was computed using a 95% confidence interval ($z_{.5\alpha} = 1.96$) and developed for this project by the Illinois Statistics Office (Amarasinghe and Cox 1990):

$$|p_a - p_b| > z_{.5\alpha} \sqrt{\left(1 - \frac{n_a}{N_a}\right) \left(\frac{p_a(1 - p_a)}{n_a - 1}\right) + \left(1 - \frac{n_b}{N_b}\right) \left(\frac{p_b(1 - p_b)}{n_b - 1}\right)}$$

Hypothesis testing One of the principal objectives of the pilot study was to evaluate the effectiveness of the stratification variable, depth to the uppermost aquifer material, for predicting the occurrence of agricultural chemicals in rural, private wells. Hypothesis testing can be used to determine if the difference in the rate of occurrence (i.e., proportion) between two study areas is statistically significant. This technique is known as pairwise comparison. One-way analysis of variance (ANOVA) can be used to simultaneously determine if the proportions for all five study areas are statistically significantly different from one another.

Results for the pair-wise comparison of the study areas are presented in table 24. The null hypothesis was that the proportions for the two study areas tested are equal. The alternate hypothesis was that the proportions are not equal. The hypothesis was tested by comparing the difference in the two proportions against a test statistic. If the absolute value of the computed difference is larger than the test statistic, then the null hypothesis was rejected, and we inferred that the alternate hypothesis was valid. Amarasinghe and Cox (1990) noted that the hypothesis test is not valid if a confidence interval based on three standard deviations contains impossible values (e.g., values less than zero) and is questionable if the proportion is very close to zero. The hypothesis test was thus not valid for the Piatt County study area and questionable for the

Table 26 Results of contingency table analysis—overall comparison.

County	Actual			Estimated		
	Occurrences	Nonoccurrences ^a	Sum	Occurrences ^b	Nonoccurrences ^c	Sum
Effingham	22	26	48	11	37	48
Kankakee	18	30	48	11	37	48
Livingston	4	44	48	11	37	48
Mason	11	37	48	11	37	48
Piatt	0	48	48	11	37	48
Calculated T = 40.10						
$\chi^2(4, 0.95) = 9.49$						

^a Number of samples collected minus the number of occurrences.

^b Calculated, used to calculate T.

^c Calculated, used to calculate T.

Table 27 Results of contingency table analysis—pairwise comparison.

County a	County b	Calc T	$\chi^2(1, 0.95)$	Statistically different? ^a
Effingham	Kankakee	0.686	3.84	No
Effingham	Livingston	17.1	3.84	Yes
Effingham	Mason	5.59	3.84	Yes
Effingham	Piatt	28.5	3.84	Yes
Kankakee	Livingston	11.6	3.84	Yes
Kankakee	Mason	2.42	3.84	No
Kankakee	Piatt	22.2	3.84	Yes
Livingston	Mason	3.87	3.84	Yes
Livingston	Piatt	4.17	3.84	Yes
Mason	Piatt	12.4	3.84	Yes

^a "No" indicates that $T \leq \chi^2$, "Yes" denotes that $T > \chi^2$.

Livingston County and Mason County study areas. The only valid pairwise comparison is between the Effingham and Kankakee County study areas and the difference is not statistically significant (table 25).

Contingency tables The use of contingency tables (CT), described by Conover (1980) and Guttman et al. (1982), is a nonparametric technique for testing the hypothesis that a number of proportions are not statistically different from one another. Contingency tables can also be used as a test for independence, that is, to test whether the sample is dependent on certain parameters. Both of these uses were applied to the results.

The first application of CT in the pilot study was to determine if the proportion of the occurrence of agricultural chemicals was equal for all study areas. This could not be checked using ANOVA because an important assumption (the variance of the proportions are equal) was not satisfied. The results of testing by CT are shown in table 26. The calculated test statistic, T, was larger than the tabulated chi-square value, so the null hypothesis (all proportions are equal) was rejected. Thus, we inferred that all proportions were not equal.

The proportions of occurrence and nonoccurrence were also tested with CT on a pairwise basis (table 27). If the calculated test statistic exceeds the chi-square value, the difference between occurrences of the tested pair is considered to be statistically significant. All pairs of occurrence were considered statistically significantly different except for the occurrences in the Effingham and Kankakee County study areas, and in the Kankakee and Mason County study areas. These results indicate that categories for areas that are not statistically different can be

combined. This combination would reduce the number of categories to be sampled and the number of samples to be collected and analyzed.

Contingency tables were also used to determine the independence of occurrence of agricultural chemicals in rural, private wells from various parameters considered to affect occurrence (table 28). Data on the parameters tested were obtained during interviews with well users. Several facts should be considered when interpreting the following results. First, most of the information gathered during the well user interview was based on the memory of the well user, not written documentation. Second, the analysis was conducted on a nonideal sample. Unlike the sample drawn to test the impact of the depth to the uppermost aquifer material, the following variables were tested using a sample of opportunity, not a sample optimally designed for testing. However, the following analysis can provide insight into the occurrence of agricultural chemicals in the rural, private wells sampled for this project. These results should not be considered definitive for all wells in Illinois. Perhaps the best use of these results is to guide future analysis and research.

Lower α values in table 28 indicate that the null hypothesis (the occurrence is independent of the tested parameter) is rejected at higher confidence intervals. A confidence interval is defined as 1 minus alpha. R1 is Cramer's contingency coefficient and ranges from 0 to 1. If R1 equals 0, there is little or no dependence; if R1 equals 1, there is strong dependence (Conover 1980). Also, Conover (1980) noted that R1 is generally larger for larger tables (tables with a larger number of rows and/or columns).

The following example should illustrate the interpretation of CT. The first parameter in table 28 is study area, which indicates the origin of the well-water sample. Samples were collected from five study areas, and five rows are in the table. The number of rows for each parameter was a function of the number of classes for the parameter. For some parameters with a large number of classes, such as well type and well depth, a second table was created. The second table had a lower number of rows indicating that some classes were combined. Each parameter tested had two columns. The two columns represent the proportions of occurrence and non-occurrence. For study area, the calculated test statistic, T, equals 40.1 and is greater than the $\chi^2(4, 0.95)$ of 9.5 (table 28). So the null hypothesis was rejected, and the occurrence was dependent on study area.

The parameters listed in table 28 were developed from the questionnaire administered to each well user (appendix B). Parameters with critical levels (alpha) less than 0.20 were considered to show dependence.

Occurrence was dependent upon the following parameters.

- Study area—the study area from which the sample is collected.
- Well type 1 and 2—for well type 1, the data were organized into six classes. These six classes were reduced to three for well type 2.
- Well depth 1 and 2—for case 1, well depth was separated into 20 classes. For case 2, well depth was separated into 12 classes.
- Well cover 1 and 2—well cover was separated into 14 classes for case 1, and 8 classes for case 2.
- Animals-past—have livestock been raised on property since 1980?
- Manure use—is manure applied within 500 feet of well?
- Tank overflow—has the sprayer tank ever overflowed?
- Mix at well—is well water used for mixing agricultural chemicals for spraying?
- Prevent seepage?—is the well cover adequate to prevent seepage?
- Backsiphoning—has the sprayer tank ever backsiphoned into the well?
- Topography—what is the topographic position of well (e.g., level land, hill slope)?

Table 28 Results of contingency table analysis—determining sample independence for various parameters (listed in order of increasing alpha).

Parameter	Rows	Columns	Calc T	Degrees of freedom	χ^2	α^a	R1 ^b
Study area	5	2	40.1	4	9.488	<0.001	0.1671
Well type 1	6	2	22.22	5	11.07	<0.001	0.0926
Well type 2	3	2	15.02	2	5.991	<0.001	0.0626
Well depth 1	20	2	36.36	19	31.41	0.01	0.1515
Well depth 2	12	2	29.03	11	19.67	0.01	0.1210
Well cover 1	14	2	25.39	13	22.36	0.025	0.1058
Well cover 2	8	2	17.64	7	14.07	0.025	0.0735
Animals, past	4	2	10.05	3	7.815	0.025	0.0419
Manure use	3	2	6.261	2	5.991	0.05	0.0261
Tank overflow	4	2	8.819	3	7.815	0.05	0.0367
Mix at well	6	2	11.23	5	11.071	0.05	0.0468
Prevent seepage?	4	2	8.994	3	7.815	0.05	0.0375
Backsiphoning	6	2	10.44	5	11.071	0.10	0.0435
Topography	5	2	9.34	4	9.488	0.10	0.0389
Ag. use	4	2	4.659	3	7.815	0.20	0.0194
Storage	3	2	3.4	2	5.991	0.20	0.0142
Nonag. use	3	2	3.615	2	5.991	0.20	0.0151
Disposal	3	2	4.2	2	5.991	0.20	0.0175
Animals, present	5	2	6.389	4	9.488	0.20	0.0266
Season 1	4	2	5.624	3	7.815	0.20	0.0234
Season 2	2	2	1.329	1	3.841	0.30	0.0055
Contaminated?	3	2	2.461	2	5.991	0.30	0.0103
Distance to field	4	2	4.447	3	7.815	0.30	0.0185
Sampling trip	24	2	24.32	23	35.17	0.40	0.1013
Dwelling type	3	2	2.39	2	5.991	0.40	0.0100
Abandoned well	4	2	3.122	3	7.815	0.40	0.0130
Nonoperating well	4	2	2.042	3	7.815	0.50	0.0085
Well age1	12	2	10.81	11	19.68	0.50	0.0450
Well age 2	9	2	0.376	8	15.507	0.99	0.0016

^a α : critical level, the smallest level of significance that would result in the rejection of the null hypothesis.

^b R1: Cramer's contingency coefficient, varies from 0 to 1, ratio of calculated T over maximum value for T, which equals $[N(q-1)]$. N is the number of samples and q is the smaller of the row or column dimension.

Occurrence was not dependent on the following parameters.

- Ag. use—are agricultural chemicals used for large-scale agricultural use?
- Storage—are agricultural chemicals stored within 500 feet of the well?
- Nonag. use—are agricultural chemicals used for nonagricultural purposes?
- Disposal—are agricultural chemicals disposed of within 500 feet of the well?
- Animals-present—are livestock currently present on property?
- Season 1 and 2—season 1 and 2 represent the season of the year when the sample was collected. For season 1, the data were grouped as four seasons. For season 2, the data are grouped as winter or other seasons.
- Contaminated?—the owner/user reported whether the well was known or was suspected to be contaminated.
- Distance to field—what is the distance from the well to the nearest field?
- Sampling trip—on what sampling trip was the sample collected?
- Dwelling type—what was the type of dwelling: farm, rural residence, or unknown?
- Abandoned well—is there an abandoned well within 500 feet of the well?
- Non-operating well—is there a nonoperating well within 500 feet of the well?
- Well age 1 and 2—well age was divided into 12 classes for case 1, and 9 classes for case 2.

The parameters that provide the strongest relation to occurrence, as evidenced by lower alpha and higher R1 values, were study area, well type, well depth, and well cover. At first, these parameters pointed to the well as the most important parameter for defining occurrence. However, the study area incorporates information regarding well type and hydrogeologic setting. Well depth and type of well cover can be related to type of well and ultimately to the study area. Based on these univariate results, there were a number of interrelated parameters that appeared to define the occurrence. A multivariate technique such as logistic regression was needed to sort through these interrelated data.

Logistic regression The purpose of logistic regression is to develop a model describing the relationship between a dependent variable and a set of independent variables. In regression analysis, "dependent" refers to a random or regress variable and "independent" refers to a nonrandom or explanatory variable. In this case, the dependent variable was the occurrence or nonoccurrence of agricultural chemicals in a sample from a rural, private well, and the independent variables might be well type, topographic position of well, and the other factors listed previously. Conceptually, logistic and linear regression, are similar techniques, but they differ in the type of variables used in the analysis. In linear regression, the dependent variable is a continuous variable. In logistic regression, the dependent variable is a binary or categorical variable (Hosmer and Lemeshow 1989). An example of a binary variable is occurrence, which can have one of two values—yes or no or, using numbers, 0 or 1.

The modeling procedure for logistic regression is similar to the procedure for linear regression and is described by Hosmer and Lemeshow (1989). The LOGIT module of SYSTAT (Steinberg and Colla 1991) was used to conduct the logistic regression modeling. The first step was to identify variables to be included in the model. This step can be accomplished by univariate logistic regression, which also provides data useful for interpretation of the multivariate model. The second step was to build the multivariate model. With LOGIT, this can be accomplished by stepwise regression. After developing a model with stepwise regression, the model should be confirmed by multivariate logistic regression using variables identified from stepwise regression.

Logistic regression was conducted using data from all five study areas to determine if there were any parameters controlling occurrence. It was expected that analyzing this larger number of samples would produce more definite results than analyzing the results from a single study area.

Univariate logistic regression was conducted for all variables found to be significant from the CT analysis. Additional parameters, those with alpha values greater than or equal to 0.20 from CT testing and thought to be possible contributing factors, were also tested by univariate logistic regression. The results of the univariate logistic regression are presented in table 29. The results are similar to the CT results, with some minor shifts in the relative strength of some parameters. The three strongest parameters still were study area, well type, and well depth.

As discussed previously with contingency tables, parameters tested were obtained during the interview of the well user. For the interpretation of the following results, several facts should be considered. First, most of the information gathered during the well user interview was based on the memory of the owner/user. Second, the analysis was conducted on a nonideal sample. Unlike the sample drawn to determine the impact of the depth to uppermost aquifer, the following variables were tested using a sample of opportunity, not a sample optimally designed for testing. However, the following analysis could be useful for providing insight into the occurrence of agricultural chemicals in the rural, private wells sampled for this project. These results should not be considered definitive for all wells in Illinois. Perhaps the best use of these results is to guide future analysis and research.

Table 29 Results of univariate logistic regression (listed in order of increasing alpha).

Parameter	Log-likelihood	G ^a	α^b
Constant ^c	-129.184		
Study area	-104.464	49.44	0.0000
Well type	-120.076	18.22	0.0011
Well depth	-118.473	21.42	0.0015
Prevent seepage?	-123.082	12.20	0.0067
Well cover	-120.261	17.85	0.0127
Animals, past	-124.365	9.64	0.0219
Topography	-123.815	10.74	0.0297
Manure use	-126.274	5.82	0.0545
Tank overflow	-125.404	7.56	0.0560
Nonag. use	-126.549	5.27	0.0717
Mix at well	-124.158	10.05	0.0738
Contaminated?	-125.113	8.14	0.0865
Disposal	-127.529	3.31	0.1912
Backsiphoning	-124.844	8.68	0.1924
Ag. use	-127.118	4.13	0.2476
Storage	-127.863	2.64	0.2669

^a G: statistic based on the difference in the log-likelihood of a model based on a parameter and a constant and a model based solely on a constant.

^b α : critical level, the smallest level of significance that would result in the rejection of the null hypothesis. It is computed based on a χ^2 statistic.

^c The model based on this constant is used for computation of G.

Stepwise logistic regression was conducted after the univariate logistic regression to assemble a multivariate logistic regression model. This multivariate model allows the determination of the relative significance, in a statistical sense, of many variables. Hosmer and Lemeshow (1989) warn that the final multivariate model must be credible on a scientific level also. In stepwise regression, the software adds to the model a variable that has the lowest significance level for the score statistic. Thus, the order in which parameters are added to the model is important; the first parameter added is the most significant and each one after it is less significant.

Stepwise regression was conducted using all parameters listed in table 29 except study area, nonag. use, disposal, backsiphoning, ag. use, and storage. Study area was excluded because it includes data on well depth, well type, and other parameters. This exclusion should lead to a model that provides additional insight into the occurrence. The other parameters were excluded because the software limited the number of parameters that could be modeled, and these were deemed the least significant based primarily on the alpha from univariate logistic regression. The remaining ten parameters were modeled using stepwise regression. Based on this modeling, five parameters were determined to be significant. These were, in order of selection, well type, prevent seepage?, tank overflow, well depth, and well cover. Based on the results of this stepwise logistic regression modeling, a multivariate model was built using these parameters.

A multivariate logistic regression model can be evaluated in a number of ways including the McFadden's Rho-squared coefficient, the odds ratio of the model parameters, and by the model prediction success table. McFadden's Rho-squared coefficient is a transformation of the G statistic intended to mimic the R-squared statistic from linear regression. Models with values of McFadden's Rho-squared coefficient between 0.20 and 0.40 are considered very satisfactory (Steinberg and Colla 1991).

The odds ratio is defined as the ratio of the odds for x equals 1 (i.e., x equals the response value) over the odds for x equals 0 (i.e., x equals the reference value) (Hosmer and Lemeshow 1989). For our model, the response value would be for an occurrence, while the reference

Table 30 Results of multivariate logistic regression.

Parameter	Odds ratio	Confidence interval ^a	
		lower	upper
Well type 1	0.826	0.217	3.14
Well type 2	1.40	0.317	6.17
Well type 3	4.75	0.990	22.7
Well type 4	0	0	0
Prevent seepage? 1	0.369	0.0599	2.27
Prevent seepage? 2	0.203	0.0236	1.75
Prevent seepage? 3	0	0	0
Tank overflow 1	3.58	1.00	12.8
Tank overflow 2		0	0
Tank overflow 3	1x10 ³²	NR ^b	0
Well depth 1	1.27	0.242	6.65
Well depth 2	0.965	0.138	6.77
Well depth 3	2.21	0.400	12.2
Well depth 4	1.89	0.345	10.4
Well depth 5	6.99	1.15	42.4
Well depth 6	1.28	0.200	8.12
Well cover 1	1.09	0.279	4.26
Well cover 2	1.39	0.275	7.05
Well cover 3	4.64	1.08	20.0
Well cover 4	2.19	0.344	14.0
Well cover 5	0.611	0.0530	7.05
Well cover 6	10.1	0.904	112
Well cover 7	0	0	0
Model prediction success table			
True occurrence	0.416	True nonoccurrence	0.826
False occurrence	0.584	False nonoccurrence	0.174

^a 95% confidence interval.

^b Value not reported by software.

value would be a nonoccurrence. If the odds ratio equals 2, an occurrence is twice as likely for the independent parameter modeled. Similarly, an odds ratio of 4 indicates that an occurrence is four times as likely. In addition, to be considered a genuine risk factor, the confidence interval for the odds ratio should not include 1.0. (An odds ratio of 1.0 would indicate that the parameter cannot be used to classify the data into reference or response categories.)

The final way to evaluate a multivariate logistic regression model is to evaluate the model prediction success table. This table provides data on the classification power of the model (Steinberg and Colla 1991).

The results of the multivariate model are presented in table 30. The model has a McFadden's Rho-squared value of 0.217, so it would be considered satisfactory. However, the confidence interval for the odds ratio of the modeled parameters contains 1.0 with only three exceptions. In addition, the model success prediction table indicates that the model could be improved. Only 41.6% of the actual occurrences would be properly predicted using the multivariate model, as shown by the true occurrence value of 0.416 (table 30). Although the multivariate model is considered satisfactory, it could be improved, perhaps by reducing the number of classes of the parameters. The univariate analysis needs to be repeated to evaluate this possibility in order to determine whether the number of classes of the parameters in table 30 can be reduced.

Overall, univariate logistic regression indicated that the study area, well type, and well depth were strong indicators for the occurrence of agricultural chemicals in rural, private wells tested in the pilot study. The results of multivariate logistic regression modeling, which accounts for the interdependence of parameters and excluded the parameter study area, indicate the most significant parameters were well type, prevent seepage?, tank overflow, well depth, and well cover.

The results of logistic regression modeling indicated that defining the parameters influencing the occurrence of agricultural chemicals will not be simple because most of the parameters are not independent, but are interrelated. These parameters can probably be defined better by looking at each study area separately; however, the smaller number of samples for one study area may hinder this analysis. Additional logistic regression should be conducted using collective data from all five study areas, and for the following study areas: Effingham, Kankakee, Livingston, and Mason.

SUMMARY AND CONCLUSIONS

The occurrence of agricultural chemicals in rural, private wells averaged 23% (range = 0% to 46%) for the five study areas. Nitrate was the most frequently occurring agricultural chemical. In addition to nitrate, nine other agricultural chemicals were detected above their respective MRLs. The remaining 28 agricultural chemicals included as analytes for this study were not detected above their respective MRLs. Only nitrate (42 occurrences) and atrazine (1 occurrence) had one or more occurrences above their respective MCLs.

For drilled or driven wells, the stratification variable, depth to the uppermost aquifer material, is useful for predicting the occurrence of agricultural chemicals in the rural, private wells tested. The dependence of occurrence on the study area was shown through analysis with contingency tables (tables 26, 27, and 28) and univariate logistic regression (table 29). Thus, the occurrence of agricultural chemicals is not uniform across different hydrogeologic environments, and the recommended statewide survey based on stratification by hydrogeologic environment is warranted. In addition, the potential for contamination map, based on depth to uppermost aquifer material (McKenna et al. 1989, McKenna and Keefer 1991), should be a reasonable guide for the design of the recommended statewide survey for drilled or driven wells. The statistical analysis indicated that certain categories of potential for contamination may be combined. Such a reduction could reduce the cost of a statewide survey, but might not be desirable if the intended use of the survey results require the originally recommended level of detail.

Well type and depth were shown to be significant predictors of occurrence of agricultural chemicals in rural, private, drinking-water wells. The dug or bored wells sampled in the Effingham County study area were shown to have the highest frequency of occurrence. For these wells, the map of potential for contamination (McKenna et al. 1989) is not valid. For drilled or driven wells, the rate of occurrence generally decreased as the depth to the uppermost aquifer materials increased. Also, the occurrence of agricultural chemicals in deep (≥ 50 feet deep) wells was shown to be significantly lower than the occurrence in shallow (< 50 feet deep) wells. In addition, for drilled or driven wells, the concentration of nitrate generally decreased with depth in the Mason County study area and possibly the Livingston County study area. Additional statistical analysis is needed. Specifically, logistic regressions should be conducted using data for a single study area. For example, logistic regression should be conducted using data from the Effingham County study area to determine which, if any, parameters influence the occurrence of agricultural chemicals in dug or bored wells. Such additional statistical analysis would be more valuable if performed on a larger data set from a statewide survey of dug and bored wells. Also, it may be fruitful to conduct logistic regression for the nitrate occurrences and the pesticide occurrences separately.

No seasonal effect in the occurrence of agricultural chemicals was observed in this study.

As stated previously, comparison of results of the pilot study and the results of other surveys of agricultural chemicals in well water must be done cautiously. Some useful information can be obtained from this type of comparison, but one must always be cognizant of the differences in the design of the various studies, the technical details of the chemical analysis, and the definition of the sample population.

A danger in conducting a pilot study is the possibility that the full-scale project will not be conducted because funding agencies are satisfied with the results of the pilot study. Some people may consider the results of a pilot study as if the results were developed from a full-scale project. This can often lead to the misapplication of the data collected and their analysis. For this project, the areal extent covered was small in comparison with the area of the entire state: about 180 square miles in the pilot study compared with more than 80,000 square miles of total area in Illinois. Only 240 samples were collected within this small area. The size of the study areas and the number of samples collected were appropriate for the purposes for which they were intended.

The pilot study demonstrated, on a gross basis, that the original classification of potential for contamination of groundwater from agricultural chemicals was valid for drilled or driven wells. It was further shown that within any area there is a great deal of variation for each parameter. Thus, general knowledge of potential for contamination by agricultural chemicals in one area will not always be helpful in predicting that every site within that area has an equal potential for contamination. Therefore, depending on the scale of the question being asked, different answers may be true for a site, area, region, or state. Furthermore, just as a larger area or greater number of samples will give a more explicit picture of the status of groundwater with respect to agricultural chemicals, a greater number of target analytes would also give a more detailed description of the status of contaminants in groundwater.

The results give an estimate of the number of occurrences of agricultural chemicals to be expected in the hydrogeologic environments studied. This information can be used to streamline the plan for the recommended statewide survey, thus allowing for greater confidence in the results of that survey at a lower cost. The pilot study also afforded staff the opportunity to fine-tune all the protocols and methodologies used in all phases of the study. This was a rare and worthwhile opportunity. The changes in protocols and methods and the increased knowledge that result from this pilot study will benefit the people of the State by making the statewide survey run more smoothly and efficiently than it otherwise would.

The results of the chemical analyses are valuable. They demonstrate that a contamination problem exists. Nitrate was shown to occur at concentrations in well water above the regulatory guidelines for public drinking water. It is important to note that sources of the problem have not been identified. However, the analytical results should not be misused as stand-alone data that are representative of the well water of the entire state. To extrapolate too much from the results of the chemical analyses would be doing a disservice to those who funded and carried out the pilot study. Most importantly, it would be a disservice to the people of Illinois who need the recommended statewide survey in its original form.

RECOMMENDATIONS

The following discussion includes recommendations to improve the original plan for a statewide survey of rural, private wells in Illinois for the occurrence of agricultural chemicals (McKenna et al. 1989). These improvements are applicable to the proposed statewide survey as well as any other large-scale survey. The recommendations here, in combination with the original plan for

the proposed statewide survey (McKenna et al. 1989), provide a tested plan for sampling wells to determine the quality of the well water.

Recommended Changes in Protocols for the Statewide Survey

Well selection For the proposed statewide survey, the following selection procedure should be used.

- Using the GIS, identify all sections, typically 1 square mile in area, in Illinois covered by each category.
- Select those sections that comprise only one category.
- Randomly select an appropriate number of sections for each category.
- Determine the land area of Illinois covered by each category.
- List and number all wells in each selected section.
- Randomly select two wells in each section for each category. If additional wells are needed, randomly select an additional well from a number of sections containing three or more wells.

Number of wells The number of wells to be sampled is determined by a number of factors and has a great impact on the cost of conducting a statewide survey of the occurrence of agricultural chemicals in rural, private wells. McKenna et al. (1989) discussed a number of factors, including the proportion of wells with an occurrence, that may have an impact on the number of wells sampled.

To determine the occurrence of agricultural chemicals on a statewide basis in Illinois, we propose the following sampling scheme. Due to the fundamental physical differences between dug or bored wells and drilled or driven wells, a separate study should be conducted for dug or bored wells. If the number of dug or bored wells statewide is 100,000, a sample of approximately 353 wells is necessary to achieve a 95% confidence interval and a precision of 5% (see table 7, McKenna et al. 1989). Furthermore, results of chemical analyses indicate that two categories may be combined (categories represented by the Mason and Kankakee County study areas). Thus, for drilled or driven wells, approximately 322 wells (95% confidence interval and 5% precision) should be sampled in each of three categories. Alternatively, it may be more cost effective, due to the differences in their occurrence, to conduct two surveys—one for nitrate and another for pesticides. For a separate nitrate survey, 322 samples from each category would be needed. The separate pesticide survey would require approximately 150 samples from each of the three categories. The additional travel and administrative costs may be offset by the reduction in the costs of the chemical analyses.

Inventory verification process Less labor-intensive options for inventorying wells should be considered for the recommended statewide survey. An alternative would be to work from aerial photographs and topographic maps to determine whether the selected areas contain residences and, therefore, a water well. When there is no reason to suspect that residences are present, an area could be deleted from the survey. County ASCS offices have aerial photographs (filed for crop reporting) that are updated each year. Residences could be identified and numbered from the photographs. A certain amount of driving would be involved, but the overall amount would be less than needed to identify all sites by driving. At the statewide level, this difference would be significant.

Interview procedure Questions should be more carefully focused during the interview process to determine if lawn-care products, self applied or professionally applied, are present near the well. Questions about the location of rights of way for utilities, railway, and road services could supply possible sources of some of the compounds detected. Lawn care and roadside inputs are perhaps as important as those from feedlots and fields, especially at residential sites.

Prior notification It is imperative that an effort be made to notify the rural residents about the study before visiting them in person. All available media should be considered. Local newspapers, radio, or television programs, and rural newsletters published by the Farm Bureau or other organizations could all be used. In cases where residents were informed about the study before they were contacted by project staff, a definite willingness to cooperate was demonstrated.

Fact sheet If a fact sheet is used to provide information to rural residents, a simplified version of the one used in the pilot study should be used. It should focus more on the benefits to the community, and particularly to the individuals selected to have the well water analyzed. The fact sheet served to inform the potential participants about the study and to provide them with a reference who could be contacted in the event that questions or comments would arise.

Information system Data should be collected and added to the information system that would allow the development of a water balance. To the extent possible, this data should be collected from existing weather stations, and a water balance could be developed at sites around the State providing a general picture of water flux. This information should be determined prior to and during the sampling period. Such data could help to explain some of the anomalies in chemical analytical results.

Chemical analysis The following paragraphs summarize the suggestions regarding the chemical analysis aspects of subsequent work.

Suitability of the NPS methods for the compounds studied Research should be conducted to find simplified or less costly analytical methods. The results indicated that certain analytes were difficult to determine reliably. A discussion of those compounds follows.

- Aldrin—Recoveries were poor for this Method 2 analyte determined in laboratory-control samples. The compound is known to degrade to dieldrin in the environment, and its use in the United States has been discontinued for many years (World Health Organization 1989, Budaveri 1989). Because of its short half-life in the environment, the inclusion of dieldrin among the analytes determined by Method 2, and the lack of any detections of aldrin in samples during this study, this compound should not be included in further studies of this type in Illinois.
- Chloramben and dinoseb—The precision and accuracy of dinoseb determination by NPS Method 3 were poor and marginally acceptable for chloramben (table 10). The average percent recovery and relative standard deviation results listed in table 10 illustrated the quality of the data produced by Method 3 for these two compounds. We suggest that Method 3 is, at best, qualitative to semiquantitative for dinoseb and is marginally acceptable for chloramben. Improved methods for their determinations should be sought.
- Heptachlor—The percent recovery of heptachlor by Method 2 was relatively low in laboratory-control samples and spiked-field samples (table 10). Heptachlor has been banned for agricultural food uses in the United States since 1975. It has a half-life of 1 to 3 days under typical environmental conditions. One of the degradation products of heptachlor is heptachlor epoxide, another compound determined by Method 2. Heptachlor epoxide has a much longer half-life, possibly on the order of years (USEPA 1979). Heptachlor was not detected in any field sample analyzed during this study. Because of its short half-life in the environment, the inclusion of heptachlor epoxide among the analytes determined by Method 2 and the lack of any detections of heptachlor in groundwater samples during this study, this compound need not be included in further studies of this type in Illinois.

- Picloram—This compound is determined by Method 3 and was among the compounds most frequently observed in the samples collected. However, the precision of its determination was poor (table 10). Because of its occurrence in Illinois groundwater, picloram should be retained in further studies, but an improved method for its determination should be sought.

Analytes to consider for subsequent studies Some potential target analytes were not selected for the pilot study. In most cases, this occurred because the compounds are comparatively new, and suitable analytical methods had not been developed or tested, when the pilot study was proposed. Possible additions for subsequent studies in Illinois include: dimethyl-tetrachlorophthalate degradates (DCPAM); 4,4'-DDD; 4,4'-DDE; pendimethalin; ethafluralin; glyphosate; clomazone; and bromoxynil.

Target analyte selection In general, we recommend that compounds, such as diazinon, that rapidly hydrolyze in soil or in water be omitted from the target analyte list. The likelihood of detecting such compounds under the sampling and analytical conditions required by this type of project is small. Also, those compounds that are rarely used in Illinois or were not found during the Pilot Study should be omitted. This could save both time and money. Degradates as well as parent compounds of high-use products should be included if they have minimum estimated half-lives of 90 days or more and are quantifiable by available methods. Examples of these types of compounds include pendimethalin, ethafluralin, glyphosate, clomazone, imazaquin, and sethoxydim.

Characterization of sample matrix Consideration should be given to a more detailed characterization of the sample matrix. It is important to evaluate whether the matrix interferences significantly affect the outcome of the analyses. Among those potential interferences are inorganic solutes such as iron, copper, and other metal cations that can interfere with the nitrate/nitrite method. Ammonium should be determined, because it may complement the nitrate/nitrite data. Inorganic anions that may affect the analytical results are unknown. Both dissolved and suspended organic carbon should be considered because their presence can interfere with extraction and target analyte detection.

Particulate matter, such as clays and organic material, can sorb analytes and, therefore, complicate the extraction processes. A count of coliform bacteria might help to distinguish feedlot runoff from field nitrate/nitrite. Such contamination may also occur from malfunctioning septic systems.

Contingency sample collection The protocol for sample collection includes carrying a set of extra bottles to allow for possible loss of containers. To allow for possible unanticipated alternative analyses, a contingency sample for each method should be collected. Carrying extra bottles for this number of methods may be prohibitive. Therefore, some thought should be given to the minimum size sample needed and possibly to the use of one sample for more than one method.

Future Research Needs

The need for research into the various aspects of the occurrence of nitrate/nitrite in well water is obvious. A procedure for determining the source of nitrate/nitrite contamination is seriously needed. A holistic approach to determine if there is a suite of analytical tests, or a set of chemical and biological tests, that can identify the source of this contamination is suggested. Research should focus on the real conditions of private well environments and attempt to define those factors that can determine the signature of the contamination source. This research is especially needed for dug and bored wells.

As discussed previously, additional statistical analysis, specifically logistic regression, should be conducted for all five study areas collectively to reduce the uncertainty in the developed mod-

els. Also, logistic regression should be conducted for each study area individually to determine if any parameters determine the occurrence of agricultural chemicals in rural, private wells.

The two most frequently cited modes for contamination of shallow wells are point-source contamination near the well and nonpoint-source contamination resulting from activities in a broad area around the well. In attempting to determine whether point or nonpoint sources of contamination leads to the occurrence of agricultural chemicals in rural, private wells, two tasks should be completed. First, additional groundwater modeling should be conducted to determine the conditions, if any, that allow agricultural chemicals to leach through the soil and into groundwater. Second, a physical test should be developed to determine if the well allows water from or near the surface to leach to the aquifer.

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APPENDIX A INVENTORY FACT SHEET

Statewide Survey for Pesticides in Rural, Private Drinking-Water Wells
carried out by

Illinois State Geologic Survey Illinois State Water Survey

Divisions of

The Illinois Department of Energy and Natural Resources

Ed Mehnert (217)-244-2765 Sue Schock (217)-333-9042

The State of Illinois is studying the occurrence of pesticides in rural private drinking water wells. As a first step in this study, all private wells in your township are being inventoried (counted).

1. Wells will be selected at random throughout the state.
2. Water will be collected from the selected wells and chemically analyzed.
3. All sampling and analysis will be done at no cost to the well user or owner.
4. The study will provide confidential information to the selected well owners/users about the quality of water in their well.
5. Published reports will not mention names, addresses or other specific well sampled.
6. Study will provide estimates of water quality for the entire state.
7. Selected well users will be interviewed at their convenience for information about the well and agricultural practices near the well.
8. The sampling will be a one time event and will occur sometime between spring of 1990 and spring of 1991.

Your local Cooperative Extension Service, Farm Bureau, ASCS, Public Health Offices, Soil and Water Conservation Districts, and County Board have been contacted about this study. Feel free to discuss it with them or ask questions. The individuals listed at the top of this form are some of the staff involved with the study, please contact either of them with any questions, comments, or for additional information about the study. Your cooperation is greatly appreciated.

APPENDIX B REVISED INTERVIEW AND WELL-SITE OBSERVATION RECORD

The State of Illinois is assessing the potential impact of pesticides and herbicides on rural private wells. It is the intent of this survey is to determine the uses and history of each domestic well.

WELL ID NUMBER (Base number for sample)_____

STAFF: FILL OUT AS MUCH OF THIS PAGE AHEAD OF TIME AS POSSIBLE

Staff member _____ Date of survey _____
Resident/Well User _____
Address _____
City _____ Zip code _____
Phone () _____
Owner (Other than resident) _____
Address _____
City _____ Zip code _____
Phone () _____
County _____ Pilot Study Site Number _____

Legal description of well: Twp _____ Rng _____ Sec _____
Quarter-quarter-quarter section _____
Status of farm: (CIRCLE ONE) active farm, residence,
residence - acres farmed by someone else, other _____
Well Type: (CIRCLE ONE) 1 = Large Diameter Bored (24" or larger)
2 = Drilled 3 = Driven 4 = Large Diameter Dug
5 = Jetted 6 = Other _____

Well depth: _____ Year or date constructed _____
Number of people using this well _____
Number of people living in this house _____
Is the well water treated? (includes softeners)
No _____ Yes _____
If yes, how? (describe) _____

- 2. Can the well be sampled? No _____ Yes _____
If yes, can the sample be collected before the treatment point?
No _____ Yes _____ Unknown _____
If yes, what is the location of the closest outlet to the well, outside the house?

(THE SAMPLING POINT IDENTIFIED SHOULD BE AGREED UPON BY THE WELL USER/OWNER, AND ANY SPECIAL INSTRUCTIONS NOTED)

Agree with the owner/user about where to discharge the water, mention sampling technique. Check whether the outside tap will be active during the winter.
(note such things as broken handle in shed; key above door)

- 3. Can the sample be collected before the holding or pressure tank, if applicable?
Yes _____ Unknown _____ No _____
If no, what is the size of the tank? _____

4. What is the topographic setting of the well? (check one)

- Level land _____
- Hilltop _____
- Hill slope _____
- Terrace _____
- Depression _____
- Floodplain _____
- Other (specify) _____

5. Is the well protected at the surface?

Yes _____ No _____

If protected, how?

- Well house or shed _____
- Concrete pad _____
- Grouted seal _____
- Covered pit _____
- Gasket in pit _____
- Other (specify) _____

6. Do you feel that this protection is adequate to prevent seepage around the well?

Yes ___ No ___ Comment: _____

After precipitation, is there standing water around the well?

Yes ___ No ___ Comment: _____

7. Is the well capped at ground surface?

Yes _____ No _____ Unknown _____

If yes, what material was used to cap or plug the well?

- Cement _____
- Plastic _____
- Steel with gasket _____
- Other (specify) _____

8. How far are any of the following from the well? (give distance)

DISTANCE

Body of water (give type)

- Drainage ditch _____
- Septic tank _____
- Septic field _____
- Cesspool _____
- Animal grazing area _____
- Animal housing facility _____
- Compost pit _____
- Garden plot _____
- Pesticide mixing point _____
- Pesticide storage _____
- Crop storage _____
- Irrigation well _____
- Cropland _____

IF CROPLAND WAS FARMED BY SOMEONE ELSE, PLEASE ENTER THE NAME OF THE FARMER, IF KNOWN, AND THE CROP TYPE IN THE CHART BELOW.

Cropland: North South East West

Now:				
Past:				

9. Do you have any livestock or other animals? (i.e. cattle, pigs, poultry, goats, etc)

Yes ___ Size of operation _____
 Kind of animals _____

No ___

10 Have you had animals in the past?

Yes ___ How long ago? _____

No ___

11. Have you or anyone else applied manure within 500' of the well within the last 3 years?

Yes ___ When _____

No ___

STAFF: Describe and show in a sketch below, the location of the sampling point. NOTE ANY LIMITATIONS ON ACCESS

Note: Include auxiliary sampling points, treatment equipment, buildings, other wells, spots of dead vegetation, septic system, flow from surface runoff, from animal shelters or manure sites, mixing points, storage areas, tanks - above or below ground, driveways, outhouses, type of ground cover; SHOW NORTH ARROW

STAFF: GET THIS INFORMATION ON SITE

(Show the user a diagram of a well to aid in the discussion of construction details, if necessary.)

12. Do you have copies of a well log form for this well?

Yes _____ No _____ Unknown _____

13. Who constructed the well? _____

14. Were you the user when the well was constructed?

Yes ___ No ___

If no, do you know who was? _____

15. What is the water level for the well? _____ Unknown _____

16. Has the well depth ever been changed?

Yes ___ from ___ to _____

No ___ Unknown _____

17. What is the diameter of the well (in inches)? _____

18. In what type of material is the well finished?
(Staff: draw a column if necessary)
- Limestone/dolomite _____
 Sandstone _____
 Sand & gravel _____
 Other material (describe) _____
 Unknown _____
19. Does this well have a casing (i.e. a protective covering used to line the well hole)?
(staff: use diagram to help explain, if needed)
- Yes _____ No _____ Unknown _____
20. What is the diameter of the casing? _____
21. What material was used to case the well? _____
- Plastic pipe (PVC) _____
 Concrete or cement _____
 Metal (steel) _____
 Tile, brick, or stone _____
 Other _____ specify _____
 Unknown _____

IF THIS IS A DUG WELL, SKIP TO QUESTION 24

22. Does the well have a screen?
 Yes ___ Describe (material, slot size) _____
 No ___ Unknown _____
23. Is the well casing grouted?
 Yes _____ With what? _____
 No _____
 Unknown _____
24. What is the depth to the water intake in the well?
 (below ground surface, in feet) _____ Unknown _____
25. What is the capacity of the pump? (How many gallons per minute CAN it pump, or how many horse power is it?)
- Gallons per minute _____
 Unknown _____
 Horsepower _____
26. Is this well used continuously?
 Yes _____ No _____
 If not continuously,
 How often is it used? _____
 When it is used? _____
 How long? _____
 Unknown _____

27. Does this well ever run dry?
 Yes _____
 Seasonally _____
 In drought _____
 Other _____ (specify) _____
 No _____

28. Have you had the water from this well tested?
 Yes _____
 For What? _____
 When? _____
 By whom? _____
 What were the results? _____
 No _____
 Unknown _____

29. Has this well ever been contaminated?
 Yes _____ By what? _____
 No _____
 Unknown _____

30. Has the well been disinfected in the last 2 years?
 Yes _____ How? _____
 No _____ Unknown _____

31. Are there any operating wells within 500 feet of this well?
 Yes _____ No _____ Unknown _____

Indicate the type of wells and the number of each type.

	Type	Number
Private drinking water supply	_____	_____
Community drinking water supply	_____	_____
Irrigation	_____	_____
Animal water supply	_____	_____
Yard use	_____	_____
Chemical mixing	_____	_____
Other	_____	_____
(specify) _____		

32. Are there any abandoned (A), or non-operating (N) wells within 500 feet of the well?
 [Non-operating can mean standby, backup, unused but operable]
 Yes _____ No _____ Unknown _____

Indicate the type of well use, and the number of each type.

	NorA	Number	Type:
Private drinking water supply	_____	_____	_____
Community drinking water supply	_____	_____	_____
Irrigation	_____	_____	_____
Animal water supply	_____	_____	_____
Other	_____	_____	_____
(describe wells) _____			

33. Describe how the above wells were abandoned_____
34. Do you use pesticides, insecticides, herbicides, or nitrogen fertilizers around your well?
Yes _____ No_____
35. Do you know of others who use pesticides, insecticides, herbicides, or nitrogen fertilizers within 500' of your well?
Yes ____ No_____
36. Do you use chemicals for other than crop purposes? (i.e. for control of bugs, vegetable garden, etc.)
Yes _____ No _____ What Kind? _____
37. Do you know of any events or factors that may have had an influence on the quality of the water from your well? (i.e. spills, tank leaks, battery storage, other incidents or problems)
Yes ____ No _____ What?_____

STAFF: REMEMBER TO DO THE SKETCH OF THE WELL-SITE

PESTICIDE, HERBICIDE AND NITROGEN
FERTILIZERS USERS QUESTIONS

FOR ACTIVE FARM SITES ONLY

This part of the survey is concerned with the usage of pesticides and herbicides near this well.

STAFF: BE SURE TO READ THIS: PESTICIDES INCLUDE ALL INSECTICIDES, PRE AND POST EMERGENT HERBICIDES, FUNGICIDES, NEMATOCIDES, RODENTICIDES, AND OTHER CHEMICAL AGENTS INCLUDING SEED TREATMENT YOU APPLY

1. Have any pesticides or herbicides been used, mixed, stored, or loaded within 500 feet of the well in the past year? (storage means kept for longer than 30 days)
Used____ Mixed____ Stored ____ Disposed____ No____

2. Is water from the well used to mix pesticides or herbicides for spraying?
Yes _____ No _____ Unknown _____

Is water taken directly from the well to the sprayer tank or do you use a water tank?
Yes _____ No _____ Unknown _____

Has the sprayer tank ever overflowed?
Yes _____ When? _____ No _____

Has the tank ever back-siphoned?
Yes _____ When? _____ No _____

Into what? _____

Do you have back-siphon prevention devices?
Yes _____ What? _____ No _____

3. Do you now, or have you within the last 5 years, **USED** pesticides or herbicides within 500 feet of the well? (Give either the brand name or the active ingredient, and the distance from the well each pesticide was used.)
4. Do you now, or have you within the last 5 years, **STORED** pesticides or herbicides within 500 feet of the well? (Give either the brand name or the active ingredient, volume, the distance from the well and how each pesticide was stored.)
5. Do you now, or have you within the last 5 years, **DISPOSED OF** pesticides or herbicides containers within 500 feet of the well? (Give either the brand name or the active ingredient, volume, concentration, and the distance from the well the containers were disposed.)
6. Have you this year, or have you within the last 5 years, **ACCIDENTALLY SPILLED** any pesticides or herbicides within 500 feet of the well? (Give either the brand name or the active ingredient, the volume, concentration, and the distance from the well of the spill.)
7. Have you this year, or have you within the last 5 years, **ACCIDENTALLY BACK-SIPHONED** pesticides or herbicides into the well? (Give either the brand name or the active ingredient, the volume and concentration.)

THE FOLLOWING QUESTIONS HAVE TO DO WITH NITROGEN
FERTILIZERS. THE COMMONLY USED TYPES ARE:

1. ANHYDROUS AMMONIA
 2. AMMONIUM NITRATE
 3. UREA
 4. AMMONIUM SULFATE
 5. SODIUM NITRATE
 6. 28%-32% NITROGEN SOLUTION
8. Do you now, or have you within the last 5 years, **APPLIED** Nitrogen Fertilizers within 500 feet of the well? (Give the type, pounds and concentration and the distance from the well it was used.)
- INDICATE FALL OR SPRING APPLICATION**
9. Have you this year, or have you within the last 5 years, **ACCIDENTALLY SPILLED** any nitrogen fertilizers within 500 feet of the well? (Give the type, volume, and the distance from the well of the spill.)